Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Tris(1,1,1,3,3,3-hexafluoroisopropyl) phosphate

Pierre-Loïc Saaidi,[a] Erwann Jeanneau[b]* and Jens Hasserodt[a]

[a]Ecole Normale Supérieure de Lyon, Laboratoire de Chimie, 46 allée d'Italie, 69364 Lyon Cedex 07, France, and [b]Centre de Diffractométrie Henri Longchambon, Université Lyon 1, 43 boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France
Correspondence e-mail: erwann.jeanneau@univ-lyon1.fr

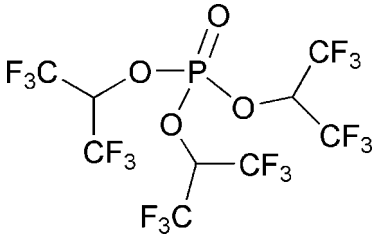
Received 4 May 2007; accepted 11 June 2007

Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.002 Å; R factor = 0.034; wR factor = 0.048; data-to-parameter ratio = 11.2.

The title compound, $C_9H_3F_{18}O_4P$, was synthesized by condensation of sodium hexafluoroisopropanolate and phosphoryl chloride. The P atom is in a distorted tetrahedral environment. The molecules are stabilized by weak O···H and F···H hydrogen-bond interactions as well as F···F interactions.

Related literature

For related literature, see: Allen *et al.* (1987); Dakternieks *et al.* (1978); Gubaidullin *et al.* (2004); Halper & Cohen (2005); Hanes *et al.* (2002); Robinson *et al.* (1971); Smart (2001); Timperley & White (2003); Timperley *et al.* (2000); Bernstein *et al.* (1995); Larson (1970); Prince (1982); Watkin (1994).



Experimental

Crystal data

$C_9H_3F_{18}O_4P$
M_r = 548.06
Monoclinic, $C2/c$
a = 18.9045 (4) Å
b = 9.9101 (3) Å
c = 19.1760 (5) Å
β = 107.044 (2)°
V = 3434.75 (16) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.37 mm^{-1}
T = 150 K
0.49 × 0.47 × 0.43 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
7697 measured reflections
4071 independent reflections
3242 reflections with $I > 3.0\sigma(I)$
R_{int} = 0.015

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.048
S = 1.1
3242 reflections
290 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.3 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P1—O2	1.5723 (11)	P1—O1	1.4545 (12)
P1—O3	1.5808 (13)	P1—O4	1.5719 (11)
O2—P1—O3	101.53 (7)	O2—P1—O4	102.00 (6)
O2—P1—O1	116.64 (7)	O3—P1—O4	102.08 (6)
O3—P1—O1	115.57 (6)	O1—P1—O4	116.66 (6)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···O1	0.97	2.57	3.022 (2)	108
C4—H4···O1	0.97	2.57	2.988 (2)	107
C7—H7···O1	0.95	2.57	3.008 (2)	108
C7—H7···O1^{i}	0.95	2.30	3.171 (2)	152
C4—H4···F10^{ii}	0.97	2.55	3.376 (3)	144

Symmetry codes: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (ii) $-x+\frac{1}{2}, -y-\frac{1}{2}, -z+1$.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *DIAMOND* (Brandenburg & Putz, 1996); software used to prepare material for publication: *CRYSTALS*.

This work was supported by the CNRS and the French Research Ministry.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CS2040).

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supplementary materials

Acta Cryst. (2007). E**63**, o3241-o3242 [**doi:10.1107/S160053680702853X**]

Tris(1,1,1,3,3,3-hexafluoroisopropyl) phosphate

P.-L. Saaidi, E. Jeanneau and J. Hasserodt

Comment

Due to its specific properties, fluorine atom has been introduced in a large variety of organic derivatives in order to modify their physical and chemical properties (Smart, 2001). The steric and electronic effects of aliphatic fluoroalkyl groups are still the subject of experimental and theoretical work (Timperley & White, 2003). We report here the X-ray structure of the title compound, (**I**), which represents one of the very few examples of crystallized polyfluorinated phosphotriester (Hanes *et al.*, 2002; Gubaidullin *et al.*, 2004).

The phosphorus atom is single bonded to three oxygen atoms from the three hexafluoroisopropoxy ligands and double bonded to a fourth oxygen atom. The coordination polyhedra of the P atom shows a tetragonal distortion with a 1.858 $Å^3$ tetrahedral volume (Robinson *et al.*, 1971). It displays a nearly regular C_3 symmetry as usually observed for P(V) atom. All bond lengths in **(I)** show expected values (Allen *et al.*, 1987).

The title compound displays three intramolecular C—H···O hydrogen interactions, similar to that found in polyfluorinated dioxaphosphepinone oxide derivatives (Gubaidullin *et al.*, 2004). These hydrogen bonds display an *S*(6) graph-set motif (Bernstein *et al.*, 1995). The crystal packing is achieved through C—H···O and C—H···F hydrogen interactions as well as F···F repulsion interactions. Indeed, the shortest intermolecular distance between two fluorine atoms is 2.873 (2) Å (Halper & Cohen, 2005).

Experimental

The title compound (**I**) was prepared according to a procedure adapted from Dakternieks *et al.* (1978): to a suspension of NaH (30 mmol) in anhydrous diethylether at 0°C, hexafluoroisopropanol (30 mmol) was added over a 10 minutes period. After 30 minutes at room temperature, the resulting turbid solution was cooled down to 0°C. $POCl_3$ (10 mmol) diluted in anhydrous diethylether was added dropwise and the reaction mixture was refluxed for 2 h. After removal of the volatile materials, the crude solid was purified by sublimation (T = 150 °C, P= 8 m mH g) to afford the title compound (2.6 mmol, 26%). ^1H, ^{13}C, ^{19}F and ^{31}P NMR were identical to the data reported by Timperley *et al.* (2000). Single crystals suitable for X-ray measurements were obtained after recrystallization at 0 °C from a 7:2 cyclohexane/diethylether mixture.

Refinement

In the absence of significant anomalous scattering effects, the Friedel pairs have been merged. All the hydrogen atoms were discernible in a difference Fourier map. They were initially refined with soft restraints on the bond length (C—H in the range 0.93–0.98 Å) and their isotropic displacement ellipsoid (U_{iso}(H) in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

Figures

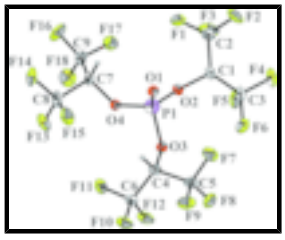


Fig. 1. View of (**I**) (30% probability displacement ellipsoids).

Tris(1,1,1,3,3,3-hexafluoroisopropyl) phosphate

Crystal data

$C_9H_3F_{18}O_4P_1$	F_{000} = 2128
M_r = 548.06	D_x = 2.12 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71069 Å
Hall symbol: -C 2yc	Cell parameters from 4008 reflections
a = 18.9045 (4) Å	θ = 0.7–27.9º
b = 9.9101 (3) Å	μ = 0.37 mm^{-1}
c = 19.1760 (5) Å	*T* = 150 K
β = 107.044 (2)º	Block, colourless
V = 3434.75 (16) Å^3	0.49 × 0.47 × 0.43 mm
Z = 8	

Data collection

Nonius KappaCCD diffractometer	R_{int} = 0.015
φ and ω scans	θ_{max} = 27.9º
Absorption correction: none	θ_{min} = 2.2º
7697 measured reflections	*h* = −24→24
4071 independent reflections	*k* = −13→12
3242 reflections with $I > 3.0\sigma(I)$	*l* = −25→25

Refinement

Refinement on *F*	H-atom parameters constrained
Least-squares matrix: full	Method, part 1, Chebychev polynomial, (Watkin, 1994, *P*rince, 1982) [*w*eight] = 1.0/[A_0*T_0(x) + A_1*T_1(x) ··· + A_{n-1}]*T_{n-1}(x)] where A_i are the Chebychev coefficients listed below and x = *F* /*F*max Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * [1-(delta*F*/6*sigma*F*)^2]^2 A_i are: 2.02 1.91 1.40
$R[F^2 > 2\sigma(F^2)]$ = 0.034	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.048	$\Delta\rho_{max}$ = 0.3 e Å^{-3}

S = 1.1	$\Delta\rho_{min}$ = −0.32 e Å^{-3}
3242 reflections	Extinction correction: Larson (1970), equation 22
290 parameters	Extinction coefficient: 47 (11)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
P1	0.285712 (18)	0.11784 (4)	0.391786 (19)	0.0248
O2	0.33023 (5)	0.19877 (11)	0.34797 (6)	0.0283
C1	0.40324 (8)	0.24709 (16)	0.38269 (8)	0.0313
H1	0.4189	0.2226	0.4339	0.0354*
C3	0.45415 (9)	0.1793 (2)	0.34444 (10)	0.042
F4	0.52180 (6)	0.23100 (16)	0.36764 (7)	0.0587
F5	0.43015 (6)	0.19094 (16)	0.27324 (6)	0.0586
F6	0.45908 (7)	0.04837 (14)	0.36086 (9)	0.0637
C2	0.40066 (11)	0.40022 (19)	0.37700 (12)	0.0462
F1	0.34688 (8)	0.44681 (12)	0.40228 (8)	0.06
F2	0.46441 (8)	0.45198 (15)	0.41796 (9)	0.0719
F3	0.38851 (10)	0.44423 (14)	0.30982 (8)	0.0713
O3	0.29796 (6)	−0.03253 (11)	0.37036 (5)	0.0286
C4	0.29168 (9)	−0.14024 (15)	0.41696 (8)	0.0307
H4	0.2749	−0.1082	0.457	0.0368*
C5	0.36786 (10)	−0.20370 (17)	0.44678 (10)	0.0427
F9	0.36608 (8)	−0.30226 (12)	0.49341 (7)	0.0593
F7	0.41562 (7)	−0.11032 (13)	0.48275 (8)	0.0652
F8	0.39356 (7)	−0.25376 (13)	0.39505 (8)	0.0586
C6	0.23308 (10)	−0.23648 (17)	0.37223 (10)	0.0384
F12	0.24868 (7)	−0.28390 (12)	0.31417 (6)	0.0525
F11	0.16861 (7)	−0.17261 (14)	0.35037 (9)	0.062
F10	0.22502 (8)	−0.34205 (12)	0.41274 (7)	0.0546
O1	0.30422 (6)	0.14500 (11)	0.46961 (6)	0.031
O4	0.20340 (5)	0.14476 (11)	0.34549 (6)	0.0297
C7	0.15810 (8)	0.23802 (16)	0.36972 (8)	0.0304
H7	0.185	0.2802	0.4143	0.0358*
C9	0.13179 (10)	0.34502 (19)	0.31043 (10)	0.041
F17	0.19015 (7)	0.40591 (13)	0.29919 (8)	0.0569
F18	0.09199 (8)	0.29449 (15)	0.24786 (7)	0.0637
F16	0.09202 (9)	0.43758 (15)	0.33152 (9)	0.0716
C8	0.09563 (9)	0.1560 (2)	0.38443 (10)	0.0415
F15	0.12421 (7)	0.06582 (15)	0.43625 (7)	0.0582
F14	0.05100 (7)	0.23522 (17)	0.40846 (8)	0.0643
F13	0.05572 (6)	0.09030 (15)	0.32645 (7)	0.0594

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.02380 (17)	0.02631 (18)	0.02450 (18)	0.00023 (12)	0.00763 (12)	−0.00099 (13)
O2	0.0260 (5)	0.0304 (5)	0.0274 (5)	−0.0036 (4)	0.0064 (4)	0.0011 (4)

C1	0.0260 (6)	0.0377 (8)	0.0299 (7)	−0.0064 (5)	0.0078 (5)	−0.0017 (6)
C3	0.0284 (7)	0.0595 (11)	0.0390 (8)	−0.0004 (7)	0.0112 (6)	−0.0023 (8)
F4	0.0268 (5)	0.0958 (10)	0.0547 (7)	−0.0081 (5)	0.0136 (4)	−0.0013 (7)
F5	0.0435 (6)	0.0997 (10)	0.0353 (5)	0.0052 (6)	0.0158 (4)	−0.0103 (6)
F6	0.0559 (7)	0.0534 (7)	0.0893 (10)	0.0158 (6)	0.0326 (7)	−0.0024 (7)
C2	0.0524 (10)	0.0369 (9)	0.0520 (10)	−0.0130 (7)	0.0195 (8)	−0.0044 (8)
F1	0.0693 (8)	0.0364 (6)	0.0819 (9)	−0.0020 (5)	0.0338 (7)	−0.0128 (6)
F2	0.0672 (8)	0.0608 (8)	0.0876 (10)	−0.0372 (7)	0.0223 (7)	−0.0217 (7)
F3	0.1083 (12)	0.0472 (7)	0.0623 (8)	−0.0113 (7)	0.0312 (8)	0.0150 (6)
O3	0.0342 (5)	0.0260 (5)	0.0274 (5)	0.0013 (4)	0.0118 (4)	0.0009 (4)
C4	0.0397 (8)	0.0271 (7)	0.0264 (6)	−0.0016 (5)	0.0114 (6)	0.0008 (5)
C5	0.0471 (9)	0.0316 (8)	0.0425 (9)	0.0016 (7)	0.0025 (7)	0.0059 (7)
F9	0.0788 (9)	0.0386 (6)	0.0499 (7)	0.0065 (5)	0.0025 (6)	0.0160 (5)
F7	0.0519 (7)	0.0470 (6)	0.0727 (9)	−0.0050 (5)	−0.0189 (6)	0.0060 (6)
F8	0.0505 (7)	0.0559 (7)	0.0741 (8)	0.0173 (5)	0.0256 (6)	0.0066 (6)
C6	0.0424 (8)	0.0346 (8)	0.0396 (8)	−0.0084 (6)	0.0140 (7)	−0.0032 (7)
F12	0.0712 (8)	0.0489 (6)	0.0383 (6)	−0.0180 (5)	0.0176 (5)	−0.0150 (5)
F11	0.0381 (6)	0.0591 (7)	0.0823 (9)	−0.0084 (5)	0.0077 (6)	−0.0036 (7)
F10	0.0751 (8)	0.0390 (6)	0.0571 (7)	−0.0198 (5)	0.0309 (6)	−0.0012 (5)
O1	0.0303 (5)	0.0356 (5)	0.0268 (5)	0.0005 (4)	0.0080 (4)	−0.0034 (4)
O4	0.0240 (5)	0.0346 (5)	0.0296 (5)	0.0008 (4)	0.0067 (4)	−0.0042 (4)
C7	0.0257 (6)	0.0367 (7)	0.0303 (7)	0.0040 (5)	0.0106 (5)	−0.0011 (6)
C9	0.0380 (8)	0.0433 (9)	0.0425 (9)	0.0090 (7)	0.0130 (7)	0.0079 (7)
F17	0.0592 (7)	0.0478 (6)	0.0689 (8)	0.0000 (5)	0.0271 (6)	0.0192 (6)
F18	0.0642 (8)	0.0772 (9)	0.0378 (6)	0.0015 (7)	−0.0034 (5)	0.0148 (6)
F16	0.0772 (9)	0.0614 (8)	0.0851 (10)	0.0398 (7)	0.0377 (8)	0.0198 (7)
C8	0.0285 (7)	0.0586 (11)	0.0390 (9)	−0.0007 (7)	0.0124 (6)	0.0060 (8)
F15	0.0504 (6)	0.0717 (8)	0.0547 (7)	−0.0052 (6)	0.0186 (5)	0.0254 (6)
F14	0.0395 (6)	0.0890 (10)	0.0762 (9)	0.0075 (6)	0.0357 (6)	0.0009 (7)
F13	0.0414 (6)	0.0755 (8)	0.0564 (7)	−0.0230 (6)	0.0065 (5)	−0.0021 (6)

Geometric parameters (Å, °)

P1—O2	1.5723 (11)	C4—C6	1.522 (2)
P1—O3	1.5808 (13)	C5—F9	1.331 (2)
P1—O1	1.4545 (12)	C5—F7	1.335 (2)
P1—O4	1.5719 (11)	C5—F8	1.322 (2)
O2—C1	1.4278 (17)	C6—F12	1.319 (2)
C1—H1	0.97	C6—F11	1.328 (2)
C1—C3	1.526 (2)	C6—F10	1.338 (2)
C1—C2	1.521 (3)	O4—C7	1.4269 (17)
C3—F4	1.327 (2)	C7—H7	0.953
C3—F5	1.312 (2)	C7—C9	1.527 (2)
C3—F6	1.332 (3)	C7—C8	1.527 (2)
C2—F1	1.331 (2)	C9—F17	1.329 (2)
C2—F2	1.333 (2)	C9—F18	1.314 (2)
C2—F3	1.315 (3)	C9—F16	1.322 (2)
O3—C4	1.4192 (18)	C8—F15	1.328 (2)
C4—H4	0.966	C8—F14	1.330 (2)

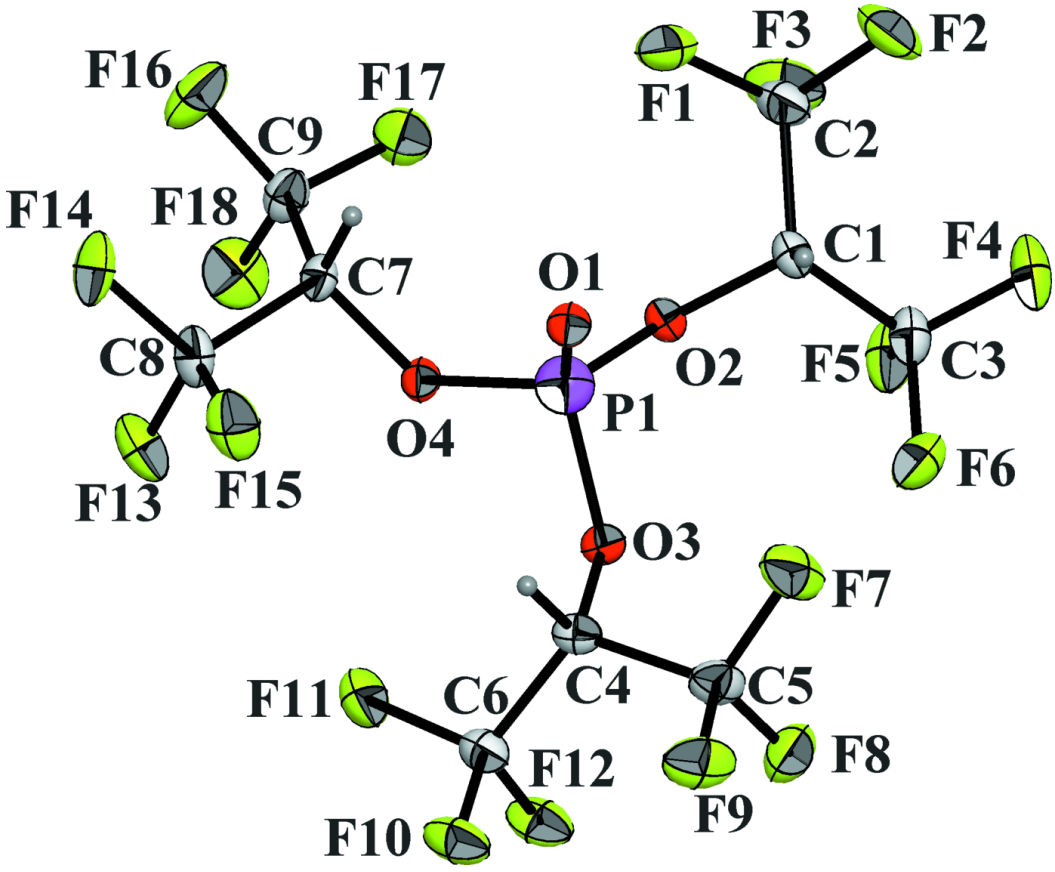
C4—C5	1.521 (2)	C8—F13	1.318 (2)
O2—P1—O3	101.53 (7)	C4—C5—F9	110.38 (16)
O2—P1—O1	116.64 (7)	C4—C5—F7	109.27 (14)
O3—P1—O1	115.57 (6)	F9—C5—F7	107.94 (15)
O2—P1—O4	102.00 (6)	C4—C5—F8	112.86 (15)
O3—P1—O4	102.08 (6)	F9—C5—F8	108.41 (15)
O1—P1—O4	116.66 (6)	F7—C5—F8	107.83 (17)
P1—O2—C1	121.17 (9)	C4—C6—F12	113.15 (14)
O2—C1—H1	110.8	C4—C6—F11	109.17 (15)
O2—C1—C3	106.74 (13)	F12—C6—F11	108.37 (16)
H1—C1—C3	109.1	C4—C6—F10	110.53 (14)
O2—C1—C2	107.15 (14)	F12—C6—F10	107.65 (14)
H1—C1—C2	108.4	F11—C6—F10	107.81 (15)
C3—C1—C2	114.57 (15)	P1—O4—C7	121.01 (9)
C1—C3—F4	110.53 (15)	O4—C7—H7	111.3
C1—C3—F5	112.79 (15)	O4—C7—C9	107.64 (12)
F4—C3—F5	108.69 (15)	H7—C7—C9	109.5
C1—C3—F6	108.99 (15)	O4—C7—C8	106.62 (14)
F4—C3—F6	107.62 (16)	H7—C7—C8	107.8
F5—C3—F6	108.07 (17)	C9—C7—C8	113.98 (13)
C1—C2—F1	109.38 (15)	C7—C9—F17	109.34 (14)
C1—C2—F2	109.70 (17)	C7—C9—F18	112.92 (16)
F1—C2—F2	107.88 (17)	F17—C9—F18	107.76 (16)
C1—C2—F3	113.19 (16)	C7—C9—F16	110.14 (15)
F1—C2—F3	108.01 (18)	F17—C9—F16	107.94 (17)
F2—C2—F3	108.53 (16)	F18—C9—F16	108.60 (16)
P1—O3—C4	119.98 (9)	C7—C8—F15	109.24 (14)
O3—C4—H4	111.1	C7—C8—F14	110.71 (16)
O3—C4—C5	107.64 (13)	F15—C8—F14	107.36 (15)
H4—C4—C5	109.4	C7—C8—F13	112.92 (14)
O3—C4—C6	107.33 (13)	F15—C8—F13	107.78 (17)
H4—C4—C6	107.5	F14—C8—F13	108.64 (15)
C5—C4—C6	113.92 (14)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O1	0.97	2.57	3.022 (2)	108
C4—H4···O1	0.97	2.57	2.988 (2)	107
C7—H7···O1	0.95	2.57	3.008 (2)	108
C7—H7···O1^{i}	0.95	2.30	3.171 (2)	152
C4—H4···F10^{ii}	0.97	2.55	3.376 (3)	144

Symmetry codes: (i) −*x*+1/2, −*y*+1/2, −*z*+1; (ii) −*x*+1/2, −*y*−1/2, −*z*+1.

Fig. 1


F16
F17
C9
F14
F18
C7
C8
F13
F15
O4
O1
O2
P1
O3
F1
F3
F2
C2
C1
F4
F5
C3
F6
F7
F11
C6
C4
C5
F12
F10
F9
F8