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Methylenebis(phosphonic difluoride)

Steffen Blaurock,[a] Axel Fischer,[a] Reinhard Schmutzler[b] and Frank T. Edelmann[a]*

[a]Chemisches Institut der Otto-von-Guericke-Universität, Universitätsplatz 2, D-39116 Magdeburg, Germany, and [b]Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany
Correspondence e-mail: frank.edelmann@ovgu.de

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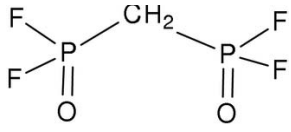
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(P–C) = 0.002 Å; R factor = 0.028; wR factor = 0.075; data-to-parameter ratio = 21.5.

The crystal structure of the title compound, $CH_2F_4O_2P_2$, is characterized by an extensive net of C—H···O hydrogen bonds.

Related literature

For related literature, see: Althoff *et al.* (1981); Maier (1965); Matczak-Jon *et al.*, (2005); Richard *et al.* (1961); Sheldrick (1975).



Experimental

Crystal data

$CH_2F_4O_2P_2$
M_r = 183.97
Orthorhombic, $Pna2_1$
a = 16.975 (2) Å
b = 5.2277 (6) Å
c = 12.9176 (14) Å
V = 1146.3 (2) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.77 mm^{-1}
T = 173 (2) K
0.43 × 0.27 × 0.13 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
T_{min} = 0.733, T_{max} = 0.907
18754 measured reflections
3500 independent reflections
3205 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.076
S = 1.05
3500 reflections
163 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}
Absolute structure: Flack (1983), with 1672 Friedel pairs
Flack parameter: −0.03 (8)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2A···O1	0.99	2.41	3.151 (2)	131
C2—H2A···O2^{i}	0.99	2.47	3.286 (3)	140
C2—H2B···O3^{i}	0.99	2.44	3.214 (2)	135
C2—H2B···O1^{i}	0.99	2.67	3.428 (2)	134
C2—H2B···F4^{ii}	0.99	2.76	3.429 (2)	125
C1—H1A···O4^{iii}	0.99	2.42	3.200 (2)	135
C1—H1A···O2^{i}	0.99	2.58	3.286 (2)	128
C1—H1A···F6^{iv}	0.99	2.71	3.404 (3)	128
C1—H1B···O3^{v}	0.99	2.46	3.310 (3)	144
C1—H1B···O4^{v}	0.99	2.56	3.298 (2)	131

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1, -y+1, z-\frac{1}{2}$; (iii) $x+\frac{1}{2}, -y+\frac{3}{2}, z$; (iv) $-x+1, -y+1, z+\frac{1}{2}$; (v) $x+\frac{1}{2}, -y+\frac{1}{2}, z$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXTL-Plus* (Bruker, 1998); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2436).

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supplementary materials

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Methylenebis(phosphonic difluoride)

S. Blaurock, A. Fischer, R. Schmutzler and F. T. Edelmann

Comment

Bis(phosphonates) form an interesting class of hydrolytically stable analogues of pyrophosphate, in which the bridging oxygen atom is replaced by a methylene group or a substituted methylene group. Several members of this class have been employed as therapeutic agents for the treatment of bone disorders such as hypercalcemia of malignancy, osteoporosis, and Paget's disease. Other bis(phosphonates) have been shown to be potent antiparasitic agents or herbicides (Matczak-Jon *et al.*; 2005, and references cited therein). The corresponding bis(phosphonicdichlorides) such as $CH_2(POCl_2)_2$ are known since 1961 (Richard *et al.*, 1961; Maier *et al.*, 1965). The crystal structure of $CH_2(POCl_2)_2$ was determined by Sheldrick (1975). Althoff *et al.* (1981) first reported the preparation and spectroscopic characterization of the corresponding fluoride, *i.e.* the title compound methylene-bis(phosphonicdifluoride), $CH_2(POF_2)_2$. Large, clear, colorless crystals (up to 2 cm in length) originating from the original work published in 1981 were found to be of excellent quality for X-ray diffraction. The crystal structure of the title compound is characterized by an extensive net of C—H···O hydrogen bonds.

Experimental

Large, clear, colorlesss crystals originating from the early work by Althoff *et al.* (1981) were used in this study.

Refinement

Refinments based on F^2 (*SHELXL97*), H atoms are refined in rinding models.

Figures

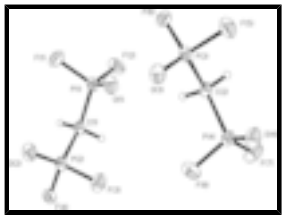

Fig. 1. The molecule of the title compound in the crystal. Thermal ellipsoids represent 50% probability levels.

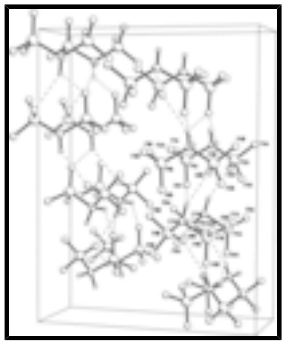

Fig. 2. The hydrogen-bonded network of the title compound in the crystal.

Methylenebis(phosphonic difluoride)

Crystal data

$CH_2F_4O_2P_2$	F_{000} = 720
M_r = 183.97	D_x = 2.132 Mg m^{-3}
Orthorhombic, *Pna*2$_1$	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: P 2 c -2 n	Cell parameters from 5368 reflections
a = 16.975 (2) Å	θ = 2.8–30.5º
b = 5.2277 (6) Å	μ = 0.77 mm^{-1}
c = 12.9176 (14) Å	*T* = 173 (2) K
V = 1146.3 (2) Å^3	Plate, colourless
Z = 8	0.43 × 0.27 × 0.13 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	3500 independent reflections
Radiation source: fine-focus sealed tube	3205 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.029
Detector resolution: 8.192 pixels mm^{-1}	θ_{max} = 30.5º
T = 173(2) K	θ_{min} = 2.4º
ω scans	*h* = −24→24
Absorption correction: multi-scan (SADABS; Sheldrick, 1997)	*k* = −7→7
T_{min} = 0.733, T_{max} = 0.907	*l* = −18→18
18754 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.028	$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.076	$(\Delta/\sigma)_{max} < 0.001$
S = 1.05	$\Delta\rho_{max}$ = 0.57 e Å^{-3}
3500 reflections	$\Delta\rho_{min}$ = −0.54 e Å^{-3}
163 parameters	Extinction correction: none
1 restraint	Absolute structure: Flack (1983), with 1672 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.03 (8)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
P1	0.55572 (3)	0.28344 (8)	0.60836 (4)	0.02034 (12)
P2	0.55486 (3)	0.02274 (8)	0.81045 (4)	0.02008 (10)
P4	0.30379 (3)	0.79236 (8)	0.76166 (4)	0.02068 (11)
P3	0.30600 (3)	0.54835 (8)	0.55714 (4)	0.01888 (10)
F2	0.59439 (9)	0.5203 (2)	0.56183 (12)	0.0347 (3)
F3	0.49330 (9)	0.1952 (2)	0.86152 (13)	0.0327 (3)
F7	0.33664 (9)	1.0365 (2)	0.80986 (13)	0.0354 (3)
F5	0.24222 (8)	0.7124 (2)	0.50573 (12)	0.0323 (3)
O3	0.27660 (9)	0.3092 (2)	0.59923 (13)	0.0248 (3)
F4	0.61055 (8)	−0.0141 (2)	0.90233 (10)	0.0296 (3)
O4	0.21851 (10)	0.7812 (3)	0.75682 (15)	0.0288 (4)
O1	0.47055 (10)	0.2938 (3)	0.61383 (15)	0.0299 (4)
O2	0.52357 (10)	−0.2127 (2)	0.76811 (15)	0.0276 (3)
F6	0.36236 (8)	0.5180 (2)	0.46534 (10)	0.0270 (2)
C2	0.35521 (12)	0.7605 (3)	0.64298 (17)	0.0179 (4)
H2A	0.4090	0.6954	0.6568	0.021*
H2B	0.3601	0.9306	0.6099	0.021*
F1	0.58654 (8)	0.0785 (3)	0.53391 (11)	0.0347 (3)
C1	0.60738 (12)	0.2305 (3)	0.72558 (17)	0.0191 (4)
H1A	0.6163	0.3964	0.7606	0.023*
H1B	0.6595	0.1547	0.7099	0.023*
F8	0.34007 (9)	0.5934 (3)	0.83358 (11)	0.0370 (3)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0220 (3)	0.01534 (18)	0.0237 (3)	0.00100 (16)	−0.0022 (2)	0.00045 (16)
P2	0.0230 (2)	0.01312 (17)	0.0241 (2)	−0.00233 (14)	0.00020 (18)	0.00064 (17)
P4	0.0224 (3)	0.01646 (18)	0.0231 (3)	0.00051 (16)	0.0025 (2)	−0.00196 (17)
P3	0.02080 (19)	0.01297 (17)	0.0229 (2)	−0.00030 (15)	−0.00179 (18)	−0.00083 (16)
F2	0.0438 (7)	0.0267 (6)	0.0335 (7)	−0.0073 (5)	−0.0018 (7)	0.0121 (5)
F3	0.0314 (7)	0.0262 (5)	0.0404 (8)	0.0013 (5)	0.0136 (6)	−0.0029 (5)

F7	0.0416 (7)	0.0296 (6)	0.0350 (7)	−0.0071 (5)	0.0048 (6)	−0.0159 (6)
F5	0.0312 (7)	0.0256 (6)	0.0403 (9)	0.0045 (5)	−0.0145 (6)	0.0006 (5)
O3	0.0265 (7)	0.0155 (6)	0.0324 (8)	−0.0045 (5)	−0.0004 (6)	−0.0007 (5)
F4	0.0439 (7)	0.0194 (5)	0.0254 (6)	−0.0008 (5)	−0.0078 (5)	0.0019 (4)
O4	0.0233 (7)	0.0256 (6)	0.0376 (10)	0.0014 (5)	0.0074 (8)	−0.0016 (6)
O1	0.0227 (8)	0.0269 (6)	0.0402 (10)	0.0032 (6)	−0.0066 (8)	−0.0007 (6)
O2	0.0313 (8)	0.0165 (5)	0.0351 (9)	−0.0070 (5)	−0.0029 (7)	−0.0007 (5)
F6	0.0385 (6)	0.0194 (5)	0.0229 (5)	0.0002 (4)	0.0046 (5)	−0.0021 (4)
C2	0.0173 (9)	0.0131 (6)	0.0231 (11)	−0.0013 (5)	0.0017 (8)	−0.0018 (6)
F1	0.0400 (8)	0.0331 (6)	0.0310 (7)	0.0070 (6)	−0.0023 (5)	−0.0132 (5)
C1	0.0167 (9)	0.0146 (6)	0.0258 (12)	−0.0007 (6)	0.0004 (9)	0.0006 (6)
F8	0.0442 (8)	0.0361 (7)	0.0306 (7)	0.0065 (6)	−0.0010 (6)	0.0119 (5)

Geometric parameters (Å, °)

P1—O1	1.4484 (17)	P4—F7	1.5256 (13)
P1—F2	1.5248 (13)	P4—C2	1.772 (2)
P1—F1	1.5320 (14)	P3—O3	1.4518 (14)
P1—C1	1.772 (2)	P3—F6	1.5318 (14)
P2—O2	1.4478 (14)	P3—F5	1.5324 (14)
P2—F4	1.5295 (13)	P3—C2	1.777 (2)
P2—F3	1.5296 (14)	C2—H2A	0.9900
P2—C1	1.782 (2)	C2—H2B	0.9900
P4—O4	1.4501 (17)	C1—H1A	0.9900
P4—F8	1.5244 (14)	C1—H1B	0.9900
O1—P1—F2	114.74 (9)	O3—P3—F6	114.55 (8)
O1—P1—F1	113.44 (9)	O3—P3—F5	113.66 (9)
F2—P1—F1	99.99 (9)	F6—P3—F5	99.42 (8)
O1—P1—C1	117.27 (11)	O3—P3—C2	117.73 (10)
F2—P1—C1	104.52 (9)	F6—P3—C2	104.72 (9)
F1—P1—C1	104.97 (8)	F5—P3—C2	104.67 (8)
O2—P2—F4	114.39 (8)	P4—C2—P3	111.53 (10)
O2—P2—F3	114.41 (9)	P4—C2—H2A	109.3
F4—P2—F3	99.31 (8)	P3—C2—H2A	109.3
O2—P2—C1	117.98 (11)	P4—C2—H2B	109.3
F4—P2—C1	104.18 (9)	P3—C2—H2B	109.3
F3—P2—C1	104.36 (8)	H2A—C2—H2B	108.0
O4—P4—F8	113.70 (9)	P1—C1—P2	111.93 (11)
O4—P4—F7	114.59 (9)	P1—C1—H1A	109.2
F8—P4—F7	100.04 (9)	P2—C1—H1A	109.2
O4—P4—C2	116.78 (11)	P1—C1—H1B	109.2
F8—P4—C2	105.32 (8)	P2—C1—H1B	109.2
F7—P4—C2	104.58 (9)	H1A—C1—H1B	107.9
O4—P4—C2—P3	−34.20 (13)	O1—P1—C1—P2	34.75 (13)
F8—P4—C2—P3	93.04 (12)	F2—P1—C1—P2	163.05 (10)
F7—P4—C2—P3	−162.01 (10)	F1—P1—C1—P2	−92.20 (12)
O3—P3—C2—P4	−44.90 (14)	O2—P2—C1—P1	48.12 (14)
F6—P3—C2—P4	−173.47 (9)	F4—P2—C1—P1	176.18 (9)
F5—P3—C2—P4	82.42 (12)	F3—P2—C1—P1	−80.12 (12)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2A···O1	0.99	2.41	3.151 (2)	131
C2—H2A···O2^{i}	0.99	2.47	3.286 (3)	140
C2—H2B···O3^{i}	0.99	2.44	3.214 (2)	135
C2—H2B···O1^{i}	0.99	2.67	3.428 (2)	134
C2—H2B···F4^{ii}	0.99	2.76	3.429 (2)	125
C1—H1A···O4^{iii}	0.99	2.42	3.200 (2)	135
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C1—H1B···O4^{v}	0.99	2.56	3.298 (2)	131

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) −*x*+1, −*y*+1, *z*−1/2; (iii) *x*+1/2, −*y*+3/2, *z*; (iv) −*x*+1, −*y*+1, *z*+1/2; (v) *x*+1/2, −*y*+1/2, *z*.

Fig. 1

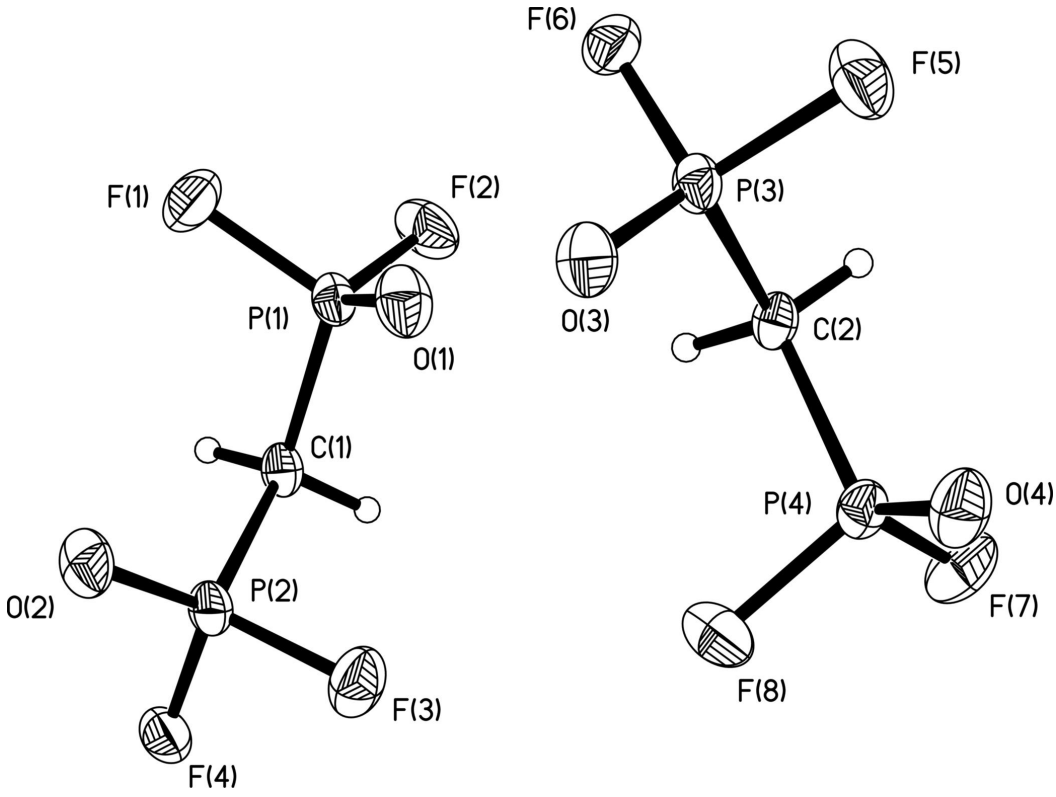
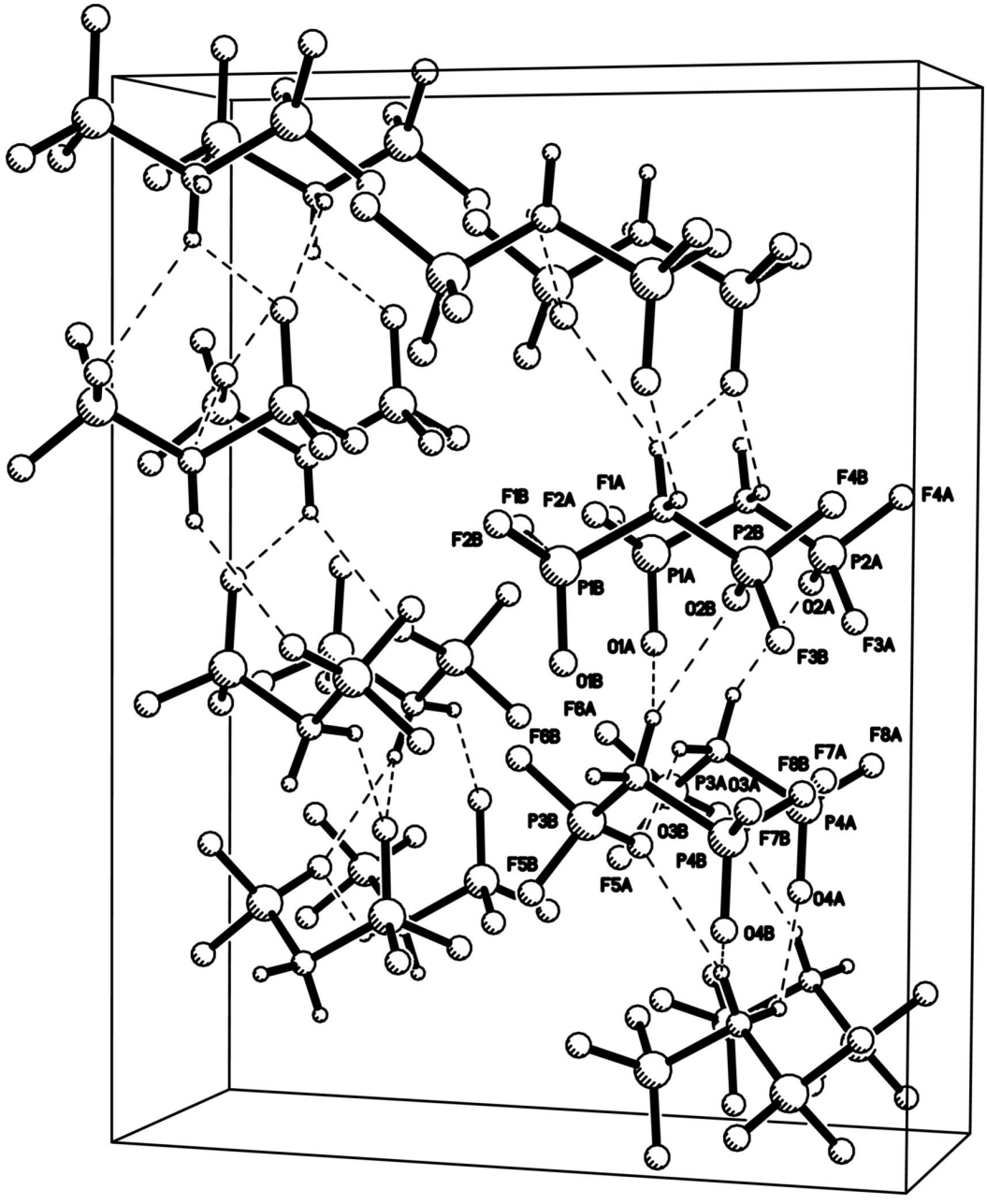


Fig. 2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