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Crystal structure of dimethyl 2,5-bis[(diphenoxyphosphoryl)oxy]cyclohexa-1,4-diene-1,4-dicarboxylate

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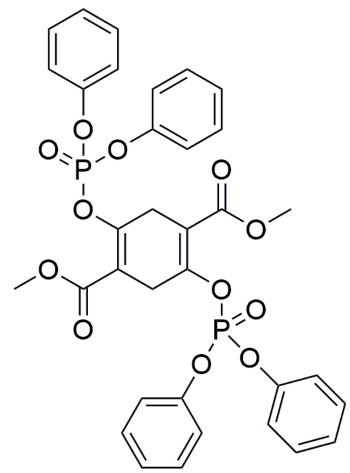
In the title compound, $C_{34}H_{30}O_{12}P_2$, which was synthesized *via* the esterification of dimethyl 2,5-dioxo-1,4-cyclohexanedicarboxylate with diphenyl chlorophosphate, the molecule has crystallographic inversion symmetry. The dihedral angles between the plane of the cyclohexa-1,4-diene ring and those of the two benzene rings of the substituent phosphate groups are 41.0 (1) and 89.5 (1)°, while that with the ester group is 3.1 (3)°. In the crystal, only weak intermolecular C—H⋯O hydrogen bonds are present.

Keywords: crystal structure; cyclohexa-1,4-diene; C—H⋯O hydrogen bonds.

CCDC reference: 1057648

1. Related literature

For background information on cyclohexa-1,4-dienes, see: El-Rayyes & Al-Hajjar (1978). For the synthesis of the title compound, see: Chaignaud *et al.* (2008).



2. Experimental

2.1. Crystal data

$C_{34}H_{30}O_{12}P_2$
$M_r = 692.52$
Monoclinic, $P2_1/c$
$a = 12.272$ (10) Å
$b = 10.629$ (8) Å
$c = 13.174$ (10) Å
$\beta = 113.644$ (10)°
$V = 1574$ (2) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.21$ mm^{-1}
$T = 113$ K
0.20 × 0.18 × 0.12 mm

2.2. Data collection

Rigaku Saturn724 CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{min} = 0.960$, $T_{max} = 0.976$
15948 measured reflections
3758 independent reflections
2264 reflections with $I > 2\sigma(I)$
$R_{int} = 0.100$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.099$
$S = 1.00$
3758 reflections
218 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.62$ e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C6—H6⋯O3^{i}	0.95	2.50	3.345 (4)	148
C9—H9⋯O5^{ii}	0.95	2.59	3.405 (4)	144
C10—H10⋯O3^{iii}	0.95	2.46	3.381 (4)	163
C15—H15B⋯O1^{iv}	0.99	2.56	3.409 (4)	144

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *CrystalStructure* (Rigaku, 2005).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: ZS2331).

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El-Rayyes, N. R. & Al-Hajjar, F. H. (1978). *J. Prakt. Chem.* **320**, 991–998.
Rigaku (2005). *CrystalClear* and *CrystalStructure*. Rigaku Corporation, Tokyo, Japan.
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supporting information

Acta Cryst. (2015). E**71**, o401–o402 [doi:10.1107/S2056989015008658]

Crystal structure of dimethyl 2,5-bis[(diphenoxyphosphoryl)oxy]cyclohexa-1,4-diene-1,4-dicarboxylate

Lei Gao, Zongshan Ma and Hong Yan

S1. Comment

1,4-Cyclohexadiene is a useful and fundamental structural motif found in a wide range of organic materials and biologically active molecules (El-Rayyes & Al-Hajjar, 1978). The synthetic routes for the preparation of derivatives of this parent compound have been reported (Chaignaud *et al.*, 2008) but their crystal structures were not described.

The title compound, $C_{34}H_{30}O_{12}P_2$, was synthesized by the esterification of dimethyl 2,5-dioxo-1,4-cyclohexanedicarboxylate with diphenyl chlorophosphate using the reported procedure of Chaignaud *et al.* (2008) and the structure is reported herein.

The molecule of the title compound has crystallographic inversion symmetry (Fig. 1), with dihedral angles between the cyclohexa-1,4-diene ring and the two benzene rings of the substituent phosphate group of 41.0 (1) [C1–C6] and 89.5 (1)° [C7–C12]. The ester group is essentially coplanar with the cyclohexadiene group [dihedral angle = 3.1 (3)°]. In the crystal, only weak intermolecular C—H···O hydrogen bonds are present (Table 1).

S2. Experimental

The title compound was synthesized using the basic procedure of Chaignaud *et al.* (2008) (Fig. 2), as follows: A solution of LiHMDS (1 M in THF, 7.9 mL) in THF (20 mL) was cooled to -78 °C under nitrogen. Subsequently, a mixture of dimethyl 2,5-dioxo-1,4-cyclohexanedicarboxylate (3.19 mmol), diphenyl chlorophosphate (6.67 mmol) and HMPA (8.90 mmol) in anhydrous THF (5 mL) were added dropwise over 5 min. The mixture was stirred at -78 °C for 1h under nitrogen and after completion of the reaction, the mixture was diluted with water (30 mL) and extracted with ethyl acetate (3×15 mL), dried with anhydrous $MgSO_4$ and filtered. Subsequently, the product obtained by evaporation of the solvent was recrystallized from ethyl acetate giving a white solid in 10% yield (m.p. 118–120 °C).

S3. Refinement

H atoms were were positioned geometrically and refined using a riding model with C—H = 0.95–0.99 Å and $U_{iso}(H)$ = $1.2U_{eq}(C)$ (aromatic) or $1.5U_{eq}(C)$ (methyl).

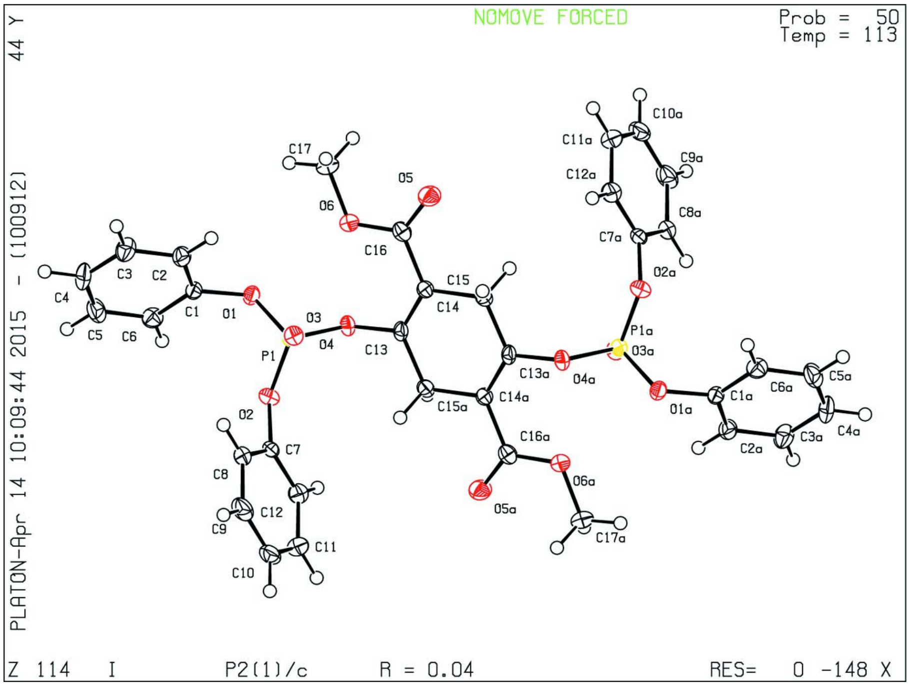

Figure 1

The molecular conformation and atom numbering scheme for the title compound, with probability ellipsoids drawn at the 50% level. For symmetry code (a): -*x*, -*y* + 1, -*z*.

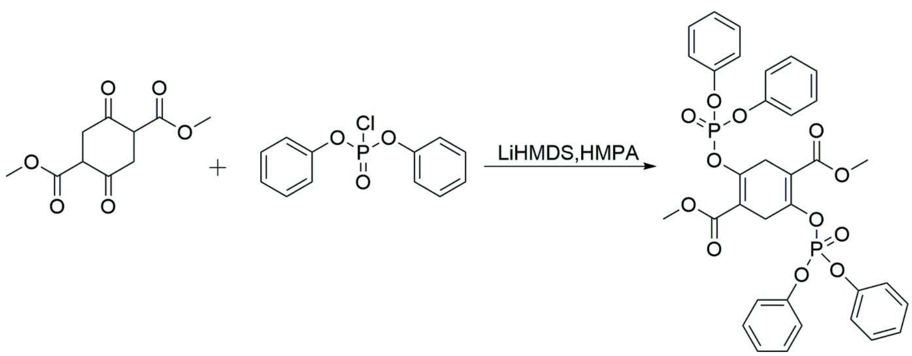

Figure 2

Synthetic route for the title compound.

Dimethyl 2,5-bis[(diphenoxyphosphoryl)oxy]cyclohexa-1,4-diene-1,4-dicarboxylate

Crystal data

$C_{34}H_{30}O_{12}P_2$
M_r = 692.52
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 12.272 (10) Å
b = 10.629 (8) Å
c = 13.174 (10) Å
β = 113.644 (10)°
V = 1574 (2) Å^3
Z = 2

F(000) = 720
D_x = 1.461 Mg m^{-3}
Melting point = 391–393 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5446 reflections
θ = 1.7–28.3°
μ = 0.21 mm^{-1}
T = 113 K
Prism, colorless
0.20 × 0.18 × 0.12 mm

Data collection

Rigaku Saturn724 CCD diffractometer
Radiation source: rotating anode
Multilayer monochromator
Detector resolution: 14.22 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.960, T_{max} = 0.976
15948 measured reflections
3758 independent reflections
2264 reflections with $I > 2\sigma(I)$
R_{int} = 0.100
θ_{max} = 28.0°, θ_{min} = 1.8°
$h = -16 \rightarrow 16$
$k = -13 \rightarrow 13$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.099
S = 1.00
3758 reflections
218 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.012P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.62 e Å^{-3}

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 $F^2 > \sigma(F^2)$ 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	0.17401 (5)	0.72276 (5)	0.24500 (4)	0.01714 (15)
O1	0.12748 (11)	0.81381 (12)	0.31240 (10)	0.0189 (3)
O2	0.26861 (12)	0.64338 (12)	0.34149 (11)	0.0211 (3)
O3	0.21532 (12)	0.77428 (12)	0.16508 (10)	0.0194 (3)
O4	0.06126 (12)	0.63451 (12)	0.19634 (10)	0.0187 (3)
O5	−0.16106 (13)	0.79217 (13)	−0.10725 (11)	0.0285 (4)
O6	−0.06056 (12)	0.82652 (13)	0.07360 (11)	0.0259 (4)
C1	0.20189 (18)	0.91573 (18)	0.36916 (16)	0.0181 (5)
C2	0.20083 (19)	1.02272 (19)	0.30979 (17)	0.0229 (5)
H2	0.1545	1.0266	0.2323	0.027*
C3	0.2684 (2)	1.1239 (2)	0.36526 (18)	0.0288 (6)
H3	0.2690	1.1986	0.3259	0.035*
C4	0.3353 (2)	1.1172 (2)	0.47791 (18)	0.0310 (6)
H4	0.3818	1.1873	0.5159	0.037*
C5	0.3350 (2)	1.0088 (2)	0.53572 (18)	0.0298 (6)
H5	0.3816	1.0046	0.6132	0.036*

C6	0.26714 (19)	0.90613 (19)	0.48111 (17)	0.0237 (5)
H6	0.2659	0.8313	0.5201	0.028*
C7	0.37059 (18)	0.58701 (19)	0.33647 (16)	0.0193 (5)
C8	0.45474 (17)	0.6591 (2)	0.31964 (15)	0.0221 (5)
H8	0.4432	0.7469	0.3063	0.027*
C9	0.55660 (19)	0.6006 (2)	0.32263 (17)	0.0294 (6)
H9	0.6158	0.6483	0.3105	0.035*
C10	0.5728 (2)	0.4722 (2)	0.34328 (17)	0.0317 (6)
H10	0.6431	0.4326	0.3455	0.038*
C11	0.4874 (2)	0.4024 (2)	0.36046 (17)	0.0290 (6)
H11	0.4987	0.3147	0.3747	0.035*
C12	0.38516 (19)	0.46028 (19)	0.35698 (17)	0.0247 (5)
H12	0.3256	0.4128	0.3687	0.030*
C13	0.02855 (17)	0.57494 (18)	0.09354 (16)	0.0173 (5)
C14	−0.04157 (18)	0.62776 (18)	−0.00080 (16)	0.0167 (5)
C15	−0.07850 (18)	0.55461 (17)	−0.10704 (15)	0.0186 (5)
H15A	−0.1664	0.5490	−0.1412	0.022*
H15B	−0.0532	0.6015	−0.1588	0.022*
C16	−0.09356 (18)	0.75651 (19)	−0.01748 (16)	0.0196 (5)
C17	−0.11425 (19)	0.95035 (18)	0.05728 (18)	0.0302 (6)
H17A	−0.0905	0.9985	0.0061	0.045*
H17B	−0.0876	0.9943	0.1286	0.045*
H17C	−0.2011	0.9420	0.0262	0.045*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0148 (3)	0.0166 (3)	0.0186 (3)	−0.0009 (2)	0.0052 (2)	−0.0017 (2)
O1	0.0177 (8)	0.0178 (8)	0.0225 (8)	−0.0025 (6)	0.0093 (7)	−0.0050 (6)
O2	0.0168 (8)	0.0239 (8)	0.0207 (8)	0.0035 (7)	0.0056 (7)	0.0029 (6)
O3	0.0193 (8)	0.0208 (8)	0.0194 (7)	−0.0011 (6)	0.0090 (7)	0.0005 (6)
O4	0.0166 (7)	0.0197 (8)	0.0182 (8)	−0.0054 (6)	0.0055 (6)	−0.0040 (6)
O5	0.0344 (9)	0.0248 (9)	0.0226 (8)	0.0067 (7)	0.0078 (8)	0.0036 (7)
O6	0.0235 (8)	0.0227 (8)	0.0258 (9)	0.0062 (7)	0.0038 (7)	−0.0043 (7)
C1	0.0165 (11)	0.0177 (11)	0.0200 (11)	−0.0006 (9)	0.0070 (9)	−0.0040 (9)
C2	0.0272 (13)	0.0221 (12)	0.0168 (11)	0.0012 (10)	0.0060 (10)	−0.0016 (9)
C3	0.0354 (14)	0.0208 (13)	0.0301 (13)	−0.0050 (11)	0.0131 (12)	−0.0028 (10)
C4	0.0334 (14)	0.0261 (14)	0.0310 (14)	−0.0123 (11)	0.0103 (12)	−0.0132 (11)
C5	0.0276 (13)	0.0379 (15)	0.0179 (12)	−0.0024 (11)	0.0029 (10)	−0.0045 (10)
C6	0.0271 (13)	0.0225 (13)	0.0217 (12)	0.0013 (10)	0.0101 (10)	0.0023 (10)
C7	0.0143 (11)	0.0238 (12)	0.0158 (11)	0.0044 (9)	0.0017 (9)	−0.0044 (9)
C8	0.0171 (11)	0.0216 (12)	0.0237 (12)	−0.0007 (10)	0.0041 (10)	−0.0038 (9)
C9	0.0161 (12)	0.0398 (15)	0.0307 (14)	−0.0035 (11)	0.0077 (11)	−0.0036 (11)
C10	0.0184 (12)	0.0442 (16)	0.0264 (13)	0.0096 (12)	0.0026 (11)	−0.0099 (11)
C11	0.0289 (13)	0.0248 (13)	0.0296 (13)	0.0069 (11)	0.0077 (11)	−0.0034 (11)
C12	0.0216 (12)	0.0228 (13)	0.0275 (12)	−0.0006 (10)	0.0074 (10)	−0.0010 (10)
C13	0.0147 (10)	0.0186 (11)	0.0189 (11)	−0.0052 (9)	0.0071 (9)	−0.0058 (9)
C14	0.0144 (10)	0.0169 (11)	0.0188 (11)	−0.0012 (9)	0.0066 (9)	−0.0009 (9)

C15	0.0154 (11)	0.0201 (12)	0.0182 (11)	−0.0005 (9)	0.0046 (9)	−0.0002 (9)
C16	0.0158 (11)	0.0240 (13)	0.0199 (11)	−0.0025 (9)	0.0079 (10)	0.0003 (9)
C17	0.0270 (13)	0.0246 (13)	0.0355 (14)	0.0094 (11)	0.0088 (12)	−0.0039 (11)

Geometric parameters (Å, º)

P1—O1	1.5677 (19)	C11—C12	1.382 (4)
P1—O2	1.5785 (19)	C13—C14	1.320 (3)
P1—O3	1.4469 (19)	C13—C15^{i}	1.489 (3)
P1—O4	1.579 (2)	C14—C15	1.503 (3)
O1—C1	1.421 (3)	C14—C16	1.489 (3)
O2—C7	1.413 (3)	C2—H2	0.9500
O4—C13	1.400 (3)	C3—H3	0.9500
O5—C16	1.201 (3)	C4—H4	0.9500
O6—C16	1.330 (3)	C5—H5	0.9500
O6—C17	1.449 (3)	C6—H6	0.9500
C1—C2	1.377 (3)	C8—H8	0.9500
C1—C6	1.371 (3)	C9—H9	0.9500
C2—C3	1.376 (3)	C10—H10	0.9500
C3—C4	1.380 (3)	C11—H11	0.9500
C4—C5	1.382 (3)	C12—H12	0.9500
C5—C6	1.386 (3)	C15—H15A	0.9900
C7—C8	1.374 (3)	C15—H15B	0.9900
C7—C12	1.371 (3)	C17—H17A	0.9800
C8—C9	1.383 (3)	C17—H17B	0.9800
C9—C10	1.390 (3)	C17—H17C	0.9800
C10—C11	1.375 (4)		
O1—P1—O2	101.02 (7)	O5—C16—C14	121.40 (18)
O1—P1—O3	119.47 (8)	O6—C16—C14	115.08 (17)
O1—P1—O4	97.92 (8)	C1—C2—H2	121.00
O2—P1—O3	115.41 (9)	C3—C2—H2	121.00
O2—P1—O4	104.54 (8)	C2—C3—H3	120.00
O3—P1—O4	115.79 (8)	C4—C3—H3	120.00
P1—O1—C1	117.75 (13)	C3—C4—H4	120.00
P1—O2—C7	124.62 (13)	C5—C4—H4	120.00
P1—O4—C13	121.73 (14)	C4—C5—H5	120.00
C16—O6—C17	114.76 (16)	C6—C5—H5	120.00
O1—C1—C2	118.23 (17)	C1—C6—H6	121.00
O1—C1—C6	118.96 (17)	C5—C6—H6	121.00
C2—C1—C6	122.74 (19)	C7—C8—H8	121.00
C1—C2—C3	118.52 (19)	C9—C8—H8	121.00
C2—C3—C4	120.2 (2)	C8—C9—H9	120.00
C3—C4—C5	120.3 (2)	C10—C9—H9	120.00
C4—C5—C6	120.3 (2)	C9—C10—H10	120.00
C1—C6—C5	118.03 (19)	C11—C10—H10	120.00
O2—C7—C8	120.56 (18)	C10—C11—H11	120.00
O2—C7—C12	117.1 (2)	C12—C11—H11	120.00

C8—C7—C12	122.2 (2)	C7—C12—H12	120.00
C7—C8—C9	118.3 (2)	C11—C12—H12	120.00
C8—C9—C10	120.3 (2)	C14—C15—H15A	109.00
C9—C10—C11	120.2 (2)	C14—C15—H15B	109.00
C10—C11—C12	119.8 (2)	H15A—C15—H15B	108.00
C7—C12—C11	119.3 (2)	C13^{i}—C15—H15A	109.00
O4—C13—C14	122.97 (18)	C13^{i}—C15—H15B	109.00
O4—C13—C15^{i}	110.99 (16)	O6—C17—H17A	109.00
C14—C13—C15^{i}	125.99 (18)	O6—C17—H17B	109.00
C13—C14—C15	119.73 (18)	O6—C17—H17C	109.00
C13—C14—C16	127.52 (18)	H17A—C17—H17B	109.00
C15—C14—C16	112.75 (16)	H17A—C17—H17C	109.00
C13^{i}—C15—C14	114.28 (16)	H17B—C17—H17C	109.00
O5—C16—O6	123.51 (19)		

O2—P1—O1—C1	75.66 (14)	C3—C4—C5—C6	−0.3 (4)
O3—P1—O1—C1	−52.09 (15)	C4—C5—C6—C1	0.4 (4)
O4—P1—O1—C1	−177.76 (12)	O2—C7—C8—C9	175.83 (17)
O1—P1—O2—C7	−151.58 (15)	C12—C7—C8—C9	0.6 (3)
O3—P1—O2—C7	−21.23 (17)	O2—C7—C12—C11	−175.66 (18)
O4—P1—O2—C7	107.15 (15)	C8—C7—C12—C11	−0.3 (3)
O1—P1—O4—C13	149.57 (14)	C7—C8—C9—C10	−0.6 (3)
O2—P1—O4—C13	−106.81 (14)	C8—C9—C10—C11	0.3 (3)
O3—P1—O4—C13	21.34 (17)	C9—C10—C11—C12	0.1 (3)
P1—O1—C1—C2	81.9 (2)	C10—C11—C12—C7	−0.1 (3)
P1—O1—C1—C6	−101.1 (2)	O4—C13—C14—C15	−176.33 (19)
P1—O2—C7—C8	59.5 (2)	O4—C13—C14—C16	2.7 (4)
P1—O2—C7—C12	−125.04 (17)	C15^{i}—C13—C14—C15	0.7 (4)
P1—O4—C13—C14	−88.2 (2)	C15^{i}—C13—C14—C16	179.7 (2)
P1—O4—C13—C15^{i}	94.39 (18)	O4—C13—C15^{i}—C14^{i}	176.67 (18)
C17—O6—C16—O5	1.1 (3)	C14—C13—C15^{i}—C14^{i}	−0.7 (3)
C17—O6—C16—C14	−178.27 (19)	C13—C14—C15—C13^{i}	−0.6 (3)
O1—C1—C2—C3	177.0 (2)	C16—C14—C15—C13^{i}	−179.77 (19)
C6—C1—C2—C3	0.2 (4)	C13—C14—C16—O5	−176.4 (2)
O1—C1—C6—C5	−177.2 (2)	C13—C14—C16—O6	2.9 (4)
C2—C1—C6—C5	−0.4 (4)	C15—C14—C16—O5	2.7 (3)
C1—C2—C3—C4	0.0 (4)	C15—C14—C16—O6	−177.98 (19)
C2—C3—C4—C5	0.1 (4)		

Symmetry code: (i) −*x*, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O5^{ii}	0.95	2.56	3.191 (4)	124
C6—H6···O3^{iii}	0.95	2.50	3.345 (4)	148
C9—H9···O5^{iv}	0.95	2.59	3.405 (4)	144

C10—H10···O3^{v}	0.95	2.46	3.381 (4)	163
C15—H15*B*···O1^{vi}	0.99	2.56	3.409 (4)	144

Symmetry codes: (ii) $-x$, $-y+2$, $-z$; (iii) x, $-y+3/2$, $z+1/2$; (iv) $x+1$, $-y+3/2$, $z+1/2$; (v) $-x+1$, $y-1/2$, $-z+1/2$; (vi) x, $-y+3/2$, $z-1/2$.