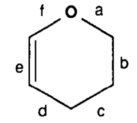
Discussion. The crystal structure of racemic 2′,3′-dimethoxywarfarin (I) contains hydrogen-bonded columnar chains of molecules related by a twofold screw operation along the *b* axis, therefore linking molecules of like configuration. An hydroxyl group on one molecule donates a hydrogen bond to a coumarin carbonyl of a neighbor, O···O = 2·812 (3), H···O = 1·97 (3) Å, O—H···O angle 173 (2)°. The hydroxy group is disposed axially and the 4-aryl substituent pseudoequatorially (*trans*) on a dihydropyran ring, which adopts a *d*,*e*-planar conformation with ring displacement asymmetry parameter ΔC_2 = 0·0669 (12) (Nardelli, 1983). The 2′-methoxy methyl group rotates out of the phenyl plane (76°) while the 3′-methoxy methyl lies nearly in the phenyl plane (4°). The dihedral angle between the phenyl and coumarin planes is 78°. An *ORTEP* drawing (Johnson, 1976) of the molecule is given in Fig. 1.

The crystal structure of (+)-4′-methylwarfarin (II) is pseudoisomorphous with that of (*S*)-(−)-warfarin (Valente, Trager & Jensen, 1975). Hydrogen bonding occurs between screw related molecules along the *b* axis with donor hydroxyls and acceptor carbonyls, the O···O and H···O separations are 2·746 (3) and 1·95 (3) Å, respectively, with an O—H···O angle of 174 (3)°. As in (I), the hydroxyl group is disposed axially, the 4′-methylphenyl group is pseudoequatorial and its plane is inclined at 70° with respect to the coumarin plane. The embedded dihydropyran ring is a nearly undistorted half-chair; ring displacement asymmetry parameter ΔC_2 = 0·0156 (17). A drawing of the structure is given in Fig. 2; intraring torsion angles for (I) and (II) are given in Table 5.

Table 5. *Torsion angles* (°) *in the dihydropyran rings*

E.s.d.'s are at most about 0·4°; common configuration.



	a	*b*	*c*	*d*	*e*	*f*
(I)	−51·9	58·9	−34·2	2·0	5·4	20·9
(II)	−44·2	62·1	−47·5	16·4	0·4	14·2

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Structure of Tris(pentafluorophenyl)phosphine

BY ANASTAS KARIPIDES AND CONNIE MILLER COSIO

Department of Chemistry, Miami University, Oxford, Ohio 45056, *USA*

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Abstract. $C_{18}F_{15}P$, M_r = 532·1, monoclinic, $P2_1/c$, a = 7·194 (2), b = 17·930 (4), c = 13·834 (2) Å, β = 94·29 (2)°, V = 1779 Å^3, Z = 4, D_m = 2·00, D_x = 1·99 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 3·3 cm^{-1}, $F(000)$ = 1032, $T \simeq$ 296 K, final R = 0·055 for 2352 unique observed reflections. The three planar C_6F_5 groups are twisted about the C—P bonds to give extensive deviations from molecular C_3 symmetry similar to those in the crystal structure of triphenylphosphine. The P—C bond lengths and C—P—C bond angles are 1·834 (4), 1·832 (4), 1·824 (4) Å and 104·4 (2), 106·0 (2), 99·6 (1)°, respectively. There are two short C···F non-bonded distances in the structure (2·99, 2·79 Å).

Introduction. Although the structural characteristics of free triphenylphosphine as well as $(C_6H_5)_3P$ fragments have been extensively studied (Daly, 1964; Brock & Ibers, 1973; Bye, Schweizer & Dunitz, 1982), there have been very few reported structural

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investigations of the corresponding fluoro-substituted triarylphosphines (Hunter, Muir & Sharp, 1986; Naae & Lin, 1979). Substitution of fluorine for hydrogen can often lead to significant changes in properties. For example, there is a sizeable difference in the melting points of $(C_6F_5)_3P$ (390 K) and $(C_6H_5)_3P$ (352 K) (Wall, Donadio & Pummer, 1960). As part of a program to study the structural effects of fluorine substitution in aryl organometallic compounds, we have determined the crystal structure of tris(pentafluorophenyl)phosphine.

Experimental. The title compound was prepared from the reaction of the Grignard reagent, C_6F_5MgBr, and PCl_3 in diethyl ether solution. The isolated crude $(C_6F_5)_3P$ was purified by sublimation, and colorless needles suitable for X-ray diffraction were grown from absolute ethanol. The density was determined by flotation in a potassium iodide solution. Crystal size: 0·20 × 0·20 × 0·10 mm (mounted in air). Cell parameters and an orientation matrix for data collection were determined from 25 centered reflections ($8 < 2\theta < 38°$) at 296 ± 1 K. Intensity data out to $(\sin\theta)/\lambda = 0·59$ Å^{-1} collected on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite-crystal incident-beam monochromator using the $\theta/2\theta$-scan mode. Each of three control reflections measured every 40 min showed no significant change in intensity. Index range: h 0 to 8; k 0 to 21; l −16 to 16. Total number of unique reflections measured was 3248. Of these, 2352 had $F_o > 1/2\sigma(F_o)$ and were used for refinement. Corrections for absorption and secondary extinction were not applied. The structure was solved by Patterson and difference Fourier methods and refined by a full-matrix least-squares procedure using established programs (Karipides, 1979). Anisotropic refinement (on F) of all atoms converged to $R = 0·055$, $wR = 0·056$; error in an observation of unit weight = 1·31; $w^{-1} = [\sigma(F_o)]^2 + (0·02F_o)^2$. Maximum shift/e.s.d. in the final least-squares refinement was 0·01. Scattering factors and anomalous-dispersion corrections for phosphorus were from Cromer & Waber (1974). Maxima and minima in the final difference map: 0·27, −0·34 e Å^{-3}. Final atom coordinates are given in Table 1.*

Table 1. *Fractional coordinates with e.s.d.'s and equivalent isotropic displacement parameters for tris(pentafluorophenyl)phosphine*

$B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ where the anisotropic β_{ij} parameters are defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	B_{eq}(Å^2)
P	0·1484 (1)	0·24321 (6)	0·91799 (7)	3·70
C(1*a*)	0·2559 (4)	0·2439 (2)	1·0424 (2)	3·44
C(2*a*)	0·3778 (5)	0·3022 (2)	1·0654 (3)	4·17
C(3*a*)	0·4832 (5)	0·3063 (2)	1·1510 (3)	4·54
C(4*a*)	0·4709 (5)	0·2510 (2)	1·2179 (3)	4·25
C(5*a*)	0·3556 (5)	0·1914 (2)	1·1983 (3)	3·95
C(6*a*)	0·2509 (5)	0·1878 (2)	1·1112 (2)	3·52
C(1*b*)	−0·0118 (5)	0·3228 (2)	0·9132 (2)	3·67
C(2*b*)	−0·0626 (5)	0·3708 (2)	0·9856 (3)	4·06
C(3*b*)	−0·1745 (6)	0·4312 (2)	0·9677 (3)	4·94
C(4*b*)	−0·2429 (6)	0·4465 (2)	0·8746 (4)	5·29
C(5*b*)	−0·2015 (5)	0·4003 (3)	0·8009 (3)	4·90
C(6*b*)	−0.0877 (5)	0·3407 (2)	0·8211 (3)	4·21
C(1*c*)	−0·0201 (5)	0·1670 (2)	0·9126 (2)	3·35
C(2*c*)	−0·1797 (5)	0·1632 (2)	0·9624 (2)	3·76
C(3*c*)	−0·3098 (5)	0·1082 (2)	0·9463 (3)	4·12
C(4*c*)	−0·2849 (5)	0·0545 (2)	0·8777 (3)	4·42
C(5*c*)	−0·1276 (6)	0·0556 (2)	0·8278 (3)	4·47
C(6*c*)	−0·0001 (5)	0·1113 (2)	0·8450 (2)	3·99
F(2*a*)	0·3945 (3)	0·3566 (1)	0·9996 (2)	5·95
F(3*a*)	0·5993 (3)	0·3639 (1)	1·1699 (2)	6·79
F(4*a*)	0·5716 (3)	0·2548 (1)	1·3033 (2)	5·82
F(5*a*)	0·3444 (3)	0·1367 (1)	1·2633 (2)	5·15
F(6*a*)	0·1425 (3)	0·1280 (1)	1·0952 (1)	4·73
F(2*b*)	0·0001 (3)	0·3585 (1)	1·0782 (2)	5·53
F(3*b*)	−0·2158 (4)	0·4763 (1)	1·0398 (2)	6·84
F(4*b*)	−0·3537 (4)	0·5058 (2)	0·8574 (2)	8·00
F(5*b*)	−0·2683 (3)	0·4143 (2)	0·7097 (2)	7·23
F(6*b*)	−0·0525 (3)	0·2953 (1)	0·7468 (2)	5·40
F(2*c*)	−0·2091 (3)	0·2146 (1)	1·0300 (2)	5·18
F(3*c*)	−0·4642 (3)	0·1076 (1)	0·9942 (2)	6·46
F(4*c*)	−0·4146 (3)	0·0027 (1)	0·8598 (2)	6·73
F(5*c*)	−0·1053 (4)	0·0041 (1)	0·7596 (2)	6·94
F(6*c*)	0·1508 (3)	0·1105 (1)	0·7937 (2)	6·16

Discussion. There is no crystallographic symmetry imposed by the space group. The crystal structure consists of discrete $(C_6F_5)_3P$ molecules linked by a network of van der Waals interactions. Views of the molecular structure and packing are illustrated in Figs. 1 and 2, respectively. Bond distances and angles are given in Table 2.

The molecular structure may be conveniently described in terms of the conformations of the three perfluorophenyl groups. Following Bye, Schweizer & Dunitz (1982), these aryl-ring conformations are succinctly expressed in terms of three positive torsion angles, each defined by $(\tau_1 + \tau_2 + \tau)/2$, where τ_1 and τ_2 are the two D—P—C—C torsion angles involving the apical C atom and the two *ortho*-C atoms in each ring. The reference atom D is a 'dummy' point placed at the centroid of the three apical C atoms [C(1*a*), C(1*b*), C(1*c*)]. For $(C_6F_5)_3P$ these torsion angles are 62, 45 and 10° for rings '*a*', '*b*' and '*c*', respectively. The molecular structure thus deviates extensively from ideal C_3 symmetry. Corresponding angles in triphenylphosphine are 59, 28 and 25° (Daly, 1964).

The P—C lengths and C—P—C and C—C—P angles are similar to values observed in $(C_6H_5)_3P$. The pentafluorophenyl group presents a smaller steric demand than mesityl or 2,6-dimethylphenyl groups, where C—P—C angles open to about 109·5° (av.) leading to a greater flattening of the phosphorus pyramid (Blount, Maryanoff & Mislow, 1975; Sobolev, Chetkina, Romm & Gur'yanova, 1976).

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* Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52006 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

All three independent pentafluorophenyl rings are planar within experimental error. The apical bond angles, C(2*a*)—C(1*a*)—C(6*a*) 116·0 (3), C(2*b*)—C(1*b*)—C(6*b*) 114·3 (3), C(2*c*)—C(1*c*)—C(6*c*) 115·6 (3)°, are smaller than the corresponding angles of 119·3 (4), 119·6 (4), 120·6 (5)° in the hydrocarbon analog, $(C_6H_5)_3P$. This compression of about 4·5° in the apical angle in $(C_6F_5)_3P$ is consistent with the arguments of Domenicano, Vaciago & Coulson (1975*a*,*b*) concerning the large σ-electron withdrawing properties of a C_6F_5 ring.

The shortest intermolecular and intramolecular C···F non-bonded interactions are C(6*b*)—F(6*b*)···C(4*a*)($x-1$, $0·5-y$, $z-0·5$) 2·985 (4) and C(1*a*)···F(6*a*) 2·793 (4) Å, respectively. These non-bonded contacts are shorter than the 3·1 to 3·2 Å predicted for a C···F non-bonded distance from van der Waals radii (Bondi, 1964; Nyburg & Faerman, 1985). The effect of the polar nature of C—F bonds on the charge distribution in this unsymmetrical molecule is evident from the observation that $(C_6F_5)_3P$ is considerably less basic than $(C_6H_5)_3P$ (Wall, Donadio & Pummer, 1960). Such polarization in the charge distribution could lead to enhancement of the electrostatic component of the non-bonded crystal-lattice energy and thus contribute to a tighter degree of molecular packing.

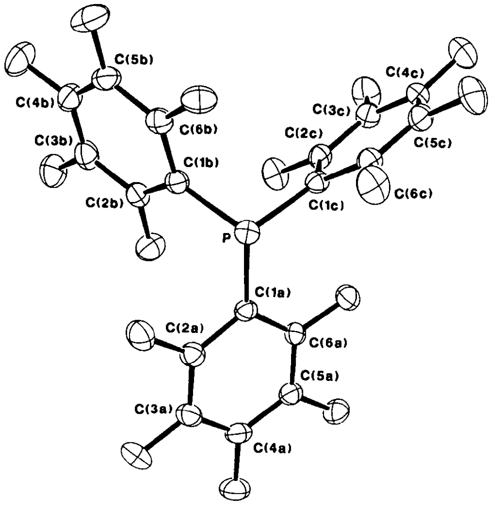

Fig. 1. A perspective view of the $(C_6F_5)_3P$ molecular structure. The ring C atoms are numbered serially C(1)···C(6) for each ring, '*a*', '*b*', or '*c*'. F atoms have the same serial number as the C atom to which they are bonded, but labels have been omitted for clarity.

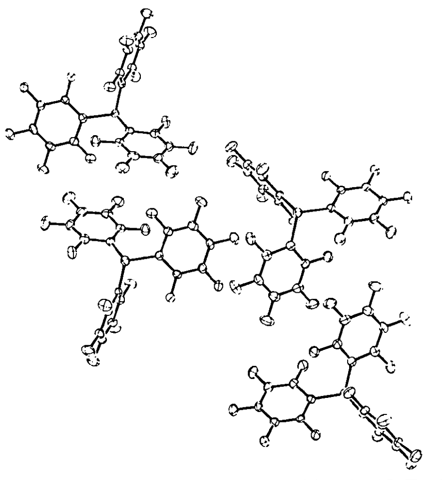

Fig. 2. A view of the molecular packing in $(C_6F_5)_3P$.

Table 2. *Selected bond lengths* (Å) *and angles* (°) *with e.s.d.'s for tris(pentafluorophenyl)phosphine*

P—C(1*a*)	1·834 (4)	C(4*b*)—C(5*b*)	1·363 (6)
P—C(1*b*)	1·832 (4)	C(5*b*)—C(6*b*)	1·363 (5)
P—C(1*c*)	1·824 (4)	C(2*b*)—F(2*b*)	1·344 (5)
C(1*a*)—C(2*a*)	1·386 (5)	C(3*b*)—F(3*b*)	1·334 (5)
C(1*a*)—C(6*a*)	1·387 (5)	C(4*b*)—F(4*b*)	1·339 (5)
C(2*a*)—C(3*a*)	1·360 (6)	C(5*b*)—F(5*b*)	1·339 (4)
C(3*a*)—C(4*a*)	1·365 (6)	C(6*b*)—F(6*b*)	1·350 (4)
C(4*a*)—C(5*a*)	1·367 (4)	C(1*c*)—C(2*c*)	1·384 (5)
C(5*a*)—C(6*a*)	1·373 (5)	C(1*c*)—C(6*c*)	1·384 (5)
C(2*a*)—F(2*a*)	1·346 (4)	C(2*c*)—C(3*c*)	1·367 (5)
C(3*a*)—F(3*a*)	1·341 (4)	C(3*c*)—C(4*c*)	1·373 (5)
C(4*a*)—F(4*a*)	1·341 (4)	C(4*c*)—C(5*c*)	1·369 (5)
C(5*a*)—F(5*a*)	1·338 (4)	C(5*c*)—C(6*c*)	1·364 (5)
C(6*a*)—F(6*a*)	1·335 (4)	C(2*c*)—F(2*c*)	1·342 (4)
C(1*b*)—C(2*b*)	1·391 (5)	C(3*c*)—F(3*c*)	1·335 (4)
C(1*b*)—C(6*b*)	1·386 (5)	C(4*c*)—F(4*c*)	1·326 (4)
C(2*b*)—C(3*b*)	1·360 (5)	C(5*c*)—F(5*c*)	1·340 (4)
C(3*b*)—C(4*b*)	1·372 (6)	C(6*c*)—F(6*c*)	1·341 (4)
P—C(1*a*)—C(2*a*)	115·8 (3)	C(1*a*)—P—C(1*b*)	104·4 (2)
P—C(1*a*)—C(6*a*)	127·5 (3)	C(1*a*)—P—C(1*c*)	106·0 (2)
P—C(1*b*)—C(2*b*)	130·9 (3)	C(1*b*)—P—C(1*c*)	99·6 (1)
P—C(1*b*)—C(6*b*)	114·6 (3)	C(2*a*)—C(1*a*)—C(6*a*)	115·0 (3)
P—C(1*c*)—C(2*c*)	126·2 (3)	C(2*b*)—C(1*b*)—C(6*b*)	116·0 (3)
P—C(1*c*)—C(6*c*)	117·8 (3)	C(2*c*)—C(1*c*)—C(6*c*)	114·3 (3)

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