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Crystal structure of [bis(2,6-diisopropylphenyl) phosphato-κO]tris(methanol-κO)lithium methanol monosolvate

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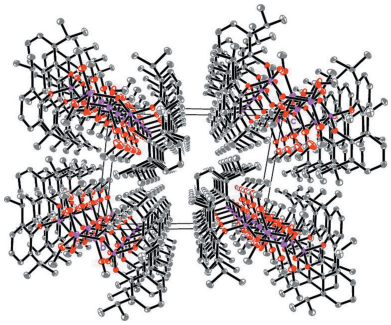
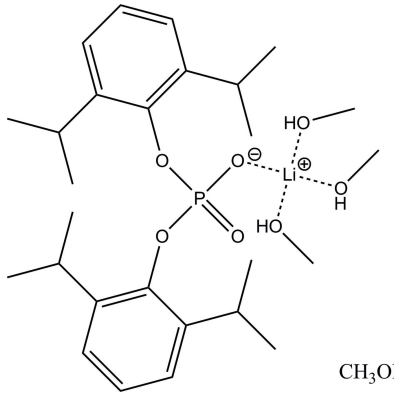
Crystals of the title compound, $[Li\{OOP(O\text{-}2,6\text{-}^{i}Pr_2C_6H_3)_2\}(CH_3OH)_3]\cdot CH_3OH$ or $[Li(C_{24}H_{34}O_4P)(CH_3OH)_3]\cdot CH_3OH$, have been formed in the reaction between $HOOP(O\text{-}2,6\text{-}^{i}Pr_2C_6H_3)_2$ and LiOH in methanol. The title compound is of interest as it represents the first reported crystal structure of the family of lithium phosphate diesters. The $\{Li(CH_3OH)_3[O_2P(O\text{-}^{i}Pr_2C_6H_3)_2]\}$ unit displays the Li atom in a slightly distorted tetrahedral coordination environment and exhibits one intramolecular O—H···O hydrogen bond between a coordinating methanol molecule and the terminal non-coordinating O atom of the phosphate group. The unit is connected with two non-coordinating methanol molecules through two intermolecular O—H···O hydrogen bonds, and with a neighbouring unit through two other O—H···O interactions. These intermolecular hydrogen bonds lead to the formation of infinite chains along [100]. There are no significant interactions between the chains.

1. Chemical context

Alkali metal phosphate diesters are of interest not only because of their fundamental biological importance (see, for example: Gerus & Lis, 2013, and references therein), but also because they are direct synthetic precursors of organophosphate *d*- and *f*-metal complexes, which may find applications in various catalytic reactions. For example, rare-earth tris-(diaryl phosphate) complexes may be successfully used in polymerization reactions of 1,4-dienes (Nifant'ev *et al.*, 2013, 2014).





Crystals of the title compound, $[Li(CH_3OH)_3\{OOP(O\text{-}2,6\text{-}^{i}Pr_2C_6H_3)_2\}]\cdot CH_3OH$, have been obtained from the reaction between $HOOP(O\text{-}2,6\text{-}^{i}Pr_2C_6H_3)_2$ and LiOH in methanol followed by cooling the reaction mixture. Bis(2,6-diisopropylphenyl)phosphoric acid (for its synthesis, see: Blonski *et*

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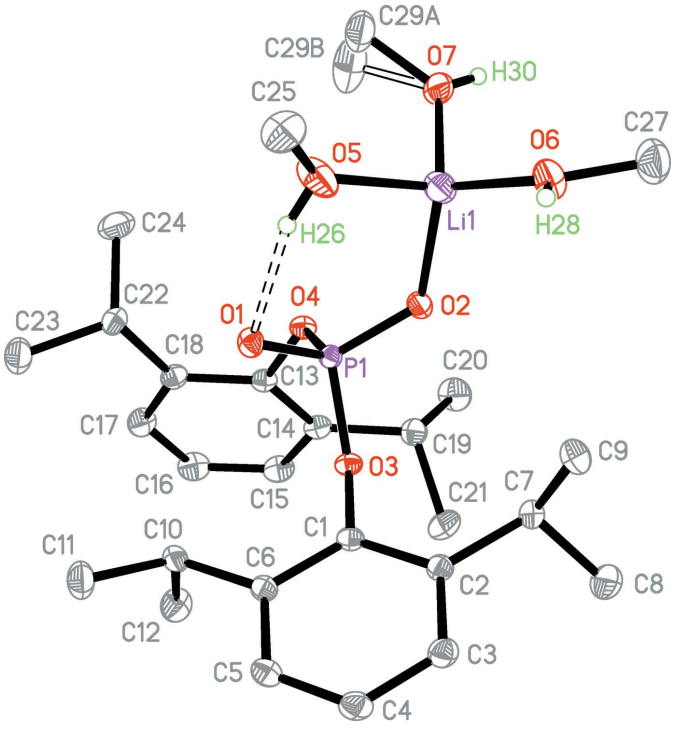

Figure 1
The molecular structure of the $\{Li(CH_3OH)_3[OOP(O\text{-}2,6\text{-}^iPr_2C_6H_3)_2]\}$ unit. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. All but hydroxy hydrogen atoms are omitted for clarity. The intramolecular hydrogen bond is shown by a dashed line. The minor component of disorder in one of the methanol molecules, C29*B*, is shown with a solid open line.

al., 1982; Kosolapoff *et al.*, 1968) was prepared from phosphoryl trichloride and 2,6-diisopropylphenol.

2. Structural commentary

In the crystal structure of the title solvate, $[Li(CH_3OH)_3\text{-}\{OOP(O\text{-}2,6\text{-}^iPr_2C_6H_3)_2\}]\cdot CH_3OH$, the $\{Li(CH_3OH)_3[OOP\text{-}(O\text{-}2,6\text{-}^iPr_2C_6H_3)_2]\}$ unit contains the Li^+ cation coordinated by three methanol molecules through the O5, O6 and O7 oxygen atoms (Fig. 1). One of the coordinating methanol molecules has its methyl group disordered over two positions [occupancy ratio 0.75 (2):0.25 (2)]. The coordination sphere of Li^+ is completed by the O2 oxygen atom of the diaryl phosphate group, $[OOP(O\text{-}2,6\text{-}^iPr_2C_6H_3)_2]^-$. This configuration is stabilized by an intramolecular hydrogen bond O5—H26···O1 (Fig.1, Table 1).

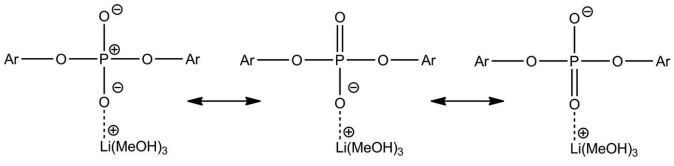

Figure 2
Plausible resonance forms of the $[OOP(O\text{-}2,6\text{-}^iPr_2C_6H_3)_2]^-$ anion.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H26···O1	0.79 (2)	2.00 (2)	2.7482 (11)	158.2 (19)
O6—H28···O8^{i}	0.85 (2)	1.86 (2)	2.7013 (14)	174 (2)
O7—H30···O2^{ii}	0.83 (2)	1.89 (2)	2.7152 (11)	170.7 (19)
O8—H32···O1	0.82 (2)	1.88 (2)	2.6929 (12)	171.8 (19)

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

Table 2
Selected bond lengths (Å).

P1—O1	1.4934 (7)	Li1—O5	1.932 (2)
P1—O2	1.4965 (7)	Li1—O6	1.915 (2)
P1—O3	1.5993 (7)	Li1—O7	1.931 (2)
P1—O4	1.6003 (7)	O3—C1	1.4035 (11)
Li1—O2	1.945 (2)	O4—C13	1.4040 (11)

The phosphorus and lithium atoms are in approximately tetrahedral environments with the corresponding bond angles ranging from 99.06 (4)–115.86 (4)° for the phosphate group and 101.32 (9)–118.40 (11) ° for the $[LiO_4]$ unit. The Li—O bond lengths range from 1.915 (2) Å to 1.945 (2) Å (Table 2). The P—O bonds can be grouped into two sets. The P1—O1 (P═O) and P1—O2 (P—O—Li) bonds have similar lengths and are ≃ 0.1 Å shorter than the P1—O3 and P1—O4 (P—O—C_{ipso}) bonds (Table 2), *i.e.* regular single P—O bonds. Since the O3—C1 and O4—C13 (O—C_{ipso}) bond lengths also correspond to single bonds, there is no charge redistribution between the PO_4 core and the two aryl fragments. These observations could best be rationalized by three major resonance forms of the anion (Fig. 2).

3. Supramolecular features

All vibrational absorption bands (*e.g.* C—H, C—C, CCH, O—H *etc.*) in the IR spectrum of the solid are fully consistent with the formula with only one exception. Regardless of the O—H absorption bands at 3636, 3576 cm^{-1}, the usual methanol C—O absorption bands at 1025–1030 cm^{-1} are missing. A possible explanation is that the methanol molecules are coordinating to lithium and form a hydrogen-bonding network. Consequently, the C—O stretching frequency may be shifted to lower wavenumbers and can be camouflaged by the phosphate absorption band at 912 cm^{-1}. This explanation would correspond to the structure data as determined by X-ray diffraction in the current study.

The $\{[Li(CH_3OH)_3][OOP(O\text{-}2,6\text{-}^iPr_2C_6H_3)_2]\}$ unit is involved in four intermolecular hydrogen bonds (Table 1, Fig. 3). Two symmetry-related O7—H30···O2 bonds connect two neighbouring units. O6—H28···O8 and O8—H32···O1 bonds link one unit and two non-coordinating methanol molecules, which are further connected to another unit. These four intermolecular hydrogen bonds result in an infinite chain extending along [100], connecting the $\{[Li(CH_3OH)_3]\text{-}[OOP(O\text{-}2,6\text{-}^iPr_2C_6H_3)_2]\}$ units and non-coordinating methanol molecules. Neighbouring molecules are related by

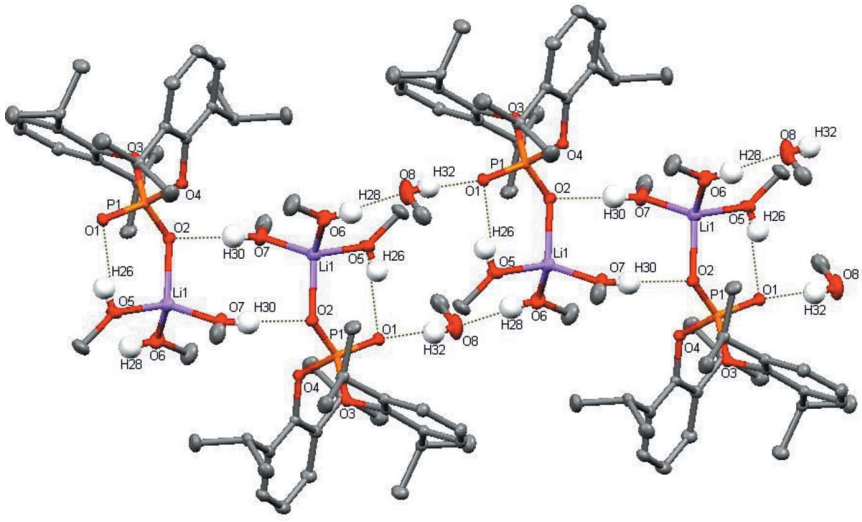

Figure 3
One-dimensional framework of {[Li(CH$_3$OH)$_3$][OOP(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$]}(CH$_3$OH). All intermolecular and intramolecular O—H···O hydrogen bonds are shown. All but hydroxy hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

inversion centers. Therefore, the orientations of the cations and anions switch in such a way as to allow the ions of neighbouring molecules in the chains to be involved in additional intermolecular Coulombic interactions (Fig. 3).

The packing of the title compound is shown in Fig. 4. No significant hydrogen-bonding interactions are found between neighbouring chains. However, some short intrachain contacts between methyl groups are present, probably due to crystal-packing effects.

4. Database survey

According to the Cambridge Structural Database (CSD version 5.35 with updates, Groom & Allen, 2014), the number of (*R*O)$_2$PO$_2$*M*(solv)$_x$ structures (*M* is an alkali metal, solv is a solvent molecule) is rather small. Structures containing additional transition metal atoms have been excluded from the search.

For related structures of potassium or sodium phosphate diesters, see: Kumara Swamy *et al.* (2001), CSD refcode ADAKUL; Gerus & Lis (2013), AGACIW; Kommana & Swamy (2003), BEDSOT; Hilken *et al.* (2014), NIZFEJ; Kumara Swamy & Kumaraswamy (2001), TIJCUK; Lugmair & Tilley (1998), VADMES; Ślepokura (2008), VIVRAU, VIVREY, VIVRIC. A mixed potassium and calcium phosphate diester has been described by Ślepokura (2008), VIVRUO. All ten found crystal structures are sodium or potassium salts. No lithium compound phosphate diesters has been structurally characterized up to date. Therefore, crystal structures of alkali metal dialkyl and diaryl phosphates remain virtually unexplored.

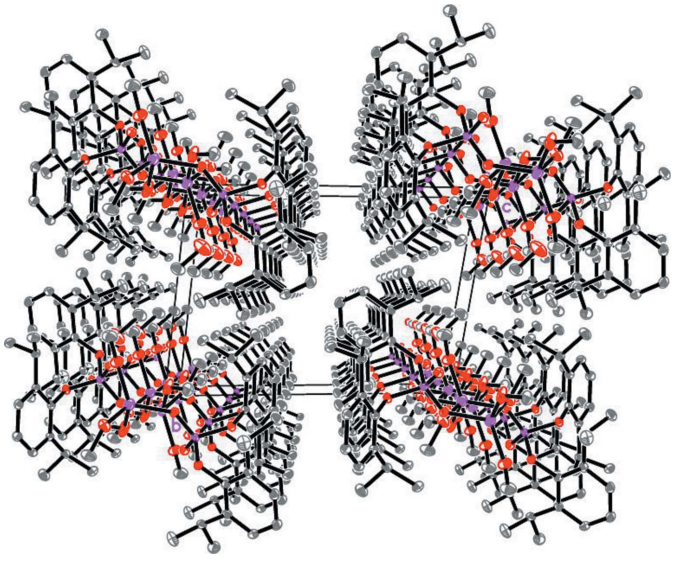

Figure 4
Packing diagram parallel to (100). All H atoms are omitted and hydrogen bonds are not shown. Infinite chains of [{Li(CH$_3$OH)$_3$[OOP(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$]}$_2$(CH$_3$OH)$_2$]$_n$ extend along [100].

5. Synthesis and crystallization

Synthesis of bis(2,6-diisopropylphenyl) phosphoric acid. Phosphoryl trichloride (12.6 ml, 21.0 g, 137 mmol, d = 1.67 g/ml) was added to a stirred solution of 2,6-diisopropylphenol (52.60 g, 295 mmol) in benzene (60 ml). Et$_3$N (44.0 ml, 32.0 g, 317 mmol, d = 0.728 g/ml, distilled over NaOH prior to use) was carefully added in small parts to the reaction mixture, while it was stirred vigorously. The reaction mixture consisted of a pale-yellow solution and an off-white precipitate of triethylamine hydrochloride. The mixture was heated under reflux for 2 days with occasional stirring. Then, water was added, and after stirring for 1 h, the organic and water layers were separated. The organic phase was evaporated under reduced pressure to produce a yellow oil. A mixture of acetone (85 ml) and water (25 ml, 1.39 mol) was added to the residue. The reaction mixture was then heated under reflux for five hours without stirring. All solvent was evaporated under

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Li(C_{24}H_{34}O_4P)(CH_4O)_3]\cdot CH_4O$
M_r	552.59
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	123
a, b, c (Å)	11.1853 (6), 11.5046 (6), 14.5237 (7)
α, β, γ (°)	90.855 (2), 102.859 (2), 118.683 (1)
V (Å^3)	1582.21 (14)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.13
Crystal size (mm)	0.60 × 0.20 × 0.10
Data collection	
Diffractometer	Bruker APEXII CCD area-detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2003)
T_{min}, T_{max}	0.872, 0.986
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22920, 10353, 8544
R_{int}	0.021
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.732
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.112, 1.02
No. of reflections	10353
No. of parameters	382
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.77, −0.53

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SHELXS2013* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).

reduced pressure from the mixture. The resulting precipitate was recrystallized from petroleum ether (70/100, ≃ 250 ml), filtered off, washed with cold (273 K) hexane and dried under dynamic vacuum. The yield of white crystals was 40.89 g (97.70 mmol, 71.3%). Melting point 432–433 K. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 [24H, *d*, –CH(C***H*****$_3$**)$_2$], 3.34 [4H, septet, –C***H***$(CH_3)_2$], 7.02–7.14 (6H, *m*, ***H*****$_{Aryl}$**), 11.08 [1H, *br.s*, P(O)O***H***]; ^{31}P NMR (162 MHz, $CDCl_3$): δ = −10.19.

Synthesis and crystallization of tris(methanol)-lithium bis(2,6-diisopropylphenyl) phosphate methanol solvate. Bis(2,6-diisopropylphenyl) phosphoric acid (15.07 g, 36.0 mmol) was dissolved in methanol (50 ml). Lithium hydroxide (0.86 g, 36 mmol) was added in small parts to the mixture until pH = 7–8. The reaction mixture was filtered, and the resulting solution was placed into a freezer (258 K) for 3 days. The grown crystals were filtered off, washed with cold methanol (≃ 273 K). Several colorless needles were selected for X-ray structure determination analysis. The remaining crystals were dried under dynamic vacuum. Yield 7.72 g (14.0 mmol, 39%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 [24H, *d*, –CH(C***H*****$_3$**)$_2$, $^3J_{HH}$ = 6.85 Hz], 2.63 (4H, *br.s*, CH_3O***H***), 3.25 (12H, *s*, C***H*****$_3$**OH), 3.60 [4H, septet, –C***H***$(CH_3)_2$, $^3J_{HH}$ = 6.85 Hz], 7.03–7.09 (6H, *m*, ***H*****$_{Aryl}$**). ^{31}P NMR (162, MHz, $CDCl_3$): δ = −10.23.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The positions of hydroxy hydrogen atoms were found from a difference map. These atoms were refined with individual isotropic displacement parameters. All other hydrogen atoms were also found from the difference map but positioned geometrically (C—H distance = 0.95 Å for aromatic, 0.98 Å for methyl, 1.00 Å for –C***H***Me_2 hydrogen atoms) and refined as riding atoms with relative isotropic displacement parameters [U_{iso}(H) = 1.2U_{eq}(C) for aromatic and –C***H***Me_2, 1.5U_{eq}(C) for methyl hydrogen atoms]. One of the coordinating methanol molecules showed disorder of its methyl group, with restrained occupancies of 0.75 (2):0.25 (2) for atoms C29*A* and C29*B*. A rotating group model was applied for all methyl groups. Reflection 0 0 1 was obstructed by the beam stop and was omitted from refinement.

Acknowledgements

The authors are grateful to Ivan V. Anan'ev for assistance with the X-ray study.

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Nifant'ev, I. E., Tavtorkin, A. N., Shlyahtin, A. V., Korchagina, S. A., Gavrilenko, I. F., Glebova, N. N. & Churakov, A. V. (2013). *Dalton Trans.* **42**, 1223–1230.
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supporting information

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Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

[Bis(2,6-diisopropylphenyl) phosphato-κ*O*]tris(methanol-κ*O*)lithium methanol monosolvate

Crystal data

$[Li(C_{24}H_{34}O_4P)(CH_4O)_3]\cdot CH_4O$
M_r = 552.59
Triclinic, $P\overline{1}$
a = 11.1853 (6) Å
b = 11.5046 (6) Å
c = 14.5237 (7) Å
α = 90.855 (2)°
β = 102.859 (2)°
γ = 118.683 (1)°
V = 1582.21 (14) Å^3
Z = 2
$F(000)$ = 600
D_x = 1.160 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.710730 (9) Å
Cell parameters from 9855 reflections
θ = 2.3–31.3°
μ = 0.13 mm^{-1}
T = 123 K
Needle, colorless
0.60 × 0.20 × 0.10 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.872, T_{max} = 0.986
22920 measured reflections
10353 independent reflections
8544 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 31.3°, θ_{min} = 2.0°
h = −16→16
k = −16→16
l = −21→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.112
S = 1.02
10353 reflections
382 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0628P)^2 + 0.329P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.77$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
P1	0.62300 (2)	0.88864 (2)	0.82666 (2)	0.01132 (6)	
Li1	0.7224 (2)	1.0298 (2)	1.03455 (14)	0.0216 (4)	
O1	0.71418 (7)	0.82744 (7)	0.85725 (5)	0.01552 (14)	
O2	0.64407 (7)	0.99757 (7)	0.89696 (5)	0.01510 (13)	
O3	0.63126 (7)	0.93432 (7)	0.72374 (5)	0.01310 (13)	
O4	0.45827 (7)	0.78087 (7)	0.80228 (5)	0.01346 (13)	
C1	0.75457 (9)	0.99858 (9)	0.69226 (6)	0.01272 (16)	
C2	0.82677 (10)	1.13862 (9)	0.70219 (7)	0.01421 (17)	
C3	0.94480 (11)	1.19980 (10)	0.66505 (7)	0.01713 (18)	
H3A	0.9972	1.2947	0.6711	0.021*	
C4	0.98609 (11)	1.12365 (10)	0.61952 (7)	0.01835 (19)	
H4A	1.0670	1.1667	0.5954	0.022*	
C5	0.90964 (11)	0.98439 (10)	0.60897 (7)	0.01706 (18)	
H5A	0.9383	0.9336	0.5767	0.020*	
C6	0.79173 (10)	0.91821 (9)	0.64503 (7)	0.01379 (17)	
C7	0.78093 (11)	1.22290 (10)	0.75072 (7)	0.01677 (18)	
H7A	0.6876	1.1609	0.7628	0.020*	
C8	0.76209 (14)	1.32155 (12)	0.68757 (9)	0.0267 (2)	
H8A	0.6950	1.2724	0.6260	0.040*	
H8B	0.8533	1.3862	0.6772	0.040*	
H8C	0.7259	1.3691	0.7191	0.040*	
C9	0.88650 (13)	1.29710 (11)	0.84741 (8)	0.0234 (2)	
H9A	0.8916	1.2320	0.8885	0.035*	
H9B	0.8554	1.3507	0.8777	0.035*	
H9C	0.9800	1.3561	0.8377	0.035*	
C10	0.70174 (10)	0.76631 (10)	0.62834 (7)	0.01561 (17)	
H10A	0.6566	0.7390	0.6823	0.019*	
C11	0.78739 (13)	0.69543 (11)	0.62659 (9)	0.0243 (2)	
H11A	0.8629	0.7261	0.6858	0.036*	
H11B	0.8287	0.7163	0.5721	0.036*	
H11C	0.7253	0.5985	0.6207	0.036*	
C12	0.58316 (12)	0.72179 (11)	0.53609 (8)	0.0228 (2)	
H12A	0.5282	0.7665	0.5397	0.034*	
H12B	0.5212	0.6246	0.5281	0.034*	
H12C	0.6242	0.7459	0.4816	0.034*	

C13	0.37172 (10)	0.70309 (9)	0.71375 (7)	0.01358 (16)	
C14	0.30293 (10)	0.75513 (10)	0.64912 (7)	0.01566 (17)	
C15	0.20879 (11)	0.67082 (11)	0.56457 (7)	0.01988 (19)	
H15A	0.1599	0.7025	0.5193	0.024*	
C16	0.18558 (11)	0.54178 (11)	0.54579 (8)	0.0221 (2)	
H16A	0.1214	0.4862	0.4881	0.027*	
C17	0.25624 (11)	0.49414 (10)	0.61134 (8)	0.02018 (19)	
H17A	0.2401	0.4060	0.5977	0.024*	
C18	0.35065 (10)	0.57348 (10)	0.69699 (7)	0.01573 (17)	
C19	0.32711 (11)	0.89620 (10)	0.66694 (7)	0.01742 (18)	
H19A	0.3980	0.9406	0.7299	0.021*	
C20	0.19082 (13)	0.89471 (14)	0.67174 (9)	0.0277 (2)	
H20A	0.1560	0.8457	0.7232	0.042*	
H20B	0.1194	0.8506	0.6109	0.042*	
H20C	0.2100	0.9868	0.6842	0.042*	
C21	0.38705 (12)	0.97881 (12)	0.58994 (8)	0.0239 (2)	
H21A	0.4731	0.9779	0.5866	0.036*	
H21B	0.4093	1.0713	0.6061	0.036*	
H21C	0.3170	0.9400	0.5280	0.036*	
C22	0.42568 (11)	0.52122 (10)	0.77067 (7)	0.01739 (18)	
H22A	0.5211	0.5984	0.8025	0.021*	
C23	0.44768 (15)	0.41384 (12)	0.72666 (9)	0.0283 (2)	
H23A	0.4917	0.4461	0.6742	0.042*	
H23B	0.3563	0.3322	0.7022	0.042*	
H23C	0.5092	0.3944	0.7754	0.042*	
C24	0.34634 (14)	0.46943 (14)	0.84766 (9)	0.0294 (3)	
H24A	0.3386	0.5414	0.8779	0.044*	
H24B	0.3981	0.4396	0.8959	0.044*	
H24C	0.2516	0.3941	0.8185	0.044*	
O5	0.81065 (10)	0.91990 (11)	1.04939 (6)	0.0312 (2)	
C25	0.92769 (13)	0.92434 (13)	1.11483 (9)	0.0284 (2)	
H25A	0.9020	0.8346	1.1315	0.043*	
H25B	0.9552	0.9860	1.1726	0.043*	
H25C	1.0070	0.9554	1.0857	0.043*	
O6	0.86571 (9)	1.20747 (8)	1.09305 (6)	0.02504 (17)	
C27	0.84869 (16)	1.31713 (13)	1.11945 (11)	0.0339 (3)	
H27A	0.8725	1.3800	1.0729	0.051*	
H27B	0.9113	1.3628	1.1829	0.051*	
H27C	0.7505	1.2842	1.1207	0.051*	
O7	0.56431 (9)	0.94990 (8)	1.09033 (6)	0.02329 (17)	
C29A	0.5209 (6)	0.8252 (4)	1.1245 (4)	0.0311 (8)	0.75 (2)
H29A	0.5812	0.7894	1.1136	0.047*	0.75 (2)
H29B	0.4225	0.7624	1.0905	0.047*	0.75 (2)
H29C	0.5290	0.8372	1.1929	0.047*	0.75 (2)
C29B	0.4900 (14)	0.8055 (11)	1.084 (2)	0.044 (3)	0.25 (2)
H29D	0.4135	0.7671	1.0245	0.066*	0.25 (2)
H29E	0.4504	0.7794	1.1384	0.066*	0.25 (2)
H29F	0.5558	0.7723	1.0829	0.066*	0.25 (2)

O8	0.85286 (11)	0.68825 (11)	0.87815 (8)	0.0382 (2)
C31	0.78917 (14)	0.59808 (13)	0.93888 (10)	0.0308 (3)
H31A	0.7034	0.5192	0.9011	0.046*
H31B	0.7646	0.6413	0.9843	0.046*
H31C	0.8550	0.5706	0.9738	0.046*
H26	0.799 (2)	0.8875 (19)	0.9979 (15)	0.045 (5)*
H28	0.953 (2)	1.236 (2)	1.0986 (14)	0.051 (5)*
H30	0.507 (2)	0.9752 (19)	1.0954 (14)	0.049 (5)*
H32	0.814 (2)	0.7331 (19)	0.8674 (14)	0.047 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.01157 (11)	0.01212 (11)	0.01118 (11)	0.00666 (8)	0.00276 (8)	0.00173 (8)
Li1	0.0244 (9)	0.0239 (9)	0.0188 (8)	0.0142 (8)	0.0046 (7)	0.0014 (7)
O1	0.0157 (3)	0.0174 (3)	0.0161 (3)	0.0110 (3)	0.0025 (3)	0.0020 (3)
O2	0.0175 (3)	0.0154 (3)	0.0139 (3)	0.0094 (3)	0.0039 (2)	0.0008 (2)
O3	0.0117 (3)	0.0157 (3)	0.0126 (3)	0.0066 (2)	0.0048 (2)	0.0041 (2)
O4	0.0119 (3)	0.0149 (3)	0.0119 (3)	0.0055 (2)	0.0028 (2)	0.0017 (2)
C1	0.0109 (4)	0.0150 (4)	0.0121 (4)	0.0060 (3)	0.0034 (3)	0.0024 (3)
C2	0.0147 (4)	0.0143 (4)	0.0132 (4)	0.0070 (3)	0.0033 (3)	0.0018 (3)
C3	0.0159 (4)	0.0147 (4)	0.0177 (4)	0.0052 (3)	0.0048 (3)	0.0021 (3)
C4	0.0145 (4)	0.0194 (5)	0.0195 (5)	0.0059 (4)	0.0075 (3)	0.0031 (4)
C5	0.0160 (4)	0.0196 (4)	0.0168 (4)	0.0091 (4)	0.0060 (3)	0.0016 (3)
C6	0.0135 (4)	0.0149 (4)	0.0126 (4)	0.0070 (3)	0.0028 (3)	0.0013 (3)
C7	0.0202 (4)	0.0146 (4)	0.0178 (4)	0.0098 (4)	0.0064 (4)	0.0027 (3)
C8	0.0362 (6)	0.0272 (6)	0.0286 (6)	0.0231 (5)	0.0124 (5)	0.0112 (4)
C9	0.0284 (5)	0.0191 (5)	0.0205 (5)	0.0106 (4)	0.0056 (4)	−0.0021 (4)
C10	0.0174 (4)	0.0139 (4)	0.0160 (4)	0.0077 (4)	0.0056 (3)	0.0008 (3)
C11	0.0265 (5)	0.0194 (5)	0.0326 (6)	0.0147 (4)	0.0100 (4)	0.0039 (4)
C12	0.0221 (5)	0.0180 (5)	0.0215 (5)	0.0068 (4)	0.0008 (4)	−0.0004 (4)
C13	0.0107 (4)	0.0145 (4)	0.0132 (4)	0.0044 (3)	0.0034 (3)	0.0021 (3)
C14	0.0131 (4)	0.0188 (4)	0.0152 (4)	0.0079 (4)	0.0040 (3)	0.0045 (3)
C15	0.0155 (4)	0.0248 (5)	0.0167 (4)	0.0092 (4)	0.0012 (3)	0.0041 (4)
C16	0.0174 (5)	0.0225 (5)	0.0180 (5)	0.0051 (4)	0.0005 (4)	0.0000 (4)
C17	0.0183 (4)	0.0157 (4)	0.0198 (5)	0.0043 (4)	0.0025 (4)	0.0003 (4)
C18	0.0139 (4)	0.0148 (4)	0.0163 (4)	0.0053 (3)	0.0044 (3)	0.0035 (3)
C19	0.0170 (4)	0.0208 (5)	0.0179 (4)	0.0123 (4)	0.0039 (3)	0.0044 (4)
C20	0.0249 (5)	0.0372 (6)	0.0314 (6)	0.0226 (5)	0.0089 (5)	0.0077 (5)
C21	0.0248 (5)	0.0250 (5)	0.0236 (5)	0.0137 (4)	0.0062 (4)	0.0105 (4)
C22	0.0187 (4)	0.0143 (4)	0.0184 (4)	0.0078 (4)	0.0040 (4)	0.0037 (3)
C23	0.0388 (7)	0.0247 (5)	0.0270 (6)	0.0213 (5)	0.0058 (5)	0.0031 (4)
C24	0.0357 (6)	0.0361 (6)	0.0252 (6)	0.0215 (6)	0.0146 (5)	0.0156 (5)
O5	0.0379 (5)	0.0508 (6)	0.0161 (4)	0.0356 (5)	−0.0045 (3)	−0.0052 (4)
C25	0.0228 (5)	0.0342 (6)	0.0244 (5)	0.0151 (5)	−0.0029 (4)	0.0048 (5)
O6	0.0241 (4)	0.0222 (4)	0.0292 (4)	0.0115 (3)	0.0080 (3)	−0.0014 (3)
C27	0.0407 (7)	0.0261 (6)	0.0443 (8)	0.0197 (6)	0.0210 (6)	0.0057 (5)
O7	0.0300 (4)	0.0268 (4)	0.0267 (4)	0.0213 (4)	0.0144 (3)	0.0105 (3)

C29A	0.0370 (16)	0.0231 (11)	0.0440 (17)	0.0190 (11)	0.0200 (14)	0.0109 (11)
C29B	0.034 (4)	0.026 (4)	0.080 (11)	0.017 (3)	0.025 (5)	0.013 (5)
O8	0.0365 (5)	0.0451 (6)	0.0568 (7)	0.0329 (5)	0.0243 (5)	0.0282 (5)
C31	0.0285 (6)	0.0269 (6)	0.0361 (7)	0.0144 (5)	0.0046 (5)	0.0098 (5)

Geometric parameters (Å, º)

P1—O1	1.4934 (7)	C16—H16A	0.9500
P1—O2	1.4965 (7)	C17—C18	1.3971 (14)
P1—O3	1.5993 (7)	C17—H17A	0.9500
P1—O4	1.6003 (7)	C18—C22	1.5214 (14)
Li1—O2	1.945 (2)	C19—C20	1.5335 (15)
Li1—O5	1.932 (2)	C19—C21	1.5352 (15)
Li1—O6	1.915 (2)	C19—H19A	1.0000
Li1—O7	1.931 (2)	C20—H20A	0.9800
O3—C1	1.4035 (11)	C20—H20B	0.9800
O4—C13	1.4040 (11)	C20—H20C	0.9800
C1—C2	1.4003 (13)	C21—H21A	0.9800
C1—C6	1.4053 (13)	C21—H21B	0.9800
C2—C3	1.4019 (13)	C21—H21C	0.9800
C2—C7	1.5224 (13)	C22—C23	1.5276 (15)
C3—C4	1.3875 (14)	C22—C24	1.5320 (15)
C3—H3A	0.9500	C22—H22A	1.0000
C4—C5	1.3930 (14)	C23—H23A	0.9800
C4—H4A	0.9500	C23—H23B	0.9800
C5—C6	1.3960 (13)	C23—H23C	0.9800
C5—H5A	0.9500	C24—H24A	0.9800
C6—C10	1.5219 (13)	C24—H24B	0.9800
C7—C8	1.5325 (15)	C24—H24C	0.9800
C7—C9	1.5342 (15)	O5—C25	1.4144 (14)
C7—H7A	1.0000	O5—H26	0.79 (2)
C8—H8A	0.9800	C25—H25A	0.9800
C8—H8B	0.9800	C25—H25B	0.9800
C8—H8C	0.9800	C25—H25C	0.9800
C9—H9A	0.9800	O6—C27	1.4225 (14)
C9—H9B	0.9800	O6—H28	0.85 (2)
C9—H9C	0.9800	C27—H27A	0.9800
C10—C11	1.5309 (14)	C27—H27B	0.9800
C10—C12	1.5339 (15)	C27—H27C	0.9800
C10—H10A	1.0000	O7—C29A	1.415 (3)
C11—H11A	0.9800	O7—C29B	1.447 (11)
C11—H11B	0.9800	O7—H30	0.83 (2)
C11—H11C	0.9800	C29A—H29A	0.9800
C12—H12A	0.9800	C29A—H29B	0.9800
C12—H12B	0.9800	C29A—H29C	0.9800
C12—H12C	0.9800	C29B—H29D	0.9800
C13—C18	1.4016 (14)	C29B—H29E	0.9800
C13—C14	1.4032 (13)	C29B—H29F	0.9800

C14—C15	1.4021 (14)	O8—C31	1.3996 (16)
C14—C19	1.5196 (14)	O8—H32	0.82 (2)
C15—C16	1.3901 (16)	C31—H31A	0.9800
C15—H15A	0.9500	C31—H31B	0.9800
C16—C17	1.3885 (15)	C31—H31C	0.9800
O1—P1—O2	115.86 (4)	C18—C17—H17A	119.4
O1—P1—O3	110.98 (4)	C17—C18—C13	117.37 (9)
O2—P1—O3	111.66 (4)	C17—C18—C22	121.75 (9)
O1—P1—O4	112.44 (4)	C13—C18—C22	120.87 (9)
O2—P1—O4	105.46 (4)	C14—C19—C20	111.38 (9)
O3—P1—O4	99.06 (4)	C14—C19—C21	111.12 (9)
O6—Li1—O7	114.81 (10)	C20—C19—C21	110.04 (9)
O6—Li1—O5	106.80 (10)	C14—C19—H19A	108.1
O7—Li1—O5	107.49 (10)	C20—C19—H19A	108.1
O6—Li1—O2	118.40 (11)	C21—C19—H19A	108.1
O7—Li1—O2	106.73 (10)	C19—C20—H20A	109.5
O5—Li1—O2	101.32 (9)	C19—C20—H20B	109.5
P1—O2—Li1	128.08 (7)	H20A—C20—H20B	109.5
C1—O3—P1	125.61 (6)	C19—C20—H20C	109.5
C13—O4—P1	126.90 (6)	H20A—C20—H20C	109.5
C2—C1—O3	118.35 (8)	H20B—C20—H20C	109.5
C2—C1—C6	123.54 (9)	C19—C21—H21A	109.5
O3—C1—C6	117.87 (8)	C19—C21—H21B	109.5
C1—C2—C3	117.12 (9)	H21A—C21—H21B	109.5
C1—C2—C7	122.36 (9)	C19—C21—H21C	109.5
C3—C2—C7	120.52 (9)	H21A—C21—H21C	109.5
C4—C3—C2	120.88 (9)	H21B—C21—H21C	109.5
C4—C3—H3A	119.6	C18—C22—C23	113.01 (9)
C2—C3—H3A	119.6	C18—C22—C24	110.50 (9)
C3—C4—C5	120.38 (9)	C23—C22—C24	110.65 (9)
C3—C4—H4A	119.8	C18—C22—H22A	107.5
C5—C4—H4A	119.8	C23—C22—H22A	107.5
C4—C5—C6	121.16 (9)	C24—C22—H22A	107.5
C4—C5—H5A	119.4	C22—C23—H23A	109.5
C6—C5—H5A	119.4	C22—C23—H23B	109.5
C5—C6—C1	116.89 (9)	H23A—C23—H23B	109.5
C5—C6—C10	121.63 (8)	C22—C23—H23C	109.5
C1—C6—C10	121.37 (8)	H23A—C23—H23C	109.5
C2—C7—C8	111.88 (8)	H23B—C23—H23C	109.5
C2—C7—C9	110.51 (8)	C22—C24—H24A	109.5
C8—C7—C9	110.68 (9)	C22—C24—H24B	109.5
C2—C7—H7A	107.9	H24A—C24—H24B	109.5
C8—C7—H7A	107.9	C22—C24—H24C	109.5
C9—C7—H7A	107.9	H24A—C24—H24C	109.5
C7—C8—H8A	109.5	H24B—C24—H24C	109.5
C7—C8—H8B	109.5	C25—O5—Li1	135.51 (10)
H8A—C8—H8B	109.5	C25—O5—H26	111.9 (14)

C7—C8—H8C	109.5	Li1—O5—H26	106.6 (14)
H8A—C8—H8C	109.5	O5—C25—H25A	109.5
H8B—C8—H8C	109.5	O5—C25—H25B	109.5
C7—C9—H9A	109.5	H25A—C25—H25B	109.5
C7—C9—H9B	109.5	O5—C25—H25C	109.5
H9A—C9—H9B	109.5	H25A—C25—H25C	109.5
C7—C9—H9C	109.5	H25B—C25—H25C	109.5
H9A—C9—H9C	109.5	C27—O6—Li1	128.27 (10)
H9B—C9—H9C	109.5	C27—O6—H28	108.3 (14)
C6—C10—C11	113.23 (8)	Li1—O6—H28	122.7 (13)
C6—C10—C12	109.69 (8)	O6—C27—H27A	109.5
C11—C10—C12	110.98 (9)	O6—C27—H27B	109.5
C6—C10—H10A	107.6	H27A—C27—H27B	109.5
C11—C10—H10A	107.6	O6—C27—H27C	109.5
C12—C10—H10A	107.6	H27A—C27—H27C	109.5
C10—C11—H11A	109.5	H27B—C27—H27C	109.5
C10—C11—H11B	109.5	C29A—O7—Li1	122.16 (15)
H11A—C11—H11B	109.5	C29B—O7—Li1	117.0 (7)
C10—C11—H11C	109.5	C29A—O7—H30	108.0 (14)
H11A—C11—H11C	109.5	C29B—O7—H30	106.9 (14)
H11B—C11—H11C	109.5	Li1—O7—H30	129.6 (14)
C10—C12—H12A	109.5	O7—C29A—H29A	109.5
C10—C12—H12B	109.5	O7—C29A—H29B	109.5
H12A—C12—H12B	109.5	H29A—C29A—H29B	109.5
C10—C12—H12C	109.5	O7—C29A—H29C	109.5
H12A—C12—H12C	109.5	H29A—C29A—H29C	109.5
H12B—C12—H12C	109.5	H29B—C29A—H29C	109.5
C18—C13—C14	123.15 (9)	O7—C29B—H29D	109.5
C18—C13—O4	118.19 (8)	O7—C29B—H29E	109.5
C14—C13—O4	118.51 (8)	H29D—C29B—H29E	109.5
C15—C14—C13	117.02 (9)	O7—C29B—H29F	109.5
C15—C14—C19	119.91 (9)	H29D—C29B—H29F	109.5
C13—C14—C19	123.07 (9)	H29E—C29B—H29F	109.5
C16—C15—C14	121.25 (10)	C31—O8—H32	108.1 (14)
C16—C15—H15A	119.4	O8—C31—H31A	109.5
C14—C15—H15A	119.4	O8—C31—H31B	109.5
C17—C16—C15	120.01 (10)	H31A—C31—H31B	109.5
C17—C16—H16A	120.0	O8—C31—H31C	109.5
C15—C16—H16A	120.0	H31A—C31—H31C	109.5
C16—C17—C18	121.20 (10)	H31B—C31—H31C	109.5
C16—C17—H17A	119.4		

O1—P1—O2—Li1	−22.98 (11)	C3—C2—C7—C9	−70.95 (12)
O3—P1—O2—Li1	−151.34 (9)	C5—C6—C10—C11	34.55 (13)
O4—P1—O2—Li1	102.06 (10)	C1—C6—C10—C11	−149.58 (9)
O1—P1—O3—C1	−42.03 (8)	C5—C6—C10—C12	−90.02 (11)
O2—P1—O3—C1	88.89 (8)	C1—C6—C10—C12	85.85 (11)
O4—P1—O3—C1	−160.39 (7)	P1—O4—C13—C18	95.20 (10)

Li1—P1—O3—C1	68.81 (10)	P1—O4—C13—C14	−89.13 (10)
O1—P1—O4—C13	−88.42 (8)	C18—C13—C14—C15	0.30 (14)
O2—P1—O4—C13	144.44 (7)	O4—C13—C14—C15	−175.14 (8)
O3—P1—O4—C13	28.84 (8)	C18—C13—C14—C19	−179.32 (9)
Li1—P1—O4—C13	175.22 (8)	O4—C13—C14—C19	5.24 (14)
P1—O3—C1—C2	−94.01 (10)	C13—C14—C15—C16	−0.31 (15)
P1—O3—C1—C6	91.40 (10)	C19—C14—C15—C16	179.32 (10)
O3—C1—C2—C3	−176.33 (8)	C14—C15—C16—C17	0.00 (17)
C6—C1—C2—C3	−2.06 (14)	C15—C16—C17—C18	0.36 (17)
O3—C1—C2—C7	3.54 (13)	C16—C17—C18—C13	−0.38 (15)
C6—C1—C2—C7	177.81 (9)	C16—C17—C18—C22	178.27 (10)
C1—C2—C3—C4	0.79 (14)	C14—C13—C18—C17	0.04 (15)
C7—C2—C3—C4	−179.08 (9)	O4—C13—C18—C17	175.49 (8)
C2—C3—C4—C5	0.71 (16)	C14—C13—C18—C22	−178.61 (9)
C3—C4—C5—C6	−1.07 (16)	O4—C13—C18—C22	−3.16 (13)
C4—C5—C6—C1	−0.11 (14)	C15—C14—C19—C20	62.20 (13)
C4—C5—C6—C10	175.93 (9)	C13—C14—C19—C20	−118.20 (11)
C2—C1—C6—C5	1.72 (14)	C15—C14—C19—C21	−60.88 (12)
O3—C1—C6—C5	176.02 (8)	C13—C14—C19—C21	118.73 (10)
C2—C1—C6—C10	−174.33 (9)	C17—C18—C22—C23	28.37 (14)
O3—C1—C6—C10	−0.04 (13)	C13—C18—C22—C23	−153.04 (10)
C1—C2—C7—C8	−127.00 (10)	C17—C18—C22—C24	−96.23 (12)
C3—C2—C7—C8	52.86 (13)	C13—C18—C22—C24	82.36 (12)
C1—C2—C7—C9	109.19 (11)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H26···O1	0.79 (2)	2.00 (2)	2.7482 (11)	158.2 (19)
O6—H28···O8^{i}	0.85 (2)	1.86 (2)	2.7013 (14)	174 (2)
O7—H30···O2^{ii}	0.83 (2)	1.89 (2)	2.7152 (11)	170.7 (19)
O8—H32···O1	0.82 (2)	1.88 (2)	2.6929 (12)	171.8 (19)

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