

ring. It also occurs in ethylbenzene and its derivatives (Kataeva, Litvinov, Strobykina & Kataev, 1990; Scharfenberg, Roszondai & Hargittai, 1980).

Fourth, the N(1)—C(7)—C(8)—O(1) moiety has the *sc* conformation with C(8)—O(1) pointing towards the C(6) side of the pyrimidine ring. The *sc* conformation seems the usual form for the moiety irrespective of whether the trigonal N is part of a ring or not (Kataev, 1990). In this respect the N—C—C—OH moiety in (1)–(4) follows the conformational behaviour of 2-aminoethanol in which heavy-atom *gauche* forms are favoured over heavy-atom *trans* forms (Van Alsenoy, Stam, Ewbank & Schafer, 1986).

We now turn to the H-bonding scheme and note that the molecules in (1) form infinite zigzag chains along the *b* axis, O(1)—H \cdots N(3')(-*x*, $\frac{1}{2} + y$, 2 - *z*) with the following parameters: O(1)—H 0.88 (5), H \cdots N(3') 2.11 (5), O(1) \cdots N(3') 2.920 (5) Å, O(1)—H \cdots N(3') 156 (1)°. In contrast, compounds (2)–(4) all primarily form dimers instead of polymers. One consequence of the O(1)—H \cdots N(3') bridge in (1) is that O(2) is not an acceptor to an H bond. Thus, the C(2)=O(2) bond length is 1.225 (5) Å, very close to the value expected (1.225 Å) for a free, unbridged C=O bond (Popelier, Lenstra, Van Alsenoy & Geise, 1990). In the related compound (2), C(2)=O(2) is engaged in H bonding and the bond is indeed lengthened [1.246 (2) Å]. Another consequence is the value $\varphi = 169$ (3)° for the torsion angle C(7)—C(8)—O(1)—H. We also calculated this angle for compounds (2)–(4) using the data retrieval system of the Cambridge Structural Database (Allen *et al.*, 1979), and found -111 (2)° in (2), 93 (2)° in (3) and 78 (3)° in (4). The scatter means that the conformation of

the C(7)—C(8)—O(1)—H moiety is dictated by the H-bonding scheme adopted by the particular compound.

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Structure of Difluorotriphenylphosphorane

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Abstract. C₁₈H₁₅F₂P, *M_r* = 300.29, orthorhombic, *Pbcn*, *a* = 6.105 (2), *b* = 16.634 (3), *c* = 14.356 (3) Å, *V* = 1458 (1) Å³, *Z* = 4, *D_x* = 1.368 Mg m⁻³, λ(Mo Kα) = 0.71069 Å, μ = 0.194 mm⁻¹, *F*(000) = 624, *T* = 294 K, *R* = 0.045 for 729 observed independent reflections. Difluorotriphenylphosphorane [(C₆H₅)₃PF₂] displays a trigonal bipyramidal geometry about the P atom, with the two F atoms

occupying axial positions. The three phenyl groups in the equatorial positions are not 'geared' in a regular propeller arrangement; one of the three rings is twisted in the opposite direction to that of the other two.

Introduction. Fluorophosphoranes have featured prominently in studies of pentavalent phosphorus

Table 1. Atomic fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (\AA^2) with *e.s.d.'s* in parentheses for independent atoms

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
P(1)	5000	2499.0 (9)	2500	3.12 (6)
F(1)	7631 (3)	2514 (3)	2801 (2)	3.9 (1)
C(1)	5662 (6)	1947 (2)	1438 (3)	3.1 (2)
C(2)	4112 (8)	1460 (3)	1016 (3)	4.0 (2)
C(3)	4601 (9)	1055 (3)	210 (3)	4.8 (3)
C(4)	6613 (10)	1138 (3)	-198 (4)	5.3 (3)
C(5)	8184 (9)	1616 (3)	211 (4)	4.9 (3)
C(6)	7705 (8)	2007 (3)	1021 (3)	4.2 (2)
C(7)	5000	3595 (3)	2500	3.4 (3)
C(8)	6778 (8)	4023 (3)	2169 (3)	4.4 (2)
C(9)	6740 (10)	4858 (3)	2154 (4)	5.5 (3)
C(10)	5000	5266 (4)	2500	5.5 (4)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) with *e.s.d.'s* in parentheses

P(1)—F(1)	1.663 (2)	C(3)—C(4)	1.368 (7)
P(1)—C(1)	1.825 (4)	C(4)—C(5)	1.378 (7)
P(1)—C(7)	1.824 (6)	C(5)—C(6)	1.364 (7)
C(1)—C(2)	1.385 (6)	C(7)—C(8)	1.383 (5)
C(1)—C(6)	1.387 (6)	C(8)—C(9)	1.389 (6)
C(2)—C(3)	1.373 (6)	C(9)—C(10)	1.355 (6)
F(1)—P(1)—F(1 ⁱ)	178.3 (2)	C(2)—C(3)—C(4)	120.4 (5)
F(1)—P(1)—C(1)	90.6 (1)	C(3)—C(4)—C(5)	120.1 (5)
F(1)—P(1)—C(1 ⁱ)	90.2 (1)	C(4)—C(5)—C(6)	119.2 (5)
F(1)—P(1)—C(7)	89.2 (1)	C(1)—C(6)—C(5)	121.8 (5)
C(1)—P(1)—C(1 ⁱ)	119.6 (2)	P(1)—C(7)—C(8)	121.0 (3)
C(1)—P(1)—C(7)	120.2 (1)	C(8)—C(7)—C(8 ⁱ)	118.0 (6)
P(1)—C(1)—C(2)	120.5 (3)	C(7)—C(8)—C(9)	120.5 (5)
P(1)—C(1)—C(6)	121.6 (3)	C(8)—C(9)—C(10)	120.5 (6)
C(2)—C(1)—C(6)	117.9 (4)	C(9)—C(10)—C(9 ⁱ)	119.9 (7)
C(1)—C(2)—C(3)	120.5 (5)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

geometry and configurational stability (Luckenbach, 1973; Cavell, Gibson & The, 1977; De'Ath, Denney, Denney & Hsu, 1976; Muetterties, Mahler & Schmutzler, 1963). We recently discovered (Doxsee, Hanawalt & Weakley, 1992) a facile means for the preparation of difluorophosphoranes such as $(\text{C}_6\text{H}_5)_3\text{PF}_2$ (Muetterties, Mahler & Schmutzler, 1963; Appel & Gilak, 1974), which bear promise as fluorinating agents for organic compounds (Kobayashi & Akashi, 1968). Theoretical (Hoffmann, Howell & Muetterties, 1972) and crystallographic (Sheldrick, 1975) suggestions regarding the structural implications of π bonding in such pentavalent phosphorus compounds prompted us to examine the crystal structure of $(\text{C}_6\text{H}_5)_3\text{PF}_2$.

Experimental. Difluorotriphenylphosphorane was prepared from equimolar amounts of triphenylphosphine and mercuric fluoride in dry benzene (Doxsee, Hanawalt & Weakley, 1992) and recrystallized from dry toluene. A colorless lath ($0.07 \times 0.15 \times 0.48$ mm), cleaved under Apiezon grease from a larger crystal, was sealed in a Lindemann-glass capil-

lary. Cell parameters were determined from 25 centred reflections ($11.1 < 2\theta < 17.3^\circ$) using a Rigaku AFC-6R diffractometer, graphite monochromator, Mo $K\alpha$ radiation, ω - 2θ scan, speed 8° min^{-1} (on ω), width $(0.85 + 0.30 \tan \theta)^\circ$. 1530 reflections were measured ($2.5 \leq 2\theta \leq 50^\circ$; $0 \leq h \leq 7$, $0 \leq k \leq 20$, $-17 \leq l \leq 0$). Three standards measured every 300 reflections revealed no significant intensity variations. No absorption or extinction corrections were applied. 1530 reflections were unique, of which 729 were observed with $I \geq 3\sigma(I)$. H atoms were identified as eight strongest peaks in the difference map and refined isotropically; 12 independent P, F and C atoms were identified in the *E* map using *SHELXS86* (Sheldrick, 1985). All calculations used the *TEXSAN* program suite (Molecular Structure Corporation, 1989); 127 parameters; $\sum w(|F_o| - |F_c|)^2$ minimized in full-matrix least squares; $w = 1/\sigma^2(F)$; final maximum $|\Delta/\sigma| = 0.05$, $\Delta\rho_{\text{max}} = 0.24$ and $\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$. Final $R = 0.045$, $wR = 0.051$ and $S = 1.68$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Fractional atomic coordinates are listed in Table 1, and bond distances and angles are presented in Table 2.* The molecular structure of difluorotriphenylphosphorane is presented in Fig. 1. The structure, confirming the trigonal bipyramidal geometry of $(\text{C}_6\text{H}_5)_3\text{PF}_2$, with the two F atoms in the axial positions, is perhaps best discussed in relation to that reported for the perfluoro derivative,

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles involving H atoms, torsion angles, intermolecular close contacts, stereoscopic and packing diagrams, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54963 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0563]

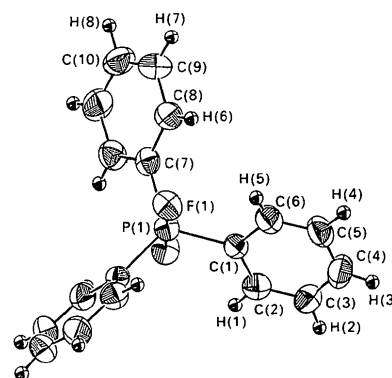


Fig. 1. Molecular structure of difluorotriphenylphosphorane.

(C₆F₅)₃PF₂ (Sheldrick, 1975). Both phosphoranes crystallize in space group *Pbcn*, with the molecule lying on a crystallographic diad axis. However, whereas the perfluoro derivative displays a regular propeller-like arrangement of the three phenyl rings, one of the phenyl rings in (C₆H₅)₃PF₂ opposes the propeller arrangement of the other two.

The P—F bond length in (C₆H₅)₃PF₂, at 1.663 (2) Å, is slightly longer than that in (C₆F₅)₃PF₂ [1.636 (2) Å], perhaps as a result of the increased electrophilicity of P in (C₆F₅)₃PF₂ owing to increased electron withdrawal by the perfluoroaryl substituents. The aryl rings in (C₆F₅)₃PF₂ display smaller dihedral angles with the equatorial plane (*ca* 33.8, 37.9 and 37.9°) than the phenyl rings in (C₆H₅)₃PF₂ (*ca* 51.5, 63.4 and 63.4°). Theoretical studies (Hoffmann, Howell & Muetterties, 1972), suggest that π donors will align their orbitals parallel to the equatorial plane of pentavalent phosphorus, while π acceptors prefer to align their orbitals perpendicular to this plane. The larger dihedral angles observed for (C₆H₅)₃PF₂, bearing better π donor substituents, suggest a shift in structure toward the predicted conformation. However, the P—C bond lengths, at approximately 1.82 Å, are not statistically different in the two phosphoranes, suggesting that π -bonding effects may be quite subtle.

Other metrical parameters in the two phosphoranes are nearly identical and in accord with near-

ideal trigonal bipyramidal geometry: the F—P—F bond angle is 178.3 (2)° in (C₆H₅)₃PF₂ and 180.0° in (C₆F₅)₃PF₂, and the C—P—C angles in both are approximately 120°.

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Three Substituted Hexahydro-5,8-dimethanonaphthalenes

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Abstract. *rel*-(4a*S*,5*S*,8*S*,8a*S*)-1,4,4a,5,8,8a-Hexahydro-2-methoxy-5-methyl-5,8-methanonaphthalene-5,8-dione (*2a*), C₁₃H₁₄O₃, *M_r* = 218.28, monoclinic, *P*2₁/*c*, *a* = 13.561 (4), *b* = 6.598 (1), *c* = 14.108 (4) Å, β = 118.37 (2)°, *V* = 1110.8 (6) Å³, *Z* = 4, *D_x* = 1.310 g cm⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 0.86 cm⁻¹, *F*(000) = 464, *T* = 298 K, *R* = 0.0969 (*wR*

= 0.0422) for 1014 reflections. *rel*-(4a*S*,5*S*,8*S*,8a*S*)-2,4a-Dibromo-1,4,4a,5,8,8a-hexahydro-5-methyl-5,8-methanonaphthalene-5,8-dione (*2b*), C₁₂H₁₀Br₂O₂, *M_r* = 346.05, monoclinic, *P*2₁/*n*, *a* = 6.556 (2), *b* = 25.739 (10), *c* = 7.436 (5) Å, β = 111.25 (4)°, *V* = 1170 (1) Å³, *Z* = 4, *D_x* = 1.970 g cm⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 68.46 cm⁻¹, *F*(000) = 672, *T* = 298 K, *R* = 0.0674 (*wR* = 0.0455) for 1389 observed reflections. *rel*-(4*R*,4a*R*,5*R*,8*S*,9*S*)-1,4,4a,5,8,8a-Hexa-

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