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Tris(pentafluorophenyl)difluorophosphorane

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Abstract. $(C_6F_5)_3PF_2$, orthorhombic, *Pbcn*, $a=8\cdot903$ (1), $b=11\cdot152$ (1), $c=18\cdot269$ (2) Å, $M=570\cdot17$, $Z=4$, $D_x=2\cdot09$ g cm^{-3}. Trigonal-bipyramidal geometry is observed for the molecule, in which the F atoms occupy the axial positions, and the pentafluorophenyl groups lie in a 'propeller-like' arrangement about the equatorial plane. A crystallographic diad axis passes through the P atom and one of the pentafluorophenyl groups. The two independent benzene ring systems make dihedral angles of 33·5 and 36·2° with the equatorial plane. The bond lengths to P (librationally corrected) are: P–F 1·638 (2), P–C 1·823 (4) and 1·815 (3) Å.

Introduction. Cell dimensions were determined by a least-squares fit to the settings for 15 reflexions ($\pm hkl$) on a Syntex $P2_1$ four-circle diffractometer (Mo $K\alpha$, 0·71069 Å). Intensities, from a prismatic crystal (approximately 0·24 × 0·28 × 0·34 mm) sealed in a Lindemann glass capillary, were collected on the diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Measurements were carried out in the θ–2θ mode ($3\cdot0 \le 2\theta \le 50\cdot0°$) at scan speeds varying linearly between 2·93° min^{-1} (150 c.p.s. and below) and 29·30° min^{-1} (5000 c.p.s. and above). Scan and background times were equal. Three standard reflexions, monitored at regular intervals, did not display any significant variations due to crystal deterioration. Lorentz and polarization but no absorption [μ(Mo $K\alpha$) = 2·6 cm^{-1}] corrections were applied. From the 1880 reflexions recorded, 1310 (69·7%) were retained for use in the structure analysis, after application of the criterion $F \ge 2\cdot5\sigma(F)$, where $\sigma(F)$ is based on the counting statistics.

The positions of 16 of the 20 independent atoms were obtained by direct methods, the remaining atoms being located from subsequent difference syntheses. Atom positional parameters and anisotropic temperature factors were refined by full-matrix least-squares calculations. The final value of the generalized index $R_G=[\sum w\Delta^2/\sum wF_o^2]^{1/2}$ was 0·059, with a weighted residual $R_w=\sum w^{1/2}\Delta/\sum w^{1/2}F_o$ of 0·048 and a corresponding unweighted R of 0·042. The weights applied were given by $w=k/(\sigma^2F_o+gF_o^2)$ where k and g refined to 1·5984 and 0·001294 respectively. Complex neutral-atom scattering factors (Cromer, 1965; Cromer & Waber, 1965) were employed. The final coordinates are in Table 1 with their anisotropic temperature-factor components in Table 2. The full covariance matrix was implemented in the estimation of the bond lengths and selected bond angles in Tables 3 and 4.

The rigid-body model of Schomaker & Trueblood (1968) was satisfactorily used to describe the thermal motion observed in an analogous trigonal-bipyramidal acyclic pentacoordinate P derivative, 2-methyl-5-(tetrafluorophosphoranyl)pyrrole (Sheldrick, 1973);

Table 1. *Positional parameters* (× 10^4)

	x	y	z
P	0	6322 (1)	2500
F(2)	1741 (2)	6323 (1)	2787 (1)
C(11)	0	7955 (3)	2500
C(12)	−350 (3)	8599 (3)	1875 (2)
C(13)	−337 (3)	9832 (3)	1874 (2)
C(14)	0	10453 (4)	2500
F(12)	−683 (2)	8031 (2)	1257 (1)
F(13)	−675 (2)	10426 (2)	1261 (1)
F(14)	0	11644 (2)	2500
C(21)	559 (3)	5500 (3)	1688 (2)
C(22)	1682 (4)	5911 (3)	1299 (2)
C(23)	2097 (4)	5310 (3)	604 (2)
C(24)	1393 (4)	4261 (3)	428 (2)
C(25)	258 (4)	3831 (3)	861 (2)
C(26)	−141 (3)	4441 (2)	1486 (2)
F(22)	2383 (2)	6955 (2)	1377 (1)
F(23)	3154 (3)	5768 (2)	168 (1)
F(24)	1777 (3)	3677 (2)	−178 (1)
F(25)	−436 (3)	2813 (2)	685 (1)
F(26)	−1219 (2)	3982 (2)	1903 (1)

Table 2. *Anisotropic temperature factors* (Å^2 × 10^3)

The anisotropic temperature factor takes the form:

$$\exp\left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{13}lhc^*a^*+2U_{12}hka^*b^*)\right].$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	32 (1)	33 (1)	41 (1)	0	0 (1)	0
F(2)	33 (1)	45 (1)	50 (1)	1 (1)	−4 (1)	−1 (1)
C(11)	34 (3)	32 (2)	37 (3)	0	−2 (2)	0
C(12)	36 (2)	41 (2)	41 (2)	−1 (2)	−3 (2)	−1 (2)
C(13)	39 (2)	42 (2)	48 (2)	12 (2)	−1 (2)	4 (2)
C(14)	33 (3)	32 (3)	64 (3)	0	2 (3)	0
F(12)	79 (2)	49 (1)	39 (1)	−1 (1)	−12 (1)	0 (1)
F(13)	84 (2)	50 (1)	60 (1)	18 (1)	−9 (1)	6 (1)
F(14)	57 (2)	31 (1)	96 (2)	0	−5 (2)	0
C(21)	34 (2)	32 (2)	42 (2)	0 (2)	−2 (2)	3 (1)
C(22)	41 (2)	40 (2)	48 (2)	−3 (2)	0 (2)	−1 (2)
C(23)	51 (2)	54 (2)	41 (2)	2 (2)	3 (2)	8 (2)
C(24)	62 (2)	49 (2)	43 (2)	−8 (2)	−5 (2)	16 (2)
C(25)	59 (2)	34 (2)	56 (2)	−6 (1)	−15 (2)	3 (2)
C(26)	42 (2)	35 (2)	47 (2)	2 (1)	−3 (1)	2 (1)
F(22)	56 (1)	54 (1)	63 (1)	−5 (1)	13 (1)	−18 (1)
F(23)	76 (2)	89 (2)	56 (1)	−3 (1)	26 (1)	−6 (1)
F(24)	104 (2)	79 (1)	53 (1)	−25 (1)	5 (1)	17 (1)
F(25)	89 (2)	41 (1)	82 (2)	−17 (1)	−16 (1)	−5 (1)
F(26)	52 (1)	44 (1)	71 (1)	1 (1)	4 (1)	−12 (1)

Table 3. *Bond lengths* (Å) *with librationally corrected values in square brackets*

P——F(2)	1·636 (2)	[1·638]
P——C(11)	1·821 (4)	[1·823]
P——C(21)	1·813 (3)	[1·815]
C(11)–C(12)	1·384 (3)	[1·386]
C(12)–C(13)	1·375 (4)	[1·376]
C(13)–C(14)	1·370 (4)	[1·372]
C(21)–C(22)	1·383 (4)	[1·384]
C(22)–C(23)	1·374 (4)	[1·376]
C(23)–C(24)	1·365 (4)	[1·367]
C(24)–C(25)	1·370 (5)	[1·371]
C(25)–C(26)	1·375 (4)	[1·377]
C(26)–C(21)	1·385 (4)	[1·386]

C(12)–F(12)	1·328 (3)	C(13)–F(13)	1·336 (3)
C(14)–F(14)	1·328 (5)	C(22)–F(22)	1·350 (4)
C(23)–F(23)	1·334 (4)	C(24)–F(24)	1·330 (4)
C(25)–F(25)	1·332 (4)	C(26)–F(26)	1·328 (3)

Table 4. *Bond angles* (°)

F(2)—P——C(11)	89·9 (1)	F(2)—P——C(21)	90·2 (1)
C(11)–P——C(21)	120·4 (1)	C(21)–P——C(21′)	119·3 (2)
C(12)–C(11)–C(12′)	117·5 (4)	C(13)–C(12)–C(11)	121·2 (3)
C(14)–C(13)–C(12)	120·4 (3)	C(13)–C(14)–C(13′)	119·3 (4)
C(26)–C(21)–C(22)	116·4 (3)	C(21)–C(22)–C(23)	122·5 (3)
C(22)–C(23)–C(24)	119·3 (3)	C(23)–C(24)–C(25)	120·2 (3)
C(24)–C(25)–C(26)	119·7 (3)	C(25)–C(26)–C(21)	121·8 (3)

a similar analysis was therefore performed on the anisotropic temperature-factor components (U_{ij}'s) of $(C_6F_5)_3PF_2$. Poor agreement was obtained between the observed and calculated U_{ij} values when all atoms were included, with a generalized index $R_G=[\sum\Delta^2/\sum U_o^2]^{1/2}$ of 0·198, which, however, subsequently improved to 0·124 (r.m.s. discrepancy = 0·0042 Å^2) when the F atoms of the C_6F_5 groups were removed from the analysis. The results of this latter analysis are given in Table 5 and have been used to apply the very small librational corrections to the relevant bond lengths listed in Table 3.*

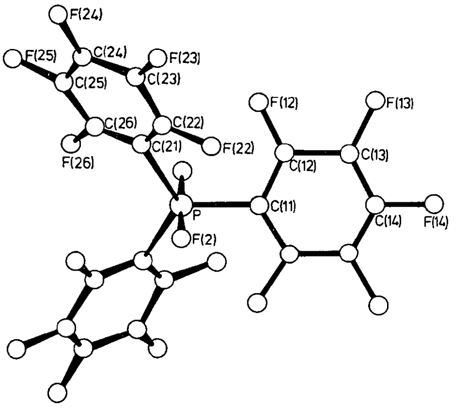

Fig. 1. Atom numbering in the molecule.

Table 5. *Rigid-body librational analysis*

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

T (Å × 10^{-4})	319 (15)	0	−36 (12)
		353 (11)	0
			414 (11)
L (rad × 10^{-4})	7 (1)	0	2 (1)
		13 (2)	0
			9 (2)
S (Å . rad × 10^{-4})	10 (2)	0	−2 (2)
	0	−4 (2)	0
	11 (3)	0	−6 (3)

Origin which gives symmetric **S**: 0, 0·5601, 0·25

Principal root-mean-square amplitudes and direction cosines

T (Å)*			
0·204	0·7387	0	−0·6741
0·188	0	1·0	0
0·171	0·6741	0	0·7387
L (rad)			
0·024	0·8204	0	−0·5717
0·037	0	1·0	0
0·032	0·5717	0	0·8204

* Reduced to keep *U* invariant.

Discussion. In a recent molecular-orbital description of the bonding of pentacoordinate P species (Hoffmann, Howell & Muetterties, 1972), it was predicted 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. The crystal structure analysis of 2-methyl-5-(tetrafluorophosphoranyl)pyrrole has confirmed that the equatorially substituted pyrrole ring, which behaves as a π donor, does in fact lie in the axial plane of the trigonal bipyramid. By analogy it might be expected, disregarding non-bonded interactions, that the potentially π-donor C_6F_5 groups in $(C_6F_5)_3PF_2$ would also lie in the axial plane. Steric considerations, however, suggest that in order to minimize non-bonded interactions between neighbouring *ortho*-substituted F atoms of the C_6F_5 groups and between these and the axial F atoms of the trigonal bipyramid, a position for the C_6F_5 plane intermediate between the axial and equatorial planes should be favoured. These considerations and the lack of structural data on compounds containing acyclic pentacoordinate P in the solid phase (Khaikin & Vilkov, 1971) prompted this study.

The molecules exhibit trigonal-bipyramidal geometry (Fig. 1), with the F atoms occupying the axial positions and the C_6F_5 groups lying in a 'propeller-like' arrangement about the equatorial plane. A crystallographic diad axis passes through the P atom and one of the C_6F_5 groups. The aromatic ring of this C_6F_5 group makes a dihedral angle of 33·5°, those of the other (symmetry-related) C_6F_5 groups 36·2°, with the equatorial plane. This intermediate position is obviously dictated by steric necessity, as shown by the short non-bonded interactions for F(12)···F(2′) and F(12)···F(22) of 2·750 and 2·990 Å respectively. A similar effect is observed in the diphosphetidine,

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30932 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

$[(C_6F_5)F_2PNCH_3]_2$, in which the C_6F_5 group makes a dihedral angle of 23·8° with the equatorial plane (Fild, Sheldrick & Stankiewicz, 1975). The librationally corrected P–C distances of 1·823 (4) and 1·815 (3) Å in $(C_6F_5)_3PF_2$ are similar to that of 1·817 (4) Å in $[(C_6F_5)F_2PNCH_3]_2$, but considerably longer than that of 1·728 (11) Å in 2-methyl-5-(tetrafluorophosphoranyl)pyrrole, where the pyrrole π system behaves as a donor. The fact that any residual donor properties of the C_6F_5 group in $(C_6F_5)_3PF_2$ must be minimal is highlighted by a comparison of the P–F(ax) distance with that in analogous molecules. Electron diffraction studies (Hansen, 1965; Bartell & Hansen, 1965; Yow & Bartell, 1973) on members of the series $(CH_3)_nPF_{5-n}$ $(0 \leq n \leq 3)$ have demonstrated a steady increase in the P–F(eq) and P–F(ax) distances with increasing methyl substitution in these trigonal-bipyramidal molecules, in agreement with the VSEPR model (Gillespie & Nyholm, 1957). Thus the value of the P–F(ax) length varies linearly between 1·577 (5) $(n=0)$ and 1·685 (1) Å $(n=3)$. In $(C_6F_5)_3PF_2$ the P–F(ax) distance of 1·638 (2) Å is shorter even than that of 1·643 (3) Å observed in $(CH_3)_2PF_3$. It may be inferred, therefore, in accordance with the VSEPR model that the electron density in the P–C bond at P, and thereby the extent of electron donation from the substituent group, is much greater in $(CH_3)_2PF_3$ than in $(C_6F_5)_3PF_2$.

A narrowing of the C–C–C angles in the C_6F_5 groups to 117·5 (4) and 116·4 (3)°, at the C bonded to P, parallels a similar observation in $[(C_6F_5)F_2PNCH_3]_2$, where an angle of 115·6 (4)° is observed. The mean values of the C–C and C–F distances are 1·377 (2) (librationally corrected) and 1·333 (3) Å respectively.

The unit cell in the *yz* projection is shown in Fig. 2.

This work was carried out within the technology programme of the Bundesministerium für Forschung und Technologie (BRD). The calculations were carried out on the Institute PDP-10 computer with the crystal structure analysis program *SHELX* (Dr G. M. Sheldrick) and programs written by myself. I am indebted to Dr M. Fild for the provision of crystals and to Frau A. Borkenstein for assistance during the data collection and for the preparation of diagrams.

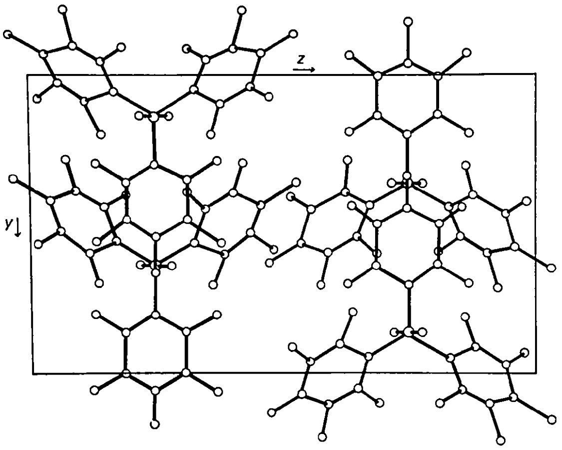

Fig. 2. Projection of the structure perpendicular to [100].

References

Bartell, L. S. & Hansen, K. W. (1965). *Inorg. Chem.* **4**, 1777–1782.

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–23.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Fild, M., Sheldrick, W. S. & Stankiewicz, T. (1975). *Z. anorg. allgem. Chem.* In the press.

Gillespie, R. J. & Nyholm, R. S. (1957). *Quart. Rev.* **11**. 339–380.

Hansen, K. W. (1965). *Inorg. Chem.* **4**, 1775–1776.

Hoffmann, R., Howell, J. M. & Muetterties, E. L. (1972). *J. Amer. Chem. Soc.* **94**, 3047–3058.

Khaikin, L. S. & Vilkov, L. V. (1971). *Russ. Chem. Rev.* **40(12)**, 1014–1029.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

Sheldrick, W. S. (1973). *J. Chem. Soc. Dalton*, pp. 2301–2304.

Yow, H. & Bartell, L. S. (1973). *J. Mol. Struc.* **15**, 209–215.

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The Dimer 2,5-Di-t-butyl-3,6-dineopentylthioeno[3,2-*b*]thiophene

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Abstract. $C_{24}H_{40}S_2$, monoclinic, $P2_1/c$, $a=9·640$ (4), $b=11·938$ (3), $c=11·796$ (6) Å, $\beta=117·86$ (4)°, $Z=2$, $D_x=1·08$ (1), $D_c=1·09$ g cm^{-3}, M.W. 392·715, $R=$ 8·0%. The dimer is planar with the center of inversion mid-way along the internal carbon–carbon bond.

Introduction. The dimer was isolated from the reaction of t-butyl neopentyl trithione with trimethyl phosphite (D. J. Anderson, unpublished results). The trithione had lost two sulfur atoms and had dimerized, but it was difficult to assign the structure of the product