Phosphorus–Fluorine Chemistry. Part XXXIV.[1] Fluorophosphoranes Involving Potential Intramolecular Donor–Acceptor Interaction. Crystal and Molecular Structure of the Product of the Reaction of Phosphorus Pentafluoride with 2-Methyl-8-trimethylsiloxyquinoline

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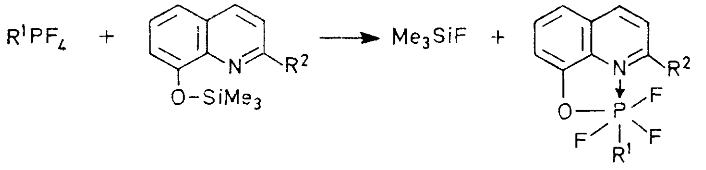
Fluorophosphoranes (RPF_4; R = F, Me, Et, or Ph) reacted with 8-trimethylsiloxyquinolines to give yellow-green monosubstituted oxinato-fluorophosphoranes, stable at 20° *in vacuo* which, on the basis of ^{31}P n.m.r. data, displayed the previously unobserved intramolecular N→P co-ordinate bond. The stability of this bond decreased with decreasing electronegativity of the ligand R, so that the product of the reaction between 8-trimethylsiloxyquinoline and trifluorodimethylphosphorane showed no evidence of six-co-ordination. Crystals of the complex $F_4P(oxMe)$ (oxMe = 2-methyl-8-oxyquinoline) are monoclinic, space group $P2_1/m$, with $a = 8{\cdot}258(4)$, $b = 6{\cdot}803(3)$, $c = 9{\cdot}453(4)$ Å, $\beta = 106{\cdot}97(5)°$, $Z = 2$. The molecule possesses a crystallographic plane of symmetry; co-ordination around phosphorus is almost perfectly octahedral. The N→P co-ordinate bond length [1·911(4) Å] is much longer than the N–P σ bond distance (1·769 Å). The structure was solved by direct methods and refined to R 0·051 for 816 unique reflections recorded on a linear diffractometer.

THE ability of PF_5 to form stable non-ionic complexes with organic donor molecules is well established;[2-5] for tetrafluorophosphoranes, RPF_4 (R = Me, Et, or Ph), however, relatively few such complexes have been reported.[6] The acceptor properties of phosphorus decline with decreasing electronegativity of the attached ligands: $PF_5 > ArPF_4 > RPF_4 \gg R_2PF_3$. All previously reported adducts between fluorophosphoranes and organic donor molecules have been intermolecular complexes. We now describe the preparation and structural characterisation of the first intramolecular complexes containing six-co-ordinated phosphorus.

RESULTS AND DISCUSSION

Preparations.—The cleavage of the Si–O bond in trimethylsiloxyquinolines with fluorophosphoranes[7] yields oxinato-fluorophosphoranes. Owing to a potentially favourable steric configuration of the 8-hydroxyquinoline skeleton, there further exists the possibility of formation of an N→P co-ordinate bond in addition to the P–O bond as in reaction (1).



(1)

R^1 = F, Me, Et, or Ph; R^2 = H or Me

All reactions between 8-trimethylsiloxyquinoline, $Me_3Si(ox)$ and fluorophosphoranes in the molar ratio 1 : 1 afford high yields of the monosubstituted products. The fluorophosphoranes display a significant gradation in their reactivity towards the silyl ethers. The reaction between PF_5 and 8-trimethylsiloxyquinoline is markedly exothermic, $PhPF_4$ shows only a slightly exothermic reaction, and in the case of $EtPF_4$ the reaction may only be brought to completion through external heating. The products are yellow-green crystalline compounds, which exhibit the following trend in their resistance to hydrolysis: $F_4P(ox) > PhF_3P(ox) > MeF_3P(ox) \sim EtF_3P(ox)$.

Monosubstitution in itself suggests the formation of a six-co-ordinated species, for aryl trimethylsilyl ethers invariably yield multisubstituted products with fluorophosphoranes such as PF_5 and RPF_4.[8] In general, the resulting stable reaction product is a difluorophosphorane, the intermediate formation of trifluorophosphoranes being demonstrated only through the use of low-temperature n.m.r. measurements.[8] Since in the case of trimethylsiloxyquinolines only monosubstitution is observed, it must be inferred that the route to multisubstitution is no longer available. After cleavage of the Si–O bond a five-co-ordinated monosubstitution product is formed, which then forms an intramolecular N→P co-ordinate bond, in preference to further substitution. Under the reaction conditions employed the six-co-ordinate complex is then incapable of further silyl ether cleavage. For fluorophosphoranes the stability of the intramolecular complexes is greater than for the comparable intermolecular complexes. No stable complexes, for example, have been isolated between RPF_4 (R = Me or Et) and pyridine at room temperature.[6] In contrast, the reaction of Me_2PF_3 with 8-trimethylsiloxyquinoline yields a white crystalline oxinatofluorophosphorane for which, however, there is no evidence for the existence of an intramolecular N→P co-ordinate bond.

A similar class of compounds exists for antimony.

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TABLE 1

Preparative, analytical, and mass spectral data for 8-hydroxyquinoline-substituted fluorophosphoranes and PF_5–base complexes

Compound	Formula	React. temp./°C	Yield (%)	M.p./°C	Solvent for recrystal.	Analyses (%) C	H	N	P	*M* Calc.	Obs.
(I) PF_4(ox)	$C_9H_6OF_4NP$	25	86	213—214	MeCN	42·2 (43·1) *	2·9 (2·4)	5·3 (5·3)	12·4 (12·3)	251·1	251
(II) $MePF_3$(ox)	$C_{10}H_9OF_3NP$	25	80	157—158	CH_2Cl_2	47·7 (48·6)	4·2 (3·7)		12·9 (12·4)	247·1	247
(III) $EtPF_3$(ox)	$C_{11}H_{11}OF_3NP$	70	89	117—118	Light pet.–CH_2Cl_2	49·2 (50·6)	4·5 (4·2)		12·5 (11·9)	261·2	261
(IV) $PhPF_3$(ox)	$C_{15}H_{11}OF_3NP$	70	82	212—213	CH_2Cl_2	57·3 (58·3)	4·1 (3·6)	4·1 (4·5)	10·4 (10·0)	309·2	309
(V) Me_2PF_2(ox)	$C_{11}H_{12}OF_2NP$	50	68	101—102	Light pet.	52·8 (54·4)	5·0 (5·0)		12·7 (12·7)	243·1	243
(VI) PF_4(oxMe)	$C_{10}H_8OF_4NP$	90	80	260 (dec.)	MeCN	45·4 (45·4)	3·6 (3·0)	5·2 (5·3)	12·2 (11·7)	265·1	265
(VII) PF_5(β-pic)	$C_6H_7F_5NP$	25	49	49—50	CH_2Cl_2	33·3 (33·0)	3·9 (3·2)	6·3 (6·4)	14·3 (14·3)		
(VIII) PF_5(quin)	$C_9H_7F_5NP$	25	66	190—196	MeCN	42·2 (42·4)	3·3 (2·8)		12·4 (12·1)		

ox = 8-Hydroxyquinoline group, oxMe = 2-Methyl-8-hydroxyquinoline group, β-pic = β-picoline, quin = quinoline.

* Calc. value in parentheses.

TABLE 2

^{31}P and ^{19}F N.m.r. data for 8-hydoxyquinoline-substituted fluorophosphoranes and PF_5–base complexes (δ in p.p.m., *J* in Hz)

Compound	δ(P) [a]	Multiplicity	δ(F) [b]	Multiplicity	Rel. intensity	*J*(P–F)	*J*(FaxFeq)	Solvent Temp./°C
(I)	118·7	qi				791 [d]		MeCN 25
(II)	105·0	q	51·0 (a) [c]	dt	1	883 (a)	62	MeCN 31
			32·0 (e)	dd	2	883 (e)		
(III)	105·0	q	60·0 (a)	dt	1	920 (a)	63	CH_2Cl_2 32
			39·0 (e)	dd	2	920 (e)		
(IV)	119·6	q	56·1 (a)	dt	1	890 (a)	56	Me_2SO 32
			39·8 (e)	dd	2	890 (e)		
(V)	9·7	tse	7·2 (a)	dse		729 (a)		CH_2Cl_2 30
(VII)	145·5	sx	82·3 (a)	dqi	1	761 (a)	58	CH_2Cl_2 32
			64·5 (e)	dd	4	803 (e)		
(VIII)	141·1	sx	80·8 (a)	dqi	1	751 (a)	57	MeCN 32
			64·5 (e)	dd	4	811 (e)		

[a] Reference ext. 85% H_3PO_4. [b] Reference internal CCl_3F. [c] (a) and (e) denote axial and equatorial fluorine atoms in the octahedral or trigonal-bipyramidal framework, respectively. [d] Because of its poor solubility no ^{19}F n.m.r. data were obtained for this compound. The value of *J*(P–F) was taken from a 36·43 MHz ^{31}P Fourier-transform spectrum.

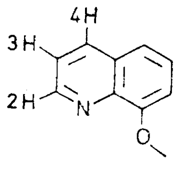
TABLE 3

^1H N.m.r. data for 8-hydroxyquinoline and some of its derivatives (δ in p.p.m., *J* in Hz)

Compound	δ(2H)	δ(4H)	*J*	δ[alkyl (aryl)]	Integration $H_{aliph.} : H_{arom.}$ Found	Calc.	*J*(HP; HF)
oxH	−8·94 dd	−8·11 dd	2/4 1·8	arom. −6·7 · · · −7·5 m			
(oxin)			2/3 4·5				
			3/4 8·5				
(ox)$SiMe_3$	−8·94 dd	−8·08 dd	2/4 1·8				
			2/3 4·5				
			3/4 8·5				
(I)	−9·19 t	−8·90 d	t 6	arom. −7·4 · · · −8·2 m			
			d 8·5				
(II)	−8·95 t	−8·50 d	t 6	Me −1·79 dq	1·0	1	HP 19·5
			d 8·5	arom. −7·0 · · · −7·8 m	2·1	2	HF 8·7
(III)	−8·97 t	−8·43 d	t 6	Me −1·4 m *	5·3	5	
			d 8·5	CH_2 −2·2 m *			
				arom. −6·8 · · · −7·8 m	6·0	6	
(IV)	−9·10 d	−8·70 d	t 6	arom. −7·4 · · · −8·2 m	2·0 †	2	
			d 8·5		9·4 †	9	
(V)	−8·96 dd	−8·16 dd	2/4 1·8	Me −2·06 dt	1·0	1	HP 16·8
			2/3 4·4	arom. −7·4 · · · −7·9 m	1·1	1	HF 12·8
			3/4 8·5				

Standard CH_2Cl_2-Lock spectrum (converted to $SiMe_4$); solvent CH_2Cl_2; temp. 30—35 °C. s = Singlet, d = doublet, t = triplet, q = quartet, qi = quintet, m = multiplet, sx = sextet, se = septet, dd = doublet of doublets, dse = doublet of septets, dt = doublet of triplets, dq = doublet of quartets, dqi = doublet of quintets, tse = triplet of septets.

* The ^1H resonance of the ethyl groups indicated a spectrum of higher order. † The integral of (2H + 4H), relative to the remaining protons, was determined.



An analogous increase in the co-ordination number of antimony from five to six through an intramolecular N→Sb co-ordinate bond is observed for the organoantimony(v) compounds, $R_nSbCl_{4-n}(ox)$ (R = Me, Bu, or Ph; n = 2—4). The stability of the N→Sb co-ordinate bond increases similarly with increasing electronegativity of the ligands attached to antimony:[9] $RSbCl_3(ox) > R_2SbCl_2(ox) \gg R_3SbCl(ox)$.

TABLE 4

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

Atom	*z/a*	*y/b*	*z/c*	$\bar{U}$
H(1)	0·547	0·358	−0·187	50(6)
H(2)	0·572	0·25	−0·308	50(6)
H(3)	0·830	0·25	−0·333	50(6)
H(4)	1·085	0·25	−0·189	50(6)
H(5)	1·299	0·25	0·090	50(6)
H(6)	1·355	0·25	0·351	50(6)
H(7)	1·191	0·25	0·526	50(6)

TABLE 5

Atom co-ordinates and anisotropic vibrational amplitudes (Å^2 × 10^3) for (VI), 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	0·7160(1)	0·25	0·2266(1)	25(1)	79(2)	30(1)	0	14(1)	0
F(1)	0·7177(2)	0·4846(4)	0·2183(3)	70(1)	68(2)	66(1)	−12(1)	34(1)	9(1)
F(2)	0·5597(2)	0·25	0·0910(4)	22(1)	121(3)	44(1)	0	12(1)	0
F(3)	0·6448(3)	0·25	0·3778(4)	44(1)	137(3)	44(1)	0	30(1)	0
O	0·8835(3)	0·25	0·3700(4)	32(1)	115(3)	32(1)	0	12(1)	0
N	0·8123(3)	0·25	0·0528(4)	25(1)	48(3)	33(2)	0	8(1)	0
C(2)	0·7623(5)	0·25	−0·1157(5)	37(2)	50(3)	35(2)	0	11(2)	0
C(3)	0·8668(5)	0·25	−0·2102(5)	47(2)	53(3)	33(2)	0	18(2)	0
C(4)	1·0140(5)	0·25	−0·1347(6)	45(2)	52(4)	47(2)	0	27(2)	0
C(5)	1·2192(5)	0·25	0·1414(7)	31(2)	54(4)	60(3)	0	18(2)	0
C(6)	1·2539(5)	0·25	0·3144(7)	22(2)	72(4)	60(3)	0	2(2)	0
C(7)	1·1457(5)	0·25	0·4011(6)	31(2)	76(4)	37(2)	0	−1(2)	0
C(8)	1·0003(4)	0·25	0·3064(5)	28(2)	64(4)	33(2)	0	9(2)	0
C(9)	0·9623(4)	0·25	0·1304(5)	27(2)	45(3)	32(2)	0	8(2)	0
C(10)	1·0700(4)	0·25	0·0432(5)	31(2)	39(3)	44(2)	0	18(2)	0
C(11)	0·6018(5)	0·25	−0·2091(6)	35(2)	100(4)	32(2)	0	4(2)	0

Two new intermolecular complexes of PF_5 with quinoline and β-picoline were synthesised as reference compounds for the ^{31}P n.m.r. investigations.

In the reactions of $PhPF_4$ with silyl ethers of the type $Me_2N\cdot[CH_2]_n\cdot OSiMe_3$ (n = 2 or 3) nearly quantitative yields of Me_3SiF were realised but formation of intramolecular complexes was not observed. The nature of the reaction could not be satisfactorily interpreted.

Preparative, analytical, and mass spectral data for all products are listed in Table 1.

N.m.r. Investigations.—^{31}P and ^{19}F N.m.r. data are listed in Table 2, and ^1H n.m.r. data in Table 3. Measurements were made difficult by the low solubility of most of these derivatives. The assumption of six-co-ordination for compounds (I)—(IV) is confirmed by the ^{31}P n.m.r. data as, in general, a highly positive shift, >100 p.p.m., is to be expected in this case.[3,10,11] In contrast, a comparison of the spectroscopic data for derivative (V) to those of $PhO(Me)_2PF_2$ [δ_F 4·2; δ_P 11·7 p.p.m.; J(P–F) 736 Hz] shows good agreement for chemical shifts and coupling constants.[8] Compound (V) is therefore a true fluorophosphorane, involving five-co-ordinated, trigonal-bipyramidal, phosphorus with two axial fluorine ligands.

The J(P–F) and δ_F values are of limited significance with regard to the question of six-co-ordination. The coupling constants, J(P–Fax) and J(P–Feq) for compounds (II)—(IV) are peculiar, in that they are identical within experimental accuracy although the fluorine atoms in these compounds have different chemical environments ($\delta_{F_{ax}} \neq \delta_{F_{eq}}$). This feature is retained with change in solvent (MeCN, CH_2Cl_2). The ^{31}P n.m.r. spectra, therefore, appear as quartets.

No n.m.r. data could be obtained for compound (VI), on account of its extremely poor solubility. Six-co-ordination in this compound is, however, confirmed by the *X*-ray diffraction study.

With the assumption of an octahedral structure for compounds (II)—(IV), it may be inferred from the ^{19}F n.m.r. spectra that no mixture of isomers is present. The spectra show in each case a doublet of doublets (intensity 2) and a doublet of triplets (intensity 1), and therefore indicate the presence of an A_2MX spin system.

The intermolecular complexes (VII), F_5P(β-picoline), and (VIII), F_5P(quinoline), display ^{19}F n.m.r. spectra which consist of a doublet of doublets and of a doublet of quintets in the intensity ratio 4 : 1, and are thereby comparable to the ^{19}F n.m.r. spectra of similar PF_5-complexes.[2,3] The values of the ^{31}P chemical shifts for (VII) and (VIII) (145 and 141 p.p.m., respectively) are of the same order as those observed for the intramolecular complexes, (I)—(IV).

X-*Ray Crystal Structure of* (VI).—The results from the final least-squares cycle are summarised in Tables 4 and 5, and were used, together with the full covariance matrix, to calculate the bond lengths and angles and their

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estimated standard deviations. Shortest non-bonded distances are summarised in Table 7. Figure 1 depicts the molecule in perspective, together with the numbering system, and Figure 2 the unit-cell contents ($y/b = 0{\cdot}25$ only) shown in projection perpendicular to [010].

TABLE 6

Interatomic distances (Å) and bond angles (°) in (VI)

(*a*) Distances

P–F(1)	1·598(3)	P–F(2)	1·572(3)
P–F(3)	1·582(3)	P–O	1·678(3)
P–N	1·911(4)	N–C(2)	1·333(5)
C(11)–C(2)	1·488(6)	C(2)–C(3)	1·426(6)
C(3)–C(4)	1·349(7)	C(4)–C(10)	1·409(6)
C(5)–C(10)	1·407(6)	C(5)–C(6)	1·369(8)
C(6)–C(7)	1·409(7)	C(7)–C(8)	1·369(6)
C(8)–C(9)	1·392(6)	C(9)–C(10)	1·407(6)
C(9)–N	1·376(5)	C(8)–O	1·353(5)
C(3)–H(3)	0·97	C(4)–H(4)	0·91
C(5)–H(5)	0·97	C(6)–H(6)	0·91
C(7)–H(7)	0·99	C(11)–H(1)	0·95
C(11)–H(2)	0·79		

(*b*) Angles

O–P–F(1)	90·6(1)	O–P–F(2)	179·5(1)
O–P–F(3)	88·5(2)	O–P–N	88·4(1)
N–P–F(1)	87·4(1)	N–P–F(2)	91·1(1)
N–P–F(3)	176·9(2)	F(1)–P–F(2)	89·3(2)
F(1)–P–F(3)	92·6(1)	F(2)–P–F(3)	92·0(1)
P–N–C(2)	133·1(3)	P–N–C(9)	107·6(3)
P–O–C(8)	115·8(3)	O–C(8)–C(7)	125·1(4)
O–C(8)–C(9)	114·5(4)	C(9)–N–C(2)	119·3(3)
N–C(2)–C(3)	118·7(4)	C(2)–C(3)–C(4)	122·2(4)
C(3)–C(4)–C(10)	120·3(4)	C(4)–C(10)–C(9)	115·2(3)
C(10)–C(9)–N	124·3(4)	C(9)–C(10)–C(6)	117·3(4)
C(4)–C(10)–C(5)	127·5(4)	C(10)–C(5)–C(6)	119·7(4)
C(5)–C(6)–C(7)	122·4(4)	C(6)–C(7)–C(8)	117·7(4)
C(7)–C(8)–C(9)	120·5(4)	C(8)–C(9)–C(10)	121·9(4)

TABLE 7

Intermolecular non-bonded distances (Å) $< 3{\cdot}5$ Å in (VI)

F(1) · · · C(4)	3·345	F(1) · · · H(1)	2·664
F(1) · · · H(4)	2·657	F(1) · · · H(5)	3·087
F(1) · · · H(7)	2·720	F(2) · · · H(1)	3·037
C(2) · · · C(5)	3·416	C(2) · · · H(5)	3·467
C(4) · · · C(9)	3·408	C(5) · · · H(1)	3·414
C(7) · · · H(3)	3·466		

The Structure of (VI).—The molecule is remarkable in that it possesses C_h symmetry. Almost perfect octahedral co-ordination is exhibited by phosphorus with angles varying between 87·4 and 92·6°. Considerable distortion is necessary at the N and C(8) atoms in order to achieve octahedral co-ordination at phosphorus. Angles of 107·6 (N) and 114·5° [C(8)] are observed within the five-membered NPOCC ring system. In contrast, however, the angle of 115·8(3)° at oxygen is only slightly larger than angles of 113·8(2) and 114·2(2)° observed in comparable five-membered ring systems containing trigonal-bipyramidal phosphorus.[12,13] Angles of 111·9(6) and 112·4(6)° have been found at oxygen in the tris-(*o*-phenylenedioxy)phosphate anion which contains six-co-ordinate phosphorus.[14]

The N→P co-ordinate bond length [1·911(4) Å] is 0·14 Å longer than the N–P bond length (1·769 Å).[15] Such a considerable increase in bond length is in accordance with kinetic studies which have established that the N→P co-ordinate bond is weaker than the similar P–P bond.[11] Definite correlation must, however, await a determination of this latter bond length and its comparison with the long P–P bond length of 2·21 Å.[16] The P–O bond length of **1·678(3)** Å is significantly shorter than the values of **1·723(7)** and **1·711(8)** Å observed in the tris-(*o*-phenylenedioxy)phosphate anion. It may be inferred from this, and from the relative widening of the angle at oxygen, that the degree of interaction between the oxygen $2p$ orbitals and any $3p$ or $3d$ orbitals available at phosphorus is greater in (VI) than in the spirophosphate anion. The shortening of the C–O bond to 1·353(5) Å, in comparison with the normal single bond length of 1·43 Å,[17] is indicative of an interaction between the oxygen $2p$ orbital perpendicular to the ring with the aromatic π-system.

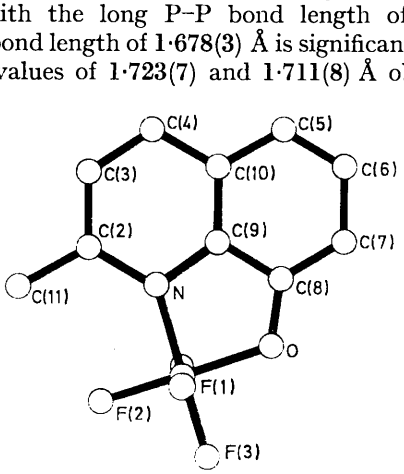

FIGURE 1 Molecular structure of (VI)

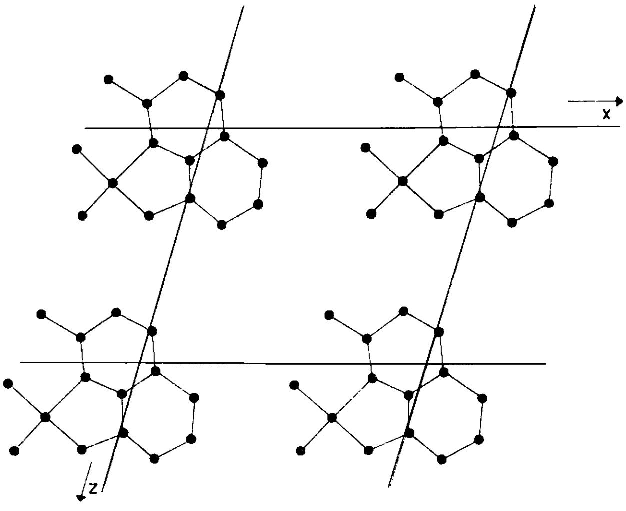

FIGURE 2 Projection of the crystal structure perpendicular to [010] showing $y/b = 0{\cdot}25$ only

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A trend (F)P–F > (N→)P–F > (O)P–F is observed for the three different P–F bond lengths which may be accounted for in terms of the electronegativity of the opposite partner in the octahedron and of the nature of its bond to phosphorus. The fact that the (N→)P–F bond is longer than the (O)P–F bond is indicative of the weakness of the N→P co-ordinate linkage. The values of the P–F bond lengths are close to that of 1·58 Å observed in the octahedral PF_6^- anion.[18]

Finally, it may be noted that some degree of bond fixation is observed, as would be expected, within the quinoline framework.

EXPERIMENTAL

Preparation of 8-Trimethylsiloxyquinoline.—8-Hydroxyquinoline (1 mol) was added to a mixture of hexamethyldisilazane (0·6 mol) and, as a catalyst, trimethylchlorosilane (0·5 ml), under dry nitrogen. The reaction mixture was then held at 100—110 °C for 2 h, with vigorous magnetic stirring. Ammonia liberated during the reaction was removed, and the product distilled under vacuum. 8-Trimethylsiloxyquinoline (94%) was obtained; b.p. 70° (0·01 Torr). By the same procedure, 2-methyl-8-trimethylsiloxyquinoline was obtained (98%), b.p. 113° (0·8 Torr) [Found: C, 65·7; H, 7·0; N, 6·0. Calc. for $C_{13}H_{18}NOSi$: C, 67·5; H, 7·4; N, 6·1%].

Adduct Formation.—All reactions were carried out by use of vacuum line techniques. In a typical preparation fluorophosphorane (or PF_5) (0·05 mol) was condensed on silyl ether (0·05 mol) contained in a heavy-walled glass tube cooled to −196 °C. Tetrafluorophenylphosphorane alone was introduced by means of an injection syringe under dry nitrogen. The tube was then sealed under vacuum and allowed to reach room temperature during 24 h. For a subsequent 48 h the tube was allowed to remain at room temperature or was heated in a steel tube at 50—90 °C, in order to facilitate completion of the reaction. After cooling to −196 °C the tube was opened to a vacuum line and the fluorotrimethylsilane produced was condensed in a trap. Its purity was subsequently checked by ^{19}F n.m.r. spectroscopy. All further manipulations (recrystallisation, making up samples) were carried out under dry nitrogen. Yields were all 80—90%. The experimental results are listed in Table 1.

N.m.r. Instrumentation.—N.m.r. spectra were recorded on a Varian HA 60A instrument at 60 MHz, 56·4 MHz, and 24·3 MHz for ^1H, ^{19}F, and ^{31}P, respectively.

Mass Spectra.—Mass spectra were obtained for the hydroxyquinoline derivatives, by use of an AEI MS 9 or Atlas CH 4. Ionisation energies of 70 eV were employed; samples were admitted into the instruments *via* a direct inlet system.

X-*Ray Diffraction.*—A long prismatic crystal of (VI) (0·3 × 1·0 × 0·3 mm) was sealed into a Lindemann glass capillary tube. Intensities were measured on a Stoe two-circle diffractometer (layers $h0$—$5l$ inclusive) using monochromated Cu-K_α radiation. Of the 852 reflections recorded, 36 were rejected because the observed intensity was not greater than the background. Measurements were carried out with stationary background counts and ω scan (0·01° step) of variable range [$\Delta\omega = 1\cdot4 \pm 0\cdot6\ (\sin\mu/\tan\theta)$]. Lorentz, polarisation, and absorption corrections were applied. Accurate unit-cell dimensions were obtained from measurements of 12 $hk0$ and 15 $h0l$ reflections on zero-layer Weissenberg photographs calibrated with tungsten (a = 3·1653 Å) by a least-squares routine which corrected for possible systematic eccentricity errors.

Crystal Data.—$C_{10}H_8F_4NOP$, M = 265·2, Monoclinic, a = 8·258(4), b = 6·803(3), c = 9·453(4), β = 106·97(5)°, U = 507·9(5) Å^3, Z = 2, D_c = 1·73. Cu-K_α radiation, λ = 1·5418 Å, μ(Cu-K_α) = 28·7 cm^{-1}. The systematic absences ($0k0$, $k = 2n + 1$) are consistent with the space groups $P2_1$ and $P2_1/m$. The distribution of normalised structure factors (E values) favoured the centrosymmetric space group $P2_1/m$, in which the molecules must lie on a crystallographic mirror plane, and all the atoms, with the exception of one fluorine and one hydrogen, occupy special positions of the type ±(x, 0·25, z). Subsequent refinement of the structure indicated this interpretation to be correct.

Structure Solution and Refinement.—The positions of the non-hydrogen atoms were located by direct methods, by use of a least-squares application of Sayre's equation,[19] with the centrosymmetric space group $P2_1/m$ being assumed. The structure was then refined by full-matrix least-squares in both possible space groups $P2_1$ and $P2_1/m$, with anisotropic temperature factors for all atoms. At this stage, before the introduction of the hydrogen atoms, values of 0·093 and 0·110 were obtained for the generalised index R_G [$= (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$ where $\Delta = |F_o| - |F_c|$] and 0·066 and 0·071 for the unweighted index $R = (\Sigma\Delta/\Sigma|F_o|)$, for refinements in the space groups $P2_1$ and $P2_1/m$, respectively. The decrease in R_G from $P2_1/m$ to $P2_1$ was clearly significant at the 99·9% confidence level.[20] However, refinement in the latter space group led to unreasonable values of the P–F bond length for those fluorine atoms [F(1) and F(1′)] related by the mirror plane in $P2_1/m$ [P–F(1) 1·40(1), P–F(1′) 1·85(1) Å]. In addition, very strong negative correlation matrix elements were observed for U_{22}(P) − U_{22}[F(1)], x/a [F(1)] − U_{22}[F(1′)], and z/c [F(1)] − U_{23} [F(1′)]. It was, therefore, inferred that $P2_1/m$ was the appropriate space group. The positions of the hydrogen atoms were located from a difference-Fourier synthesis and were included as fixed parameters, with an overall isotropic temperature factor, in the final stages of refinement. Adoption of the centrosymmetric space group was further justified by the location of the methyl atoms [C(11)] in positions related by the crystallographic mirror plane at y/b = 0·25.

The secondary extinction coefficient (ψ^* as defined by Larson[21]) refined to (0·76 ± 0·16) × 10^{-2}. Complex neutral-atom scattering factors[22,23] were employed for all atoms. The weighting scheme adopted was $w = (0\cdot49 + |F_o| + 0\cdot02955\ F_o^2)^{-1}$, which has been converted to an absolute scale of F_o.

In the final cycles of refinement a total of 102 parameters were varied simultaneously, these consisting of 33 positional parameters, 66 anisotropic temperature-factor components, 1 overall isotropic temperature factor for the hydrogen atoms, the secondary extinction coefficient, and an overall scale factor. The final weighted index R' [$= (\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}F_o)$] was 0·065 for 816 unique observed reflections with a corresponding unweighted index, R, of 0·051. A similar refinement in $P2_1$ gave values of 0·059 and 0·048, respectively. A

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final difference-Fourier synthesis revealed no unexpected features. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21019 (6 pp., 1 microfiche).*

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