

Difluoro(mesityl)phosphine

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Key indicators

Single-crystal X-ray study
 $T = 178\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$
Disorder in main residue
 R factor = 0.030
 wR factor = 0.087
Data-to-parameter ratio = 14.6

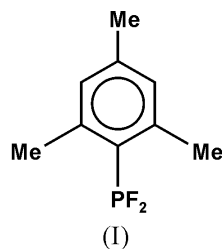
For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $\text{C}_9\text{H}_{11}\text{F}_2\text{P}$, displays mirror symmetry, with all ring C and the P atom lying in the mirror plane. The methyl H atoms are disordered across the mirror plane. Key dimensions around the P atom are P–F 1.5814 (10), P–C 1.8116 (17) Å and F–P–F 95.95 (8)°.

Comment

We are interested in organic derivatives of phosphorus trifluoride. We have published the syntheses of several compounds of the type RPF_2 (Heuer & Schmutzler, 1988, 1989; Wesemann *et al.*, 1992, and references therein), but the X-ray structure determinations have, with one exception (Heuer *et al.*, 1989), been limited to metal complexes. We present here the structure of uncomplexed difluoro(mesityl)-phosphine, (I).

The molecule is shown in Fig. 1; it possesses crystallographic mirror symmetry, with all atoms except fluorine and methyl H atoms (which are disordered, see *Experimental*) lying in the mirror planes. A closely similar arrangement was observed for the hydrogen analogue mesitylphosphine (Bartlett *et al.*, 1987), which also crystallizes in $Pnma$, but the structures do not seem to be isotopic.



The molecular dimensions of (I) may be regarded as normal (Table 1). For discussion purposes, non-corrected bond lengths

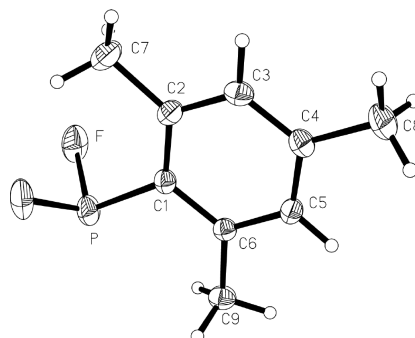


Figure 1

The molecule of the title compound in the crystal. Displacement ellipsoids are shown at the 30% probability level. H-atom radii are arbitrary.

are used, but libration-corrected values are presented in the *Experimental* section. The P–F bond length is 1.5814 (10) Å, with F–P–F 95.95 (8)°, cf. 1.572, 1.581 (2) Å and 96.3 (1)° in the anthracene-9-PF₂ dimer (Heuer *et al.*, 1989). The P–C bond length of 1.8116 (17) Å may be compared with the value of 1.807 (5) Å observed for mesitylphosphine (Bartlett *et al.*, 1987), but is rather shorter than the average of 1.833 Å observed for the series PPh₂(Mes), PPh(Mes)₂ and P(Mes)₃ (Mes is mesityl; Blount *et al.*, 1994), and much shorter than the 1.859 (2) Å in the anthracene dimer, for which steric crowding may be responsible for bond lengthening.

The orientation of the PF₂ group with respect to the ring is given by the torsion angle F–P–C1–C2 of 49.15 (4)°.

One of the methyl H atoms is involved in a short contact to the centroid (C_g) of a ring in the neighbouring layer: C9–H9A···C_g with normalized H···C_g 2.64 Å and C–H···C_g 150°. This could be considered as a C–H···π interaction.

Experimental

The title compound was prepared from the reaction of the corresponding chloride with sodium fluoride in acetonitrile. It was isolated as an oil that crystallized in the form of colourless prisms (m.p. 408–410 K), extremely sensitive to moist air (Heuer, 1989). For this reason, the crystal used for structure determination was rather larger than usual.

Crystal data

C₉H₁₁F₂P
M_r = 188.15
 Orthorhombic, *Pnma*
a = 13.261 (5) Å
b = 7.185 (2) Å
c = 9.735 (3) Å
V = 927.6 (5) Å³
Z = 4
D_x = 1.347 Mg m⁻³

Mo *Kα* radiation
 Cell parameters from 50 reflections
 θ = 8–11.5°
 μ = 0.27 mm⁻¹
T = 178 (2) K
 Block, colourless
 0.7 × 0.7 × 0.7 mm

Data collection

Nicolet R3 diffractometer
 ω scans
 2236 measured reflections
 1154 independent reflections
 1014 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.015
 θ_{\max} = 27.5°

h = 0 → 17
k = 0 → 9
l = -12 → 12
 3 standard reflections
 every 147 reflections
 intensity decay: 1.5%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.030
wR (*F*²) = 0.087
S = 1.09
 1154 reflections
 79 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.2323P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.21 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.34 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

P–F	1.5814 (10)	P–C1	1.8116 (17)
F–P–F ⁱ	95.95 (8)	F–P–C1	100.88 (5)
F–P–C1–C2	49.15 (4)		

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

The aromatic atoms H3 and H5 were refined freely. The methyl H atoms, which are disordered across the mirror plane, could nonetheless be identified in difference syntheses; the methyl groups were then idealized and refined as rigid groups allowed to rotate but not tip. The structure could also be refined with ordered methyl groups in the corresponding non-centrosymmetric space group *Pna2*₁, but with a series of restraints to improve refinement stability. The *R* values were not improved. It is unlikely that X-ray methods alone can distinguish between the two possibilities; we prefer the disordered centrosymmetric model because it is unaffected by the matrix near-singularities inherent in the *Pna2*₁ refinement. The latter is presented in the deposited material. A rigid-body libration correction (Schomaker & Trueblood, 1968) gave the following corrected bond lengths (Å): P–F 1.588, P–C1 1.819, C1–C2 1.419, C2–C3 1.397, C3–C4 1.392, C4–C5 1.391, C1–C6 1.414, C5–C6 1.398, C2–C7 1.520, C4–C8 1.518, C6–C9 1.519.

Data collection: *P3* (Nicolet, 1987); cell refinement: *P3*; data reduction: *XDISK* (Nicolet, 1987); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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