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The typical crystal structures of a few representative α-aryl-α-hydroxyphosphonates

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The crystal structures of seven α-aryl-α-hydroxyphosphonates synthesized by the Pudovik reaction of substituted benzaldehydes and dialkyl phosphites, namely dimethyl [(hydroxy)(phenyl)methyl]phosphonate, $C_9H_{13}O_4P$, dimethyl [(3,4-dimethoxyphenyl)(hydroxy)methyl]phosphonate, $C_{11}H_{17}O_6P$, dimethyl (1-hydroxy-1-phenylethyl)phosphonate, $C_{10}H_{15}O_4P$, dimethyl [1-hydroxy-1-(4-nitrophenyl)ethyl]phosphonate, $C_{10}H_{14}NO_6P$, dibenzyl [hydroxy(2-nitrophenyl)methyl]phosphonate, $C_{21}H_{20}NO_6P$, dibenzyl [(3-chlorophenyl)(hydroxy)methyl]phosphonate, $C_{21}H_{20}ClO_4P$, and dibenzyl [hydroxy(4-methylphenyl)methyl]phosphonate, $C_{22}H_{23}O_4P$, were studied to gain a better understanding of the organization in this type of molecule in the solid state. The crystals obtained for this series of compounds show a balance between C—OH···O=P chain-linked packing and the dimeric types of hydrogen-bond bridges of intermolecular pairs of such functions. The description is based on primary graph-set descriptors. Using graph-set descriptors one level deeper (*i.e.* secondary graph sets of the C—H···O type) revealed a similarity in the graph-set descriptors, suggesting a fine interplay of substituent- and shape-dependent effects on strong–weak interactions. It seems that the formation of chains or dimers is governed not only by the presence of a tertiary Cα atom, but also by the nature and crowding of the *ortho* substituents of the α-aryl group.

1. Introduction

α-Hydroxyphosphonates represent a prominent class within organophosphorus compounds due to their real or potential biological activity. Based on their enzyme inhibitory properties (Patel *et al.*, 1995), hydroxyphosphonates may have antibiotic (Kategaonkar *et al.*, 2010; Pokalwar *et al.*, 2006), antifungicidal (Kategaonkar *et al.*, 2010), antioxidant (Rao *et al.*, 2011; Naidu *et al.*, 2012), anticancer (Kalla *et al.*, 2015), anti-HIV and anti-inflammatory effects (Frechette *et al.*, 1997). Trichlorfon [or *O*,*O*-dimethyl (2,2,2-trichloro-1-hydroxyethyl)phosphonate] was an early insecticide that was the precursor of dichlorvos (2,2-dichlorovinyl dimethylphosphate) with an acetylcholine esterase paralyzing effect (Lorenz *et al.*, 1995).

A number of base- and acid-catalyzed, as well as different solid-salt-catalyzed methods were elaborated for the synthesis of α-hydroxyphosphonates (Rádai & Keglevich, 2018; Pudovik & Konovalova, 1979; Kharasch *et al.*, 1960; Ruveda & De Licastro, 1972; Timmler & Kurz, 1971; Texierboullet & Foucard, 1980, 1982*a*,*b*; Hudson *et al.*, 2008; Sardarian & Kaboudin, 1997; Smahi *et al.*, 2008; Solhy *et al.*, 2010; Kaboudin & Nazari, 2002). Thiourea-based organo-catalysts have also been used for the synthesis of tertiary α-hydroxyphosphonates

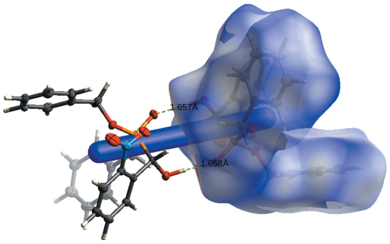

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Table 1
Experimental details for the preparation and characterization of α-hydroxyphosphonates **1** and **3**.

Product	Time (min)	Yield (%)	^{31}P NMR δP	^{31}P NMR δP (reference)	M.p. (°C)	M.p. (reference) (°C)	$[M + H]^+$	Entry
1a	10	95	23.8	24.3[a]	100–101	101–102[e,f]	217.1	1
1b	120	86	24.1	23.8[b]	125–126	124[b]	277.1	2[#]
3a	30	91	21.1	21.1[c]	124–125	-	414.1114	3
3b	30	88	22.3	22.3[c]	103–104	-	403.0881	4
3c	330	94	22.4	22.4[d]	110–111	87–88[d]	383.1392	5

Notes: (#) In this case, 0.3 equivalents of triethylamine was used. References: (*a*) Rowe & Spilling (2001); (*b*) Hudson *et al.* (2008); (*c*) Rádai *et al.* (2018); (*d*) Pawar *et al.* (2006); (*e*) Keglevich *et al.* (2011); (*f*) Abramov (1952).

(Kong *et al.*, 2012). Keglevich and co-workers reported a microwave-assisted, solvent-free preparation of hydroxyphosphonates (Keglevich *et al.*, 2011). Although a number of green variations were developed for the synthesis of the phosphonates under discussion, in these approaches the reaction conditions were green only with respect to the catalyst and the lack of solvents. The work-up involved the extensive use of solvents as extractants, eluants in chromatography and as media for recrystallizations (Kumar *et al.*, 2012; Nandre *et al.*, 2012; Kong *et al.*, 2014; Kulkarni *et al.*, 2013; Ramananarivo *et al.*, 2013; Santhisudha *et al.*, 2015; Liu *et al.*, 2014). Keglevich and co-workers could, however, elaborate a green method, when the hydroxyphosphonate simply crystallized out in a pure form from the reaction mixture. In this case, only a minimal amount of acetone and pentane was necessary as the solvent (Keglevich *et al.*, 2017). A convenient functionalization of α-hydroxyphosphonates was also reported recently (Cytlak *et al.*, 2018) *en route* to the synthesis of α-aminophosphonates. Several such novel α-aminophosphonate crystal structures were also reported (Cytlak *et al.*, 2018). The structure determination of phosphonates was soon undertaken as their economic value grew. The crystal structure of trichlorfon was reported 50 years ago (Höhne & Lohs, 1969). Several related tertiary Cα α-hydroxyphosphonate ester crystal structures have been reported recently, *viz.* diphenyl (hydroxyphenylmethyl)phosphonate (Fang *et al.*, 2006*c*), diethyl [hydroxy(phenyl)methyl]phosphonate (An *et al.*, 2008; Fang *et al.*, 2010; Ouksel *et al.*, 2017), dimethyl [hydroxy(phenyl)methyl]phosphonate (Fang *et al.*, 2006*b*) and diisopropyl (hydroxyphenylmethyl)phosphonate (Fang *et al.*, 2006*a*). Of interest are the three known independent room-temperature structure determinations of diethyl [hydroxy(phenyl)methyl]phosphonate derivative. One determination reports disorder of the ethyl ester groups (An *et al.*, 2008), but the three have different volumes of 1296.5, 1263.5 and 1315.2 Å^3 [Cambridge Structural Database (CSD; Groom *et al.*, 2016) refcodes KODYOS (An *et al.*, 2008), KODYOS01 (Fang *et al.*, 2010) and KODYOS02 (Ouksel *et al.*, 2017)]. Some closely related Cα methyl-group-containing crystal structures are dimethyl (*S*)-[cyano(hydroxy)phenylmethyl]phosphonate (Kong *et al.*, 2012), diphenyl (1-hydroxy-1-phenylethyl)phosphonate (Lane *et al.*, 1996), dimethyl (1-hydroxy-1,2-diphenylethyl)phosphonate (Acar *et al.*, 2009), dimethyl (1-hydroxy-1,2-diphenylethyl)phosphonate (Tahir *et al.*, 2009*a*,*b*) and diethyl (1-hydroxy-1-phenylethyl)phosphonate (Tahir *et al.*, 2009*c*).

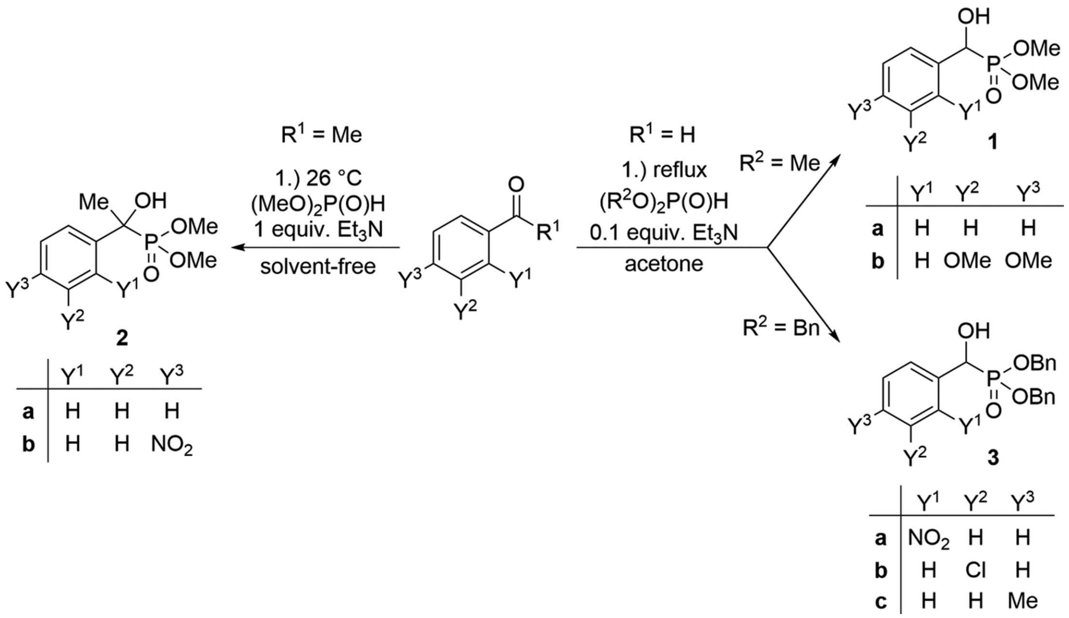

Figure 1
The synthesis of α-hydroxyphosphonates **1**, **2** and **3**.

Table 2
Experimental details for the preparation and characterization of α-hydroxyphosphonates **2a** and **2b**.

			^{31}P NMR					
Product	Time (min)	Yield (%)	δP	δP (reference)	M.p. (°C)	M.p. (reference) (°C)	[*M* + H]$^+$	Entry
2a	7	48	26.2	26.0[a]	130–131	130[c]	231.1	1
2b	2	82	24.8	24.8[b]	167–168	170–171[b]	276.1	2[#]

Notes: (#) ^{13}C NMR (CDCl$_3$): δ 25.8 (*d*, ^2J = 3.3 Hz, CH$_3$), 53.8 (*d*, ^2J = 8.0 Hz, OCH$_3$), 54.7 (*d*, ^2J = 7.3 Hz, OCH$_3$), 73.7 (*d*, ^1J = 160.1 Hz, PCH), 123.1 (*d*, ^4J = 2.7 Hz, C3), 126.8 (*d*, ^3J = 4.2 Hz, C2), 147.2 (*d*, ^5J = 3.3 Hz, C4), 148.6 (C1). References: (*a*) Seven *et al.* (2011); (*b*) Keglevich *et al.* (2017); (*c*) Hudson *et al.* (2008).

Table 3
Crystallization summary of compounds **1**, **2** and **3** at 26 °C.

Compound	Solvent	Precipitant	Crystallization time
1a[a]	methanol	pentane	5 min
1b[b]	acetone	–	48 h
2a[b]	acetone	–	48 h
2b[b]	acetone	–	48 h
3a[b]	diethyl ether	–	24 h
3b[b]	diethyl ether	–	24 h
3c[b]	diethyl ether	–	72 h

Notes: (*a*) crystals were obtained from the reaction mixture; (*b*) crystals were obtained by recrystallization.

Here we aim at describing some fundamental association patterns in the solid state which may govern the formation of macroscopic ordered solid objects, *i.e.* crystals. Structures in general and the crystal structure in particular may be important not only in structure–activity relationships, but also in many simple practical properties of pharmaceuticals, such as preparing solid dosage forms (tablettability), bio-availability (solubility and polymorphy), storage and metabolic pathway identification, and many others (Ye *et al.*, 2014). Crystal structure descriptions of phosphonates usually allude to a description of the association patterns observed in the solid phase *via* characterization of hydrogen-bond bridges and/or other putative favourable interactions contributing towards the build-up of the macroscopic crystal. This and similar issues are relevant and are the subject of recent discussions (Edwards *et al.*, 2017; Mackenzie *et al.*, 2017). Another series of studies has dealt with the two different ways of looking at intermolecular interactions either with an emphasis on specific atom–atom contacts (whether interactions or bonds) or rather as a whole-of-molecule approach that is sort of blind to atom–atom interactions (Dunitz, 2015; Lecomte *et al.*, 2015; Thakur *et al.*, 2015).

2. Experimental

2.1. Syntheses and crystallizations

The ^{31}P, ^{13}C and ^{1}H NMR spectra were taken on a Bruker Avance-300 instrument operating at 121.5, 75.5 and 300 MHz, respectively. The exact mass measurements were performed using a Q-TOF Premier mass spectrometer in positive electrospray mode. The melting points were determined by differential scanning calorimetry (DSC) measurements using a Setaram DSC 92 instrument.

2.1.1. General procedure for the preparation of dimethyl [hydroxy(phenyl)methyl]phosphonates, 1, and dibenzyl [hydroxy(phenyl)methyl]phosphonates, 3. A mixture of 11.0 mmol of aromatic aldehyde (benzaldehyde: 1.2 g; 2-nitrobenzaldehyde: 1.7 g; 3-chlorobenzaldehyde: 1.5 g; 4-methylbenzaldehyde: 1.3 g; 3,4-dimethoxybenzaldehyde: 1.8 g), 11.0 mmol of phosphite (dimethyl phosphite: 1.1 ml; dibenzyl phosphite: 2.4 ml) and triethylamine (1.1 mmol, 0.15 ml) was stirred in acetone (1 ml) under reflux for 10–330 min (for details, see Table 1). After adding pentane (6 ml) to the reaction mixture, the product crystallized on cooling. Filtration of the crystals afforded products **1a**, **1b**, **3b** and **3c** as white crystals, and **3a** as orange crystals in yields of 86–95% in a pure form.

2.1.2. General procedure for the preparation of dimethyl (1-hydroxy-1-phenylethyl)phosphonates, 2. A mixture of 11.0 mmol of aromatic ketone (acetophenone: 1.2 g; 4-nitroacetophenone: 1.7 g), dimethyl phosphite (11.0 mmol, 1.1 ml) and triethylamine (11.0 mmol, 1.5 ml) was stirred at 26 °C for 2–7 h. The product appeared as a white precipitate. The reaction mixture was cooled to 5 °C. After crystallization was complete, the product was isolated by simple filtration. The white crystals were washed with hexane (2 × 5 ml), affording hydroxyphosphonates **2a** and **2b** in yields of 48/82% in a purity of >98% (Table 2).

Crystals were obtained by slow evaporation of various solvents (see Table 3).

The differing crystallization times may suggest different factors that control the process, as the almost instant crystallization of **1a** may suggest kinetic control of the crystal growth, while others may well be governed by thermodynamic control.

2.2. Data collection, structure solution and refinement

The crystal structure of compound **1a** has been reported at room temperature (Fang *et al.*, 2006*b*) and thus a redetermination at low temperature was carried out. Hydroxy H atoms were located in difference Fourier maps and refined keeping the isotropic displacements adjusted to 20% greater than that of the O-atom $U_{\rm iso}$ value. All C—H hydrogens were placed at idealized positions and treated as riding atoms, with isotropic parameters 20 or 50% (for methyl C atoms) greater than for the C atoms to which they are attached. The crystal of **3b** is the only in this series which crystallized in a chiral space group. As no enantioselective agents were applied, this means that conglomerate crystallization (spontaneous resolution) occurred on crystallization. The high Flack x = 0.35 (12) and its high s.u. value indicate that the measured single crystal was a racemic twin in approximate 0.33:0.67 proportions. Further crystallographic experimental details (such as space groups, cells and

Table 4
Experimental details.

For all determinations, H atoms were treated by a mixture of independent and constrained refinement.

	1a	**1b**	**2a**	**2b**
Crystal data				
Chemical formula	$C_9H_{13}O_4P$	$C_{11}H_{17}O_6P$	$C_{10}H_{15}O_4P$	$C_{10}H_{14}NO_6P$
M_r	216.16	276.21	230.19	275.19
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $C2/c$	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
Temperature (K)	173	173	173	173
a, b, c (Å)	8.4039 (5), 7.7007 (3), 16.6012 (7)	39.464 (3), 8.5132 (4), 8.0044 (3)	8.4780 (3), 17.2370 (6), 8.1357 (3)	8.1800 (4), 8.4006 (6), 9.9661 (4)
α, β, γ (°)	90, 99.149 (4), 90	90, 100.620 (5), 90	90, 106.484 (4), 90	102.173 (5), 94.897 (4), 107.504 (5)
V (Å^3)	1060.69 (9)	2643.2 (2)	1140.05 (7)	630.26 (6)
Z	4	8	4	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.25	0.23	0.23	0.24
Crystal size (mm)	0.40 × 0.20 × 0.04	0.30 × 0.20 × 0.05	0.40 × 0.35 × 0.25	0.40 × 0.35 × 0.20
Data collection				
Diffractometer	Agilent Xcalibur Sapphire3	Agilent Xcalibur Sapphire3	Agilent Xcalibur Sapphire3	Agilent Xcalibur Sapphire3
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2014)	Multi-scan (*CrysAlis PRO*; Agilent, 2014)	Multi-scan (*CrysAlis PRO*; Agilent, 2014)	Multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min}, T_{max}	0.846, 1.000	0.956, 1.000	0.933, 1.000	0.948, 1.000
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	20344, 3209, 2491	13696, 4023, 2812	22954, 3450, 3080	12564, 3827, 3070
R_{int}	0.041	0.049	0.025	0.028
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.714	0.714	0.714	0.714
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.108, 1.02	0.047, 0.126, 1.03	0.031, 0.089, 1.04	0.041, 0.114, 1.03
No. of reflections	3209	4023	3450	3827
No. of parameters	139	178	150	176
No. of restraints	0	0	0	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.33, −0.27	0.40, −0.29	0.35, −0.19	0.34, −0.28

	3a	**3b**	**3c**
Crystal data			
Chemical formula	$C_{21}H_{20}NO_6P$	$C_{21}H_{20}ClO_4P$	$C_{22}H_{23}O_4P$
M_r	413.35	402.79	382.37
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1$	Orthorhombic, $Pbca$
Temperature (K)	133	133	173
a, b, c (Å)	10.0795 (3), 13.8530 (6), 15.9354 (5)	10.4239 (8), 7.8757 (5), 12.0461 (7)	16.7332 (8), 8.2012 (3), 28.0902 (13)
α, β, γ (°)	111.110 (4), 90.852 (3), 106.326 (3)	90, 103.775 (7), 90	90, 90, 90
V (Å^3)	1975.23 (13)	960.49 (11)	3854.9 (3)
Z	4	2	8
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.18	0.31	0.17
Crystal size (mm)	0.43 × 0.30 × 0.25	0.30 × 0.22 × 0.20	0.37 × 0.15 × 0.05
Data collection			
Diffractometer	Agilent Xcalibur Sapphire3	Agilent Xcalibur Sapphire3	Agilent Xcalibur Sapphire3
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2014)	Multi-scan (*CrysAlis PRO*; Agilent, 2014)	Multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min}, T_{max}	0.980, 1.000	0.991, 1.000	0.980, 1.000
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	39828, 11989, 8512	6934, 3407, 2955	29616, 4758, 3133
R_{int}	0.038	0.028	0.070
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.714	0.625	0.667
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.124, 1.03	0.047, 0.114, 1.05	0.056, 0.150, 1.02
No. of reflections	11989	3407	4758
No. of parameters	565	255	265
No. of restraints	0	1	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.60, −0.31	0.34, −0.20	0.45, −0.26
Absolute structure	–	Refined as an inversion twin	–
Absolute structure parameter	–	0.35 (12)	–

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *ORTEP* (Burnett & Johnson, 1996), *ORTEP-3* (Farrugia, 2012), *DIAMOND* (Brandenburg, 1999) and *PLATON* (Spek, 2009).

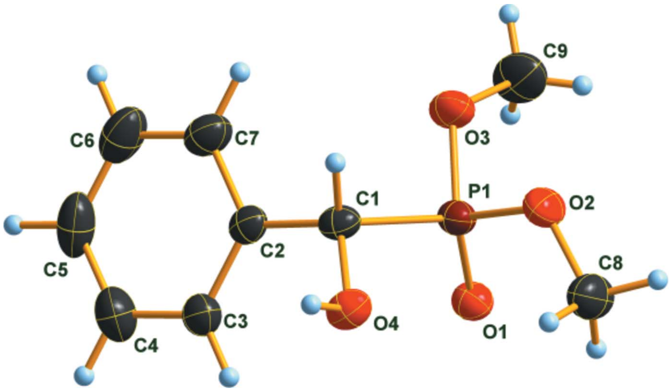

Figure 2
The molecular structure of **1a**, showing the atomic numbering and 50% probability displacement parameters for the non-H atoms.

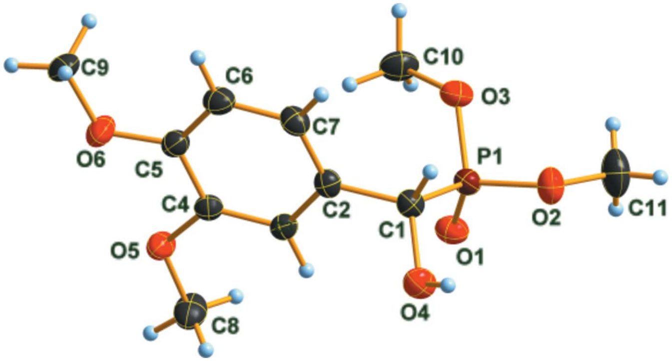

Figure 3
The molecular structure of **1b** (the asymmetric unit), showing the atomic numbering and 50% probability displacement parameters for the non-H atoms.

data collection), as well as computational results (model refinement and final notes), are summarized in Table 4.

2.3. Other computing tools

The Cambridge Structural Database (CSD; Groom *et al.*, 2016) programs *ConQuest* (Versions 1.22 and 1.23; Bruno *et al.*, 2002) and *Mercury* (Macrae *et al.*, 2008) were used with their built-in tools (such as plotting, graph-set analysis and statistical tools). Incidentally, the legacy CSD program *RPLUTO* was also applied. For an overview of some of the electronic aspects of the interactions in these crystals, *CrystalExplorer* was applied (Turner *et al.*, 2017). Underlying energy calculations were performed both at the CE-HF (Hartree–Fock) and CE B3LYP/6-31G(d,p) levels. Energy frameworks resulting from these two approaches proved to be nearly identical with respect to both the energy components magnitude and the directional features in the respective crystals. Thus, the resulting minor discrepancies either in the components (Coulombic, dispersion and repulsion forces) or in the total energies only showed hardly visible differences. However, most of these results will be reported in a later publication and only one particular aspect for **3a** is covered here.

3. Results and discussion

The structural diagrams of the seven crystal structures determined in this study are shown in Fig. 1, and the crystallographic asymmetric-unit contents are shown in Figs. 2–8.

These seven crystal structures are classified and shown in the order of their principal hydrogen-bond motifs based on the topology of the O—H$\cdots$O═P hydrogen bonds. This group simply follows the literature usage in naming 'chains' and 'dimers' as the principal propagation forms of O—H$\cdots$O hydrogen-bond bridges in the crystal packing of the individual solid forms (*e.g.* Etter, 1990; Bernstein *et al.*, 1995; Tahir *et al.*, 2009*a*; Ouksel *et al.*, 2017).

The tertiary Cα H-atom-containing and chain-forming compounds **1a**, **1b**, **3b** and **3c** are discussed first. The formation of chain-like hydrogen-bond bridges in tertiary Cα—H-containing phosphonates has been reported previously [*e.g.* in trichlophone (Höhne & Lohs, 1969) or in Ouksel *et al.* (2017)].

A packing drawing for compound **1b** (Fig. SF1 in the supporting information) shows a typical arrangement for this class of contacts.

The quaternary Cα methyl-containing derivatives which form dimers are **2a** and **2b**, while tertiary Cα—H equipped hydroxyphosphonate **3a** forms a dimer even in its asymmetric unit. The other tertiary α-H-containing counterparts, *i.e.* **3b** and **3c**, form chains.

Compound **1a** is possibly isostructural (Kálmán *et al.*, 1993) with the known diethyl [hydroxy(phenyl)methyl]phosphonate crystal structures (An *et al.*, 2008; Fang *et al.*, 2010; Ouksel *et al.*, 2017; see Table ST1 in the supporting information).

Packing drawings for **2a** and **3a** (see Figs. SF2 and SF3 in the supporting information) show the basic primary propagation forms of the O—H$\cdots$O hydrogen-bond bridges in the crystal packing for the centrosymmetric dimer and for the pseudo-centrosymmetric types.

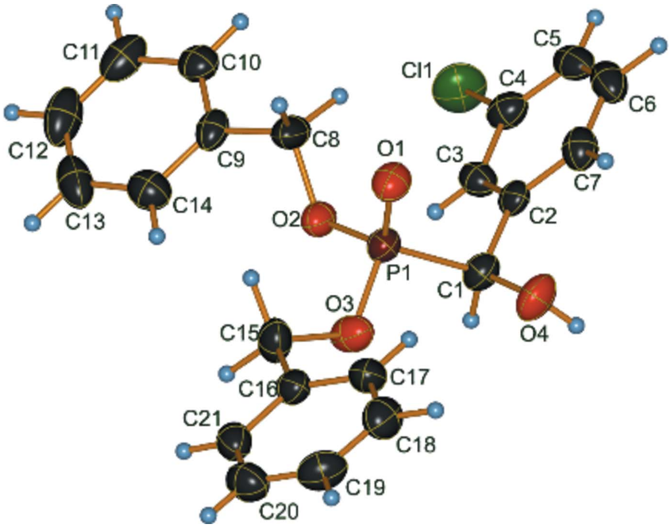

Figure 4
The molecular structure of **3b** (the asymmetric unit), showing the atomic numbering and 50% probability displacement parameters for the non-H atoms.

Table 5
OPCO torsion angles (°) in **1a**–**3c**.

Compound **3a** has two independent molecules in the asymmetric unit, hence the two values.

Compound	OPCO	Torsion (°)
1a	O1—P1—C1—O4	66.4 (1)
1b	O1—P1—C1—O4	54.6 (1)
2a	O1—P1—C1—O4	−56.5 (1)
2b	O1—P1—C5—O4	64.3 (1)
3a	O1—P1—C1—O4	−74.0 (1)
3a	O7—P2—C22—O10	73.5 (1)
3b	O1—P1—C1—O4	55.5 (3)
3c	O1—P1—C1—O4	55.4 (2)

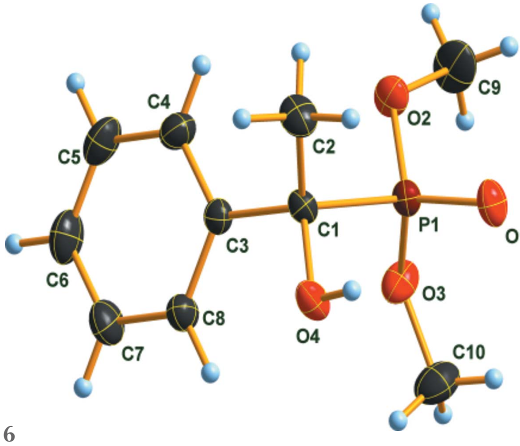

Figure 6
The molecular structure of **2a** (the asymmetric unit), showing the atomic numbering and 50% probability displacement parameters for the non-H atoms.

This work was primarily initiated in order to explain the packing formation of these seven related α-hydroxy-α-arylphosphonate target compounds. The main driving force was supposed to be the O—H···O═P-type hydrogen-bond bridge formation. About three-quarters (30 out of 40, see supporting information) of such structures adopt some form of chain. We believe that this is related partly to the crowding around the Cα atom and partly due to electronic reasons. The usual chain formation in our seven-membered mini-series is broken for the two quaternary Cα-atom structures (*i.e.* **2a** and **2b**) and, somewhat surprisingly, for a tertiary Cα-atom derivative (**3a**) also, which is a possible irregularity.

3.1. Analysis of some intra- and intermolecular features

As the synthesis and a crystal structure description of compound **1a** have been published previously (Fang *et al.*, 2006*b*), only other aspects will be reported here. Low-temperature geometry data of **1a** are consistent with the other structures presented in this article. Intramolecular bonding features will not be discussed at length as the bonding parameters conform to expected mean values within the usual significance criteria.

The only intramolecular shape descriptor we deal with is the torsion angle along the P—Cα bond, as defined by the hydroxy O atom and the O atom of the P═O unit (double-bond notation is used hereinafter in the conventional sense in conformity with database notations). The O═P—C—OH torsion angles (OPCO hereinafter) are listed for the studied crystal structures **1a**–**3c** in Table 5.

The absolute values of these eight angular angles are distributed around a mean value of 62.5°. Thus, one is inclined to believe that this torsion is swaying around 60° in the synclinal (sc) conformation range. The four molecules in the dimer-type crystal structures have a mean value of 58°, while the rest show a mean value of 67.1°. The torsion angles are rather soft parameters, hence the individual deviations from either the mean or from any other in this small sample may not have particular significance. Similar values and like deviations arise from literature data obtained from the Cambridge Structural Database (CSD; Groom *et al.*, 2016). Saying there is no particular significance just indicates that deviations and the small torsion-angle variations might well be signs of intermolecular effects that may span a range from a few tenths to a few kJ mol^{-1} energies or so (Sarkar & Row, 2017). A search for the chemical fragment (Fig. SF4 in the supporting information) with an acyclic hydroxyphosphonate ester unit and a

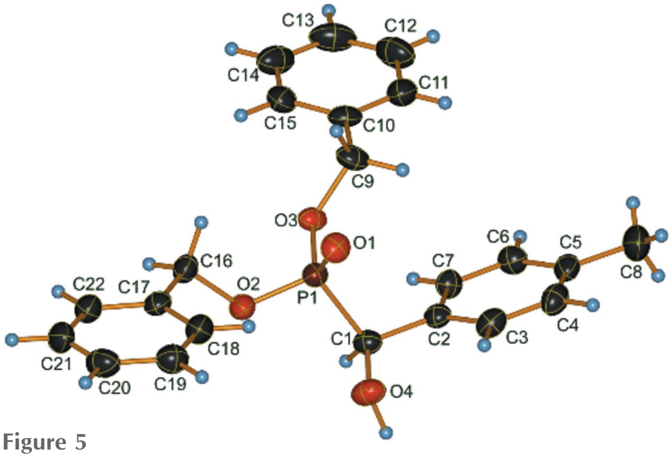

Figure 5
The molecular structure of **3c** (the asymmetric unit), showing the atomic numbering and 50% probability displacement parameters for the non-H atoms.

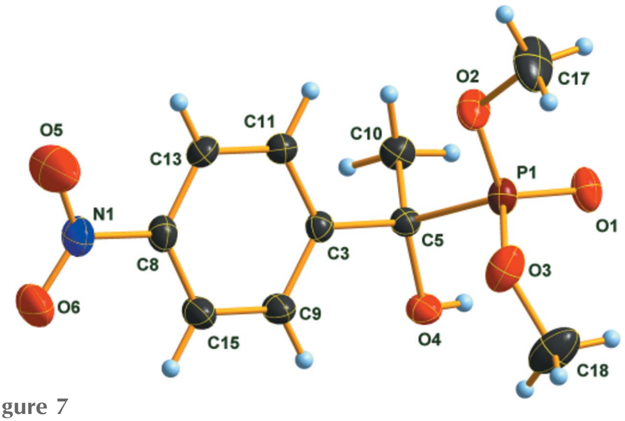

Figure 7
The molecular structure of **2b** (the asymmetric unit), showing the atomic numbering and 50% probability displacement parameters for the non-H atoms.

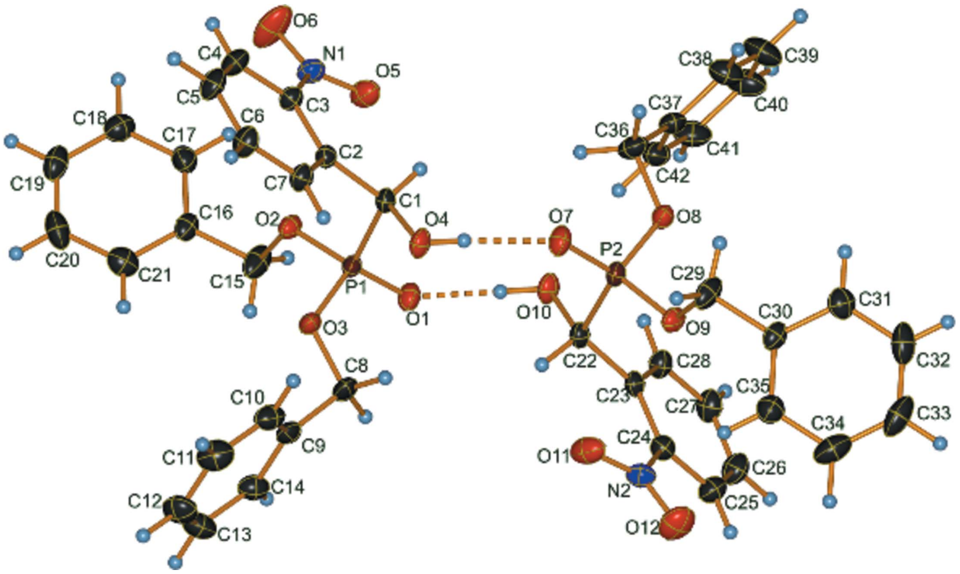

Figure 8
The molecular structure of **3a** (the asymmetric unit), showing the atomic numbering and 50% probability displacement parameters for the non-H atoms. The dimer formed by hydrogen-bond bridges is shown with broken lines. This pseudocentrosymmetric dimer is quite similar to the true centrosymmetric dimers formed in **2a** and **2b**.

Table 6
Statistic descriptors of the 36 OPCO values around the sc conformation range in the CSD.

Extracted from a full table and rounded appropriately to integer numbers. The most relevant numbers are printed in bold.

	Count	Min (°)	Max (°)	Mean (°)	Sample std dev. (°)	Mean std dev. (°)	Skewness	Kurtosis	Median (°)
OPCO	36	48	83	**64**	**9**	**7**	0.56	−0.49	**61**

C—O—H moiety within hydrogen-bond bridging distance to the P═O group. This search resulted in 36 hits (*i.e.* crystal structures) which contain 42 independent molecular fragments. Of these 42, the OPCO angle values of 36 fall in the synperiplanar/synclinal ranges (*i.e.* between −30 and 30°, and between 30 and 90° for sp and sc, respectively). Thus, when the OPCO angle values are truncated to this range, the distribution values come close to those seen in the structures here (Table 6). The OPCO torsion angle seems to favour this low synclinal conformation range just at the border of the sp region. Of historical interest is that trichlorfon has the lowest reported OPCO torsion angle (28°).

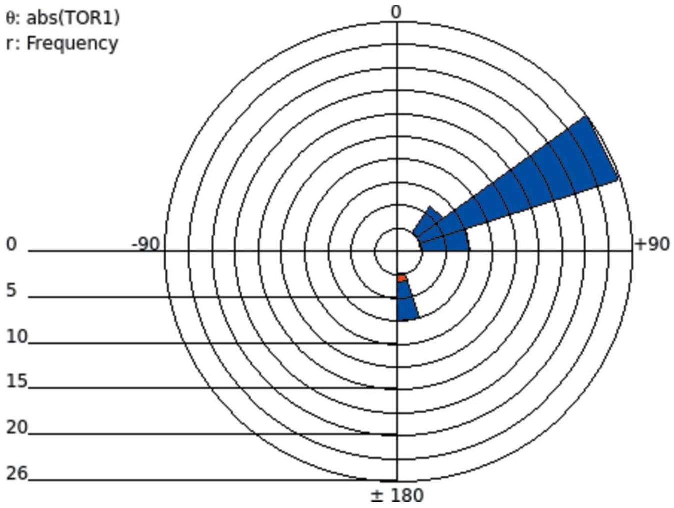

Figure 9
A polar histogram of the HO—C—P═O torsion-angle distribution in acyclic P(O*R*) esters (*i.e.* omitting cyclic constrained esters). There are still several high antiperiplanar (ap, *trans*) conformations (6 out of 42 hits).

Of further interest is that when the full search results are examined it becomes apparent (Fig. 9) that some OPCO torsions adopt values close to 180° (6 in the sample of total of 42) attaining the antiperiplanar conformation. This corresponds to the traditional *trans* disposition of the two O atoms across the P—C bond. None of our compounds adopts this conformation. The question is whether such conformational changes have any influence regarding the hydrogen-bond bridge-forming ability?

Thus, the intermolecular relationships need to be examined. A quick overview is provided by the polar scattergram of the OPCO values against the hydrogen-bond bridge angles (Fig. 10), as well as a summary of the statistics of some of the hydrogen-bond bridge distance parameters (Table 7). These both point towards nondiscriminative hydrogen-bond bridge features conforming well to expected standards, thus indicating normal and possibly well-defined hydrogen-bond bridges. Apparently, the OPCO torsion-angle values do not indicate any particular influence on the hydrogen-bond bridge geometry.

A further aspect of the intermolecular interactions is, however, their topology. As this type was recognized in the

Table 7
Statistics table of the intermolecular hydrogen-bond bridges of acyclic esters of hydroxyphosphonate fragments in the CSD.

35 crystal structures yielded 42 independent fragments containing the search moiety (the table is restricted to the most known parameters only). AHD is the P═O···H—O hydrogen-bond bridge angle and *d* is the O···H distance. The angular values are rounded to whole degrees.

Name	Count	Min.	Max.	Mean	Sample std dev.	Mean dev.	Median
AHD (°)	42	136	178	166	11	9	170
d (Å)	42	2.59	2.77	2.70	0.04	0.03	2.70

Table 8
Hydrogen-bond graph-set descriptors in compounds **1a**–**3c**.

Primary contacts are O—H···O hydrogen-bond bridges, while secondary contacts encompass additional C—H···O hydrogen-bond bridges involving those used in the primary contact as well (for a graphical overview, see Table ST2 in the supporting information.

Compound	Primary GS	Secondary GS
1a	$C(5)$	$R_2^2(8)$
1b	$C(5)$	$R_2^2(8)$
2a	$R_2^2(10)$	$R_2^2(10)$
2b	$R_2^2(10)$	$R_2^2(10)$
3a	$R_2^2(10)$	$R_2^2(10)$, with $S(6)$ and $S(5)$
3b	$C(5)$	$R_2^2(8)$
3c	$C(5)$	$C(8)$, $C_2^2(13)$, with $S(7)$

form of chain-like or dimer involvement of the P═O···H—O hydrogen-bond bridges, the quest is to try to identify conditions which would decide in favour of either option. Initially, the presence of the α-H atom at the chiral C atom (ternary C atom in compounds **1** and **3**) was supposed to be responsible for chain formation. In contrast, the presence of the α-methyl substituent (*i.e.* a quaternary C atom) would promote dimer formation, as seen in compounds **2**. Nevertheless, the crystal structure of **3a**, which is a dimer-forming tertiary Cα H-atom species, seems to be an exception in this assumption.

3.2. Graph-set characterization

Graph-set descriptions have been used since the pioneering work of Etter and Bernstein (Etter, 1990; Bernstein *et al.*, 1995) for a topological representation of the intra- and mainly intermolecular hydrogen-bond contacts. Compound **3a** is exceptional in many aspects. A representation abstracted from its crystal energy framework computation result from *CrystalExplorer* (Turner *et al.*, 2017) is shown in graphical form (Fig. 11). This serves also to exemplify the relationship between the P═O···H—O hydrogen-bond bridges, directionality and energy relations.

The Coulombic component provides here most of the total energy, with the major dispersion contribution aligned also close to parallel to the electrostatic contribution. The resulting total energy (shown as a thick blue rod) aligns very well with the direction of the O···H—O hydrogen-bond bridges, thus explaining the dominant vectorial interaction in this crystal. As the dominating electrostatic contribution comes from the O—H···O═P-type hydrogen-bond bridges, the simplest approach lists these interactions first (Table 8). Five-membered chains of one donor/acceptor each (chains) or rings twice as large of two donors/acceptors each (dimers) constitute the basic motif propagation.

The dominant O—H···O hydrogen-bond bridges are the primary component. When adding any C—H types to the possible donors, this picture is complemented by the secondary graph-set motifs such that these latter partly overlap with the primary sets. This is to say that at least one of the O atoms from the primary set is involved (*i.e.* a joint O—H···O and C—H···O motif exists). This also makes sense, as the many C—H···O interactions might be a substantial factor due to their large number alone.

Examining the primary dimer sets (*i.e.* **2a**, **2b** and **3a**), especially with regard to seeking an explanation why a dimer (even more in the asymmetric unit) is formed in species **3a**, we can establish the following: in **2a**, prevalent rings made up by

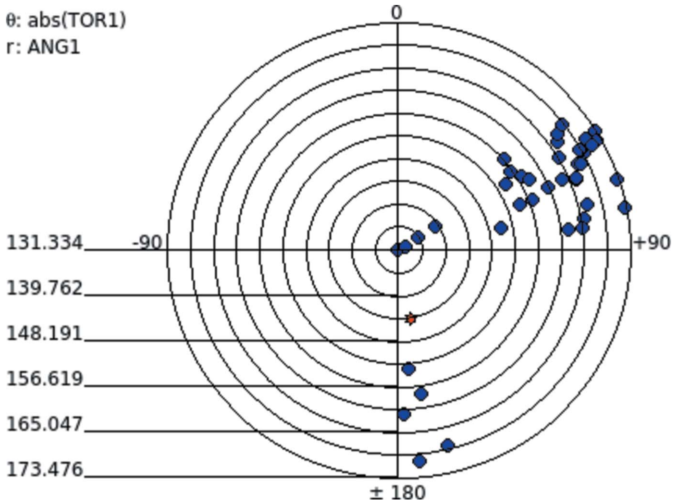

Figure 10
A polar scattergram of the HO—C—P═O torsion angles *versus* the P═O···H—O hydrogen-bond bridge angle in acyclic P(O*R*) esters.

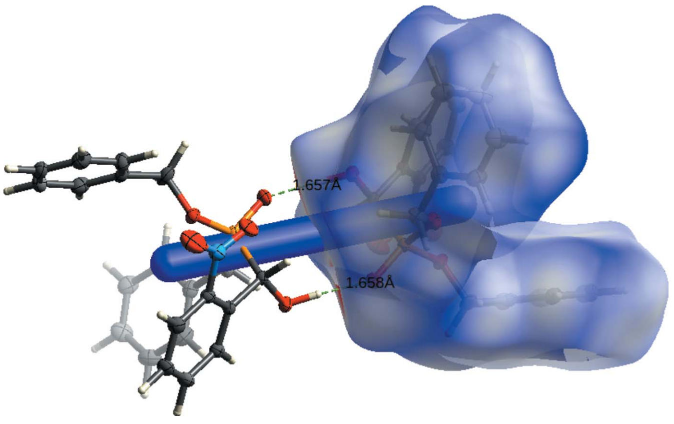

Figure 11
The largest total energy bar (blue rod) is shown in the **3a** asymmetric unit dimer from its lattice energy framework. This shows the largest cohesive total energy relationship between molecular centres. One molecule is shown with its unsigned Hirshfeld surface also, while the other is represented in a displacement ellipsoid plot only, with the two H···O-to-acceptor distances listed (with values of 1.657 and 1.658 Å).

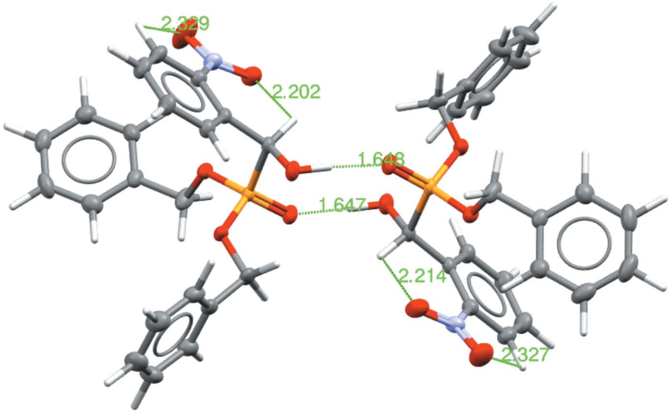

Figure 12
A view of the decisive internal hydrogen-bond bridges in the asymmetric-unit dimer of **3a**. Distances are in Å and their values stem from a normalized H-atom position geometry. As to their uncertainties, one can estimate that they are in the order of 0.01 Å.

the dominant O—H···O interactions are complemented by an $R_2^2(10)$ secondary motif involving two symmetry-related *ortho* H—C groups from the phenyl group. This points to the important role that the phenyl *ortho* substituents may play. The other quaternary C*α* compound, **2b**, has an identical ranking of rings in the secondary complement. But these are not from *o*-C—H but from two symmetry-related *α*-methyl H atoms. The **3a** primary set is the same ten-membered ring, but formed through intermolecular hydrogen-bond bridges between the two molecules of the asymmetric unit ($Z' = 2$), while the secondary set forms between symmetry-centre-related molecules. Thus, they are symmetrically identical with those in **2a** and **2b**, but they involve intermolecular C—H···O hydrogen-bond contacts in the case of **3a**. Extending the hydrogen-bond bridge functions for intramolecular C—H···O results in the *S*(6) and *S*(5) patterns. This self-binding involves the *o*-NO$_2$-group O atoms to the C*α* H atom [*S*(6) pattern] and to the neighbouring *m*-C—H group [*S*(5) form] in both **3a** molecules (Fig. 12).

Practically identical dimensions and patterns underline the important electronic and steric functions of the *o*-NO$_2$ groups towards their neighbouring units in both **3a** molecules. In the case of dimethyl [hydroxy(2-nitrophenyl)methyl]phosphonate, dimer formation with an identical $R_2^2(10)$ primary hydrogen-bonded ring was reported (Tahir *et al.*, 2009*a*), together with similar internal *o*-NO$_2$-group involvement. The *o*-NO$_2$ group forms the same *S*(6) and *S*(5) rings to the C*α* H atom and to the next *m*-C—H group, respectively. Thus, **3a**, in spite of having a tertiary C*α* atom, it does not form a chain-like packing motif but a dimer, similar to **2a** and **2b** with their quaternary C*α* atom. In such a way, the *o*-NO$_2$ groups act [torsion angles O5—N1—C3—C2 = −9.2 (2)° and O11—N2—C24—C23 = 13.7 (2)°] not only as effective steric shielding for the H atom at C*α* (Fig. SF5 in the supporting information), but also as if they were quaternary C-atom substituents. Thus, we hypothesize, that compounds with tertiary C*α* atoms are prone to form chains, while those with quaternary C*α* atoms, or with a sterically electronically shielded C*α* H atom, tend to cause dimers. Compound **3b** has a secondary set that is identical topologically and functionally with those in compounds **1** in a chiral crystal lattice. Compound **3c** has a more confusing secondary set situation. It is hard to decide the ranking as there are at least two competitive chain sets, both involving *o*-C—H H atoms. In the *S*(7) set, an intramolecular distance (2.66 Å) links one of the benzyl *o*-H atoms to the O═P group. In the other *C*(8) set, an *o*-H atom of the other benzyl ester group approaches (2.57 Å) an O—H group of the next **3c** molecule. Both of these are relatively longer distances with respect to the sum of the van der Waals radii concerned. Moreover, a $C_2^2(13)$ graph set links two more molecules to the base graph set *via* contacts both to a screw and to a glide-related molecule from the basal *α*-H atom to a screw-related O═P group (3.17 Å), which is also acting towards a glide-related *o*-H atom (2.57 Å) of that benzyl moiety.

4. Conclusions

There seem to be just too many variables and conditions, not to mention the actual crystallization conditions, that may affect the final outcome of crystal formation, *i.e.* the topology of the associates formed under particular circumstances. We think that the initial assumption concerning the crowding around the C*α* atom is an important piece of the puzzle. The simplest realization of crowding is the introduction of a methyl group at C*α*, *i.e.* for **2a** and **2b**. Electronic modification through either substituents or through noncovalent interactions may also affect a tertiary C—H group. An important role of the C—H···O interactions is seen in **3a**. In spite of having a tertiary C*α* atom, it does not form a chain-like packing motif but a dimer, like **2a** and **2b** with their quaternary C*α* atom. Thus, we postulate the hypothesis that compounds with tertiary C*α* atoms are prone to form chains, while those with quaternary C*α* atoms, or with a sterically electronically shielded C*α* H atom, tend to promote the formation of dimers. Nevertheless, we believe, even on the basis of this limited study, that we may call attention to several factors that have an influence on the hydrogen-bonding motif outcome. As mentioned here several times, grouping the compounds on the tertiary–quaternary feature of the C*α* atom is one of these factors. The role and nature of the substituents, especially in the *ortho* positions of the aromatic phenyl-type moieties, that are immediately linked to C*α* modify such a classification *via* intramolecular effects. It seems from the graph-set analysis that the dominating (primary) hydrogen-bond bridges are not only co-existent with the weaker but more numerous secondary bridges, but that these may provide a complementary vehicle towards making crystals. One may also observe a degree of similarity in the primary and secondary graph sets of the studied molecular crystals, thus reflecting molecular similarity at another more abstract level.

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supporting information

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The typical crystal structures of a few representative *α*-aryl-*α*-hydroxyphosphonates

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Computing details

For all structures, data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *ORTEP* (Burnett & Johnson, 1996), *ORTEP-3* (Farrugia, 2012), *PLATON* (Spek, 2009) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *PLATON* (Spek, 2009).

Dibenzyl [hydroxy(4-methylphenyl)methyl]phosphonate (3c)

Crystal data

$C_{22}H_{23}O_4P$
$M_r = 382.37$
Orthorhombic, *Pbca*
$a = 16.7332$ (8) Å
$b = 8.2012$ (3) Å
$c = 28.0902$ (13) Å
$V = 3854.9$ (3) Å^3
$Z = 8$
$F(000) = 1616$

$D_x = 1.318$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4004 reflections
$\theta = 4.5$–27.9°
$\mu = 0.17$ mm^{-1}
$T = 173$ K
Block, colorless
0.37 × 0.15 × 0.05 mm

Data collection

Agilent Xcalibur Sapphire3 diffractometer
Radiation source: Enhance (Mo) X-ray Source
Detector resolution: 15.9809 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)
$T_{min} = 0.980$, $T_{max} = 1.000$

29616 measured reflections
4758 independent reflections
3133 reflections with $I > 2\sigma(I)$
$R_{int} = 0.070$
$\theta_{max} = 28.3°$, $\theta_{min} = 4.4°$
$h = -22 \rightarrow 21$
$k = -10 \rightarrow 10$
$l = -36 \rightarrow 37$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.150$
$S = 1.02$
4758 reflections
265 parameters
0 restraints

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0669P)^2 + 1.3244P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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.
An Xcalibur, Sapphire3 detector equipped diffractometer was used with an Enhance Mo K*α* X-ray radiation to collect all the intensity data. The program CrysAlis PRO (CrysAlisPro, Agilent, 2014) was used for data collection, space group determination and all data reduction purposes including empirical absorption correction using spherical harmonics. The initial structure models were provided by direct methods using SHELXT (Sheldrick, 2015a) and refined using full-matrix least-squares on F^2 using SHELXL (Sheldrick, 2015b). All non-H atoms were refined anisotropically.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
P1	0.86630 (3)	0.11650 (7)	0.74859 (2)	0.02500 (16)
O1	0.88249 (10)	0.28792 (18)	0.76026 (6)	0.0334 (4)
O2	0.83579 (9)	0.00874 (17)	0.79113 (5)	0.0314 (4)
O3	0.79822 (9)	0.09657 (16)	0.71029 (5)	0.0288 (4)
C5	1.02433 (14)	0.1749 (3)	0.58777 (8)	0.0340 (5)
O4	1.01055 (11)	0.0164 (2)	0.76139 (6)	0.0395 (4)
C10	0.71903 (14)	0.1766 (3)	0.64312 (9)	0.0332 (5)
C3	1.03925 (14)	0.1711 (3)	0.67304 (9)	0.0335 (5)
H3	1.0670 (8)	0.2088 (10)	0.7011 (8)	0.040*
C11	0.73182 (17)	0.1995 (3)	0.59491 (10)	0.0421 (6)
H11	0.7791 (15)	0.2462 (15)	0.5842 (4)	0.051*
C1	0.95057 (13)	−0.0002 (3)	0.72631 (8)	0.0285 (5)
H1	0.9350	−0.1175	0.7237	0.034*
C18	0.87025 (14)	0.1879 (3)	0.87877 (9)	0.0363 (5)
H18	0.9039 (10)	0.2212 (10)	0.8520 (8)	0.044*
C2	0.97640 (13)	0.0618 (2)	0.67771 (8)	0.0272 (5)
C7	0.93737 (14)	0.0092 (3)	0.63681 (8)	0.0303 (5)
H7	0.8948 (12)	−0.065 (2)	0.63923 (10)	0.036*
C4	1.06260 (15)	0.2263 (3)	0.62880 (9)	0.0369 (6)
H4	1.1080 (12)	0.305 (2)	0.62631 (11)	0.044*
C17	0.79922 (14)	0.1056 (3)	0.87028 (8)	0.0308 (5)
C19	0.89383 (17)	0.2232 (3)	0.92481 (9)	0.0398 (6)
H19	0.9437 (15)	0.2807 (17)	0.93039 (19)	0.048*
C6	0.96076 (14)	0.0661 (3)	0.59253 (8)	0.0339 (5)
H6	0.9318 (8)	0.0289 (10)	0.5637 (8)	0.041*
C22	0.75307 (15)	0.0584 (3)	0.90880 (9)	0.0366 (6)
H22	0.7036 (14)	−0.0020 (17)	0.90344 (18)	0.044*
C16	0.77049 (14)	0.0704 (3)	0.82078 (8)	0.0334 (5)
H16A	0.7267 (8)	−0.0121 (14)	0.82201 (8)	0.040*
H16B	0.7485 (4)	0.1722 (18)	0.8064 (3)	0.040*
C15	0.64759 (15)	0.1085 (3)	0.65822 (10)	0.0381 (6)

H15	0.6377 (3)	0.0941 (5)	0.6925 (10)	0.046*
C21	0.77629 (16)	0.0958 (3)	0.95484 (9)	0.0439 (6)
H21	0.7423 (10)	0.0644 (10)	0.9818 (8)	0.053*
C20	0.84685 (17)	0.1770 (3)	0.96282 (10)	0.0439 (6)
H20	0.8624 (6)	0.2000 (8)	0.9928 (10)	0.053*
C13	0.6045 (2)	0.0829 (3)	0.57840 (12)	0.0545 (8)
H13	0.5656 (14)	0.0496 (12)	0.5561 (8)	0.065*
C12	0.6739 (2)	0.1524 (4)	0.56281 (11)	0.0543 (8)
H12	0.6819 (4)	0.1678 (7)	0.5310 (12)	0.065*
C14	0.59054 (18)	0.0609 (3)	0.62603 (11)	0.0496 (7)
H14	0.5416 (16)	0.0130 (16)	0.6367 (4)	0.060*
C8	1.05096 (18)	0.2326 (3)	0.53963 (10)	0.0510 (7)
H8A	1.0775 (11)	0.332 (2)	0.54271 (13)	0.076*
H8B	1.0066 (8)	0.246 (2)	0.5200 (4)	0.076*
H8C	1.0853 (11)	0.1559 (17)	0.5263 (4)	0.076*
C9	0.78111 (16)	0.2317 (3)	0.67775 (9)	0.0365 (6)
H9A	0.8320 (9)	0.2650 (7)	0.6600 (3)	0.044*
H9B	0.7608 (4)	0.3304 (18)	0.6965 (3)	0.044*
H40	1.0494 (17)	−0.069 (3)	0.7537 (9)	0.044*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0241 (3)	0.0235 (3)	0.0274 (3)	0.0000 (2)	−0.0007 (2)	−0.0014 (2)
O1	0.0343 (10)	0.0261 (8)	0.0398 (10)	−0.0042 (6)	−0.0002 (7)	−0.0049 (6)
O2	0.0307 (9)	0.0317 (8)	0.0318 (9)	0.0046 (7)	0.0043 (7)	0.0026 (6)
O3	0.0263 (8)	0.0233 (7)	0.0368 (9)	−0.0008 (6)	−0.0052 (6)	0.0032 (6)
C5	0.0316 (13)	0.0319 (12)	0.0385 (14)	0.0058 (10)	0.0097 (10)	0.0033 (10)
O4	0.0338 (10)	0.0462 (10)	0.0385 (10)	0.0099 (8)	−0.0069 (7)	−0.0040 (7)
C10	0.0333 (14)	0.0245 (11)	0.0417 (14)	0.0078 (9)	−0.0096 (10)	0.0001 (9)
C3	0.0285 (13)	0.0348 (12)	0.0371 (13)	−0.0001 (9)	−0.0003 (10)	−0.0092 (10)
C11	0.0348 (15)	0.0412 (14)	0.0503 (17)	0.0066 (11)	0.0032 (12)	0.0078 (11)
C1	0.0293 (12)	0.0288 (11)	0.0274 (12)	0.0041 (9)	−0.0030 (9)	−0.0032 (8)
C18	0.0315 (14)	0.0395 (13)	0.0379 (14)	0.0007 (10)	0.0035 (10)	0.0022 (10)
C2	0.0273 (12)	0.0253 (10)	0.0291 (12)	0.0046 (9)	0.0008 (9)	−0.0027 (8)
C7	0.0295 (13)	0.0295 (11)	0.0320 (12)	−0.0046 (9)	0.0000 (9)	−0.0016 (9)
C4	0.0314 (14)	0.0321 (12)	0.0472 (15)	−0.0043 (10)	0.0073 (11)	−0.0036 (10)
C17	0.0264 (12)	0.0300 (11)	0.0359 (13)	0.0063 (9)	0.0029 (9)	0.0002 (9)
C19	0.0376 (15)	0.0400 (14)	0.0417 (15)	0.0007 (11)	−0.0044 (11)	0.0001 (11)
C6	0.0356 (14)	0.0360 (12)	0.0302 (13)	0.0009 (10)	−0.0026 (10)	−0.0040 (9)
C22	0.0312 (14)	0.0390 (13)	0.0395 (15)	0.0023 (10)	0.0060 (10)	0.0030 (10)
C16	0.0274 (13)	0.0374 (12)	0.0355 (13)	0.0003 (10)	0.0059 (9)	0.0000 (10)
C15	0.0391 (15)	0.0325 (13)	0.0428 (15)	0.0028 (10)	0.0006 (11)	0.0084 (10)
C21	0.0387 (15)	0.0571 (17)	0.0358 (14)	0.0085 (12)	0.0103 (11)	0.0075 (11)
C20	0.0468 (17)	0.0520 (15)	0.0331 (14)	0.0113 (13)	−0.0048 (12)	−0.0001 (11)
C13	0.0544 (19)	0.0442 (16)	0.065 (2)	0.0061 (14)	−0.0302 (16)	−0.0060 (14)
C12	0.069 (2)	0.0599 (18)	0.0341 (15)	0.0163 (16)	−0.0069 (14)	0.0032 (12)
C14	0.0355 (16)	0.0376 (14)	0.076 (2)	−0.0033 (11)	−0.0111 (14)	0.0075 (13)

C8	0.0470 (17)	0.0616 (18)	0.0443 (17)	0.0012 (14)	0.0132 (13)	0.0092 (13)
C9	0.0404 (15)	0.0244 (11)	0.0447 (14)	0.0007 (10)	−0.0088 (11)	0.0073 (10)

Geometric parameters (Å, º)

P1—O1	1.4687 (16)	C7—H7	0.94 (3)
P1—O2	1.5716 (16)	C4—H4	1.00 (3)
P1—O3	1.5754 (15)	C17—C22	1.385 (3)
P1—C1	1.815 (2)	C17—C16	1.499 (3)
O2—C16	1.464 (3)	C19—C20	1.379 (4)
O3—C9	1.465 (3)	C19—H19	0.97 (3)
C5—C4	1.384 (3)	C6—H6	0.99 (3)
C5—C6	1.395 (3)	C22—C21	1.385 (4)
C5—C8	1.501 (3)	C22—H22	0.98 (3)
O4—C1	1.413 (3)	C16—H16A	0.998 (17)
O4—H40	0.98 (3)	C16—H16B	0.998 (17)
C10—C11	1.384 (4)	C15—C14	1.372 (4)
C10—C15	1.386 (3)	C15—H15	0.98 (3)
C10—C9	1.493 (3)	C21—C20	1.374 (4)
C3—C4	1.379 (3)	C21—H21	0.98 (3)
C3—C2	1.388 (3)	C20—H20	0.90 (3)
C3—H3	0.97 (3)	C13—C12	1.365 (4)
C11—C12	1.379 (4)	C13—C14	1.370 (4)
C11—H11	0.93 (3)	C13—H13	0.94 (3)
C1—C2	1.520 (3)	C12—H12	0.91 (3)
C1—H1	1.0000	C14—H14	0.96 (3)
C18—C19	1.383 (4)	C8—H8A	0.930 (16)
C18—C17	1.388 (3)	C8—H8B	0.930 (15)
C18—H18	0.98 (3)	C8—H8C	0.930 (15)
C2—C7	1.390 (3)	C9—H9A	1.024 (18)
C7—C6	1.385 (3)	C9—H9B	1.024 (18)

O1—P1—O2	115.37 (9)	C18—C19—H19	119.9
O1—P1—O3	112.66 (9)	C7—C6—C5	121.1 (2)
O2—P1—O3	103.06 (8)	C7—C6—H6	119.4
O1—P1—C1	115.99 (10)	C5—C6—H6	119.4
O2—P1—C1	102.59 (9)	C17—C22—C21	120.8 (2)
O3—P1—C1	105.77 (9)	C17—C22—H22	119.6
C16—O2—P1	118.73 (13)	C21—C22—H22	119.6
C9—O3—P1	119.27 (13)	O2—C16—C17	110.78 (19)
C4—C5—C6	117.9 (2)	O2—C16—H16A	109.5
C4—C5—C8	121.1 (2)	C17—C16—H16A	109.5
C6—C5—C8	121.0 (2)	O2—C16—H16B	109.5
C1—O4—H40	104.4 (15)	C17—C16—H16B	109.5
C11—C10—C15	119.2 (2)	H16A—C16—H16B	108.1
C11—C10—C9	119.3 (2)	C14—C15—C10	120.9 (3)
C15—C10—C9	121.5 (2)	C14—C15—H15	119.6
C4—C3—C2	120.8 (2)	C10—C15—H15	119.6

C4—C3—H3	119.6	C20—C21—C22	120.0 (2)
C2—C3—H3	119.6	C20—C21—H21	120.0
C12—C11—C10	119.6 (3)	C22—C21—H21	120.0
C12—C11—H11	120.2	C21—C20—C19	119.8 (3)
C10—C11—H11	120.2	C21—C20—H20	120.1
O4—C1—C2	113.10 (19)	C19—C20—H20	120.1
O4—C1—P1	105.11 (14)	C12—C13—C14	120.9 (3)
C2—C1—P1	110.74 (14)	C12—C13—H13	119.6
O4—C1—H1	109.3	C14—C13—H13	119.6
C2—C1—H1	109.3	C13—C12—C11	120.3 (3)
P1—C1—H1	109.3	C13—C12—H12	119.8
C19—C18—C17	120.5 (2)	C11—C12—H12	119.8
C19—C18—H18	119.8	C13—C14—C15	119.2 (3)
C17—C18—H18	119.8	C13—C14—H14	120.4
C3—C2—C7	118.6 (2)	C15—C14—H14	120.4
C3—C2—C1	121.1 (2)	C5—C8—H8A	109.5
C7—C2—C1	120.3 (2)	C5—C8—H8B	109.5
C6—C7—C2	120.3 (2)	H8A—C8—H8B	109.5
C6—C7—H7	119.8	C5—C8—H8C	109.5
C2—C7—H7	119.8	H8A—C8—H8C	109.5
C3—C4—C5	121.2 (2)	H8B—C8—H8C	109.5
C3—C4—H4	119.4	O3—C9—C10	108.29 (18)
C5—C4—H4	119.4	O3—C9—H9A	110.0
C22—C17—C18	118.6 (2)	C10—C9—H9A	110.0
C22—C17—C16	119.5 (2)	O3—C9—H9B	110.0
C18—C17—C16	121.9 (2)	C10—C9—H9B	110.0
C20—C19—C18	120.3 (3)	H9A—C9—H9B	108.4
C20—C19—H19	119.9		

O1—P1—O2—C16	48.40 (18)	C8—C5—C4—C3	−178.7 (2)
O3—P1—O2—C16	−74.80 (17)	C19—C18—C17—C22	−0.6 (3)
C1—P1—O2—C16	175.47 (16)	C19—C18—C17—C16	177.9 (2)
O1—P1—O3—C9	23.70 (19)	C17—C18—C19—C20	−0.1 (4)
O2—P1—O3—C9	148.69 (16)	C2—C7—C6—C5	1.0 (3)
C1—P1—O3—C9	−103.97 (17)	C4—C5—C6—C7	−1.0 (3)
C15—C10—C11—C12	−0.8 (4)	C8—C5—C6—C7	178.3 (2)
C9—C10—C11—C12	−178.4 (2)	C18—C17—C22—C21	1.5 (3)
O1—P1—C1—O4	55.39 (17)	C16—C17—C22—C21	−177.0 (2)
O2—P1—C1—O4	−71.29 (16)	P1—O2—C16—C17	−113.16 (18)
O3—P1—C1—O4	−178.96 (13)	C22—C17—C16—O2	−136.4 (2)
O1—P1—C1—C2	−67.08 (17)	C18—C17—C16—O2	45.1 (3)
O2—P1—C1—C2	166.25 (15)	C11—C10—C15—C14	1.3 (4)
O3—P1—C1—C2	58.57 (17)	C9—C10—C15—C14	178.9 (2)
C4—C3—C2—C7	0.0 (3)	C17—C22—C21—C20	−1.7 (4)
C4—C3—C2—C1	179.7 (2)	C22—C21—C20—C19	1.0 (4)
O4—C1—C2—C3	−20.6 (3)	C18—C19—C20—C21	−0.1 (4)
P1—C1—C2—C3	97.0 (2)	C14—C13—C12—C11	1.0 (4)
O4—C1—C2—C7	159.11 (19)	C10—C11—C12—C13	−0.4 (4)

P1—C1—C2—C7	−83.2 (2)	C12—C13—C14—C15	−0.5 (4)
C3—C2—C7—C6	−0.4 (3)	C10—C15—C14—C13	−0.7 (4)
C1—C2—C7—C6	179.8 (2)	P1—O3—C9—C10	175.76 (15)
C2—C3—C4—C5	0.0 (4)	C11—C10—C9—O3	−129.7 (2)
C6—C5—C4—C3	0.5 (3)	C15—C10—C9—O3	52.6 (3)

Dibenzyl [(3-chlorophenyl)(hydroxy)methyl]phosphonate (3b)

Crystal data

$C_{21}H_{20}ClO_4P$	$F(000) = 420$
$M_r = 402.79$	$D_x = 1.393$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.4239$ (8) Å	Cell parameters from 2191 reflections
$b = 7.8757$ (5) Å	$\theta = 4.4$–$25.4°$
$c = 12.0461$ (7) Å	$\mu = 0.31$ mm^{-1}
$\beta = 103.775$ (7)°	$T = 133$ K
$V = 960.49$ (11) Å^3	Block, colorless
$Z = 2$	0.30 × 0.22 × 0.20 mm

Data collection

Agilent Xcalibur Sapphire3 diffractometer	6934 measured reflections
Radiation source: Enhance (Mo) X-ray Source	3407 independent reflections
Detector resolution: 15.9809 pixels mm^{-1}	2955 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.028$
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)	$\theta_{max} = 26.4°$, $\theta_{min} = 4.3°$
$T_{min} = 0.991$, $T_{max} = 1.000$	$h = -9 \rightarrow 13$
	$k = -8 \rightarrow 9$
	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.2038P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.047$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.114$	$\Delta\rho_{max} = 0.34$ e Å^{-3}
$S = 1.05$	$\Delta\rho_{min} = -0.20$ e Å^{-3}
3407 reflections	Absolute structure: Refined as an inversion twin
255 parameters	Absolute structure parameter: 0.35 (12)
1 restraint	
Hydrogen site location: inferred from neighbouring sites	

Special details

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

Refinement. Refined as a 2-component inversion twin
An Xcalibur, Sapphire3 detector equipped diffractometer was used with an Enhance Mo Kα X-ray radiation to collect all the intensity data. The program CrysAlis PRO (CrysAlisPro, Agilent, 2014) was used for data collection, space group determination and all data reduction purposes including empirical absorption correction using spherical harmonics. The initial structure models were provided by direct methods using SHELXT (Sheldrick, 2015a) and refined using full-matrix least-squares on F^2 using SHELXL (Sheldrick, 2015b). All non-H atoms were refined anisotropically.

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

	x	y	z	U_{iso}*/U_{eq}
P1	0.39196 (10)	0.20951 (14)	0.13606 (8)	0.0314 (3)
Cl1	0.87251 (14)	0.3666 (2)	0.47865 (10)	0.0640 (4)
O2	0.4032 (3)	0.2610 (4)	0.2646 (2)	0.0368 (7)
O4	0.5090 (3)	0.2690 (5)	−0.0254 (2)	0.0483 (9)
H4	0.5506	0.3370	−0.0576	0.072*
O1	0.3842 (3)	0.0246 (4)	0.1175 (2)	0.0404 (7)
O3	0.2705 (3)	0.3148 (4)	0.0693 (3)	0.0458 (8)
C2	0.6585 (4)	0.2610 (5)	0.1657 (3)	0.0315 (9)
C3	0.7023 (4)	0.3308 (6)	0.2740 (4)	0.0357 (9)
H3	0.652 (3)	0.410 (5)	0.2999 (15)	0.043*
C9	0.4049 (4)	0.2024 (6)	0.4615 (3)	0.0366 (9)
C4	0.8229 (4)	0.2798 (7)	0.3431 (4)	0.0405 (10)
C5	0.9030 (5)	0.1650 (6)	0.3042 (4)	0.0444 (12)
H5	0.986 (5)	0.1341 (18)	0.350 (3)	0.053*
C14	0.2867 (4)	0.2884 (7)	0.4557 (4)	0.0464 (11)
H14	0.2292	0.3133	0.3837	0.056*
C21	−0.0793 (4)	0.2817 (6)	−0.0668 (4)	0.0407 (10)
H21	−0.1135 (18)	0.337 (3)	−0.011 (3)	0.049*
C20	−0.1603 (5)	0.2497 (7)	−0.1726 (4)	0.0483 (12)
H20	−0.245 (5)	0.2777 (18)	−0.1868 (9)	0.058*
C13	0.2537 (5)	0.3374 (7)	0.5567 (5)	0.0565 (14)
H13	0.1733	0.3965	0.5528	0.068*
C10	0.4860 (5)	0.1684 (6)	0.5690 (4)	0.0409 (11)
H10	0.5671	0.1100	0.5752	0.049*
C17	0.1022 (5)	0.1597 (6)	−0.1257 (4)	0.0397 (11)
H17	0.192 (5)	0.1288 (17)	−0.1098 (9)	0.048*
C1	0.5270 (4)	0.3155 (6)	0.0922 (3)	0.0363 (10)
H1	0.5172	0.4412	0.0983	0.044*
C16	0.0516 (4)	0.2340 (6)	−0.0423 (3)	0.0364 (10)
C11	0.4485 (5)	0.2199 (7)	0.6674 (4)	0.0502 (12)
H11	0.5044	0.1964	0.7404	0.060*
C18	0.0214 (5)	0.1302 (7)	−0.2335 (4)	0.0481 (12)
H18	0.058 (2)	0.079 (3)	−0.292 (3)	0.058*
C8	0.4424 (5)	0.1376 (6)	0.3573 (4)	0.0460 (11)
H8A	0.548 (4)	0.1175 (10)	0.3753 (7)	0.055*
H8B	0.3941 (17)	0.018 (4)	0.3320 (9)	0.055*
C15	0.1368 (4)	0.2643 (7)	0.0766 (4)	0.0454 (12)
H15A	0.0933 (15)	0.364 (3)	0.1186 (15)	0.054*
H15B	0.1420 (4)	0.149 (4)	0.1272 (18)	0.054*
C7	0.7381 (4)	0.1431 (6)	0.1276 (4)	0.0419 (10)
H7	0.7094	0.0942	0.0538	0.050*
C19	−0.1103 (5)	0.1741 (7)	−0.2565 (4)	0.0494 (13)
H19	−0.164 (3)	0.1531 (14)	−0.327 (4)	0.059*
C6	0.8590 (5)	0.0974 (6)	0.1974 (4)	0.0470 (12)
H6	0.918 (3)	0.009 (5)	0.1677 (16)	0.056*

C12	0.3337 (6)	0.3025 (8)	0.6596 (5)	0.0594 (15)
H12	0.3088	0.3365	0.7272	0.071*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0336 (5)	0.0304 (6)	0.0304 (5)	−0.0026 (4)	0.0082 (4)	0.0004 (4)
Cl1	0.0613 (8)	0.0802 (11)	0.0410 (6)	−0.0028 (7)	−0.0065 (5)	−0.0050 (6)
O2	0.0463 (17)	0.0322 (17)	0.0348 (14)	0.0037 (12)	0.0154 (12)	0.0014 (12)
O4	0.060 (2)	0.056 (2)	0.0313 (15)	−0.0126 (16)	0.0151 (14)	−0.0007 (14)
O1	0.0498 (19)	0.0327 (18)	0.0408 (16)	−0.0045 (14)	0.0149 (14)	−0.0031 (13)
O3	0.0353 (16)	0.047 (2)	0.0509 (17)	−0.0045 (14)	0.0029 (13)	0.0120 (15)
C2	0.030 (2)	0.031 (2)	0.0358 (19)	−0.0061 (16)	0.0123 (16)	0.0046 (16)
C3	0.032 (2)	0.030 (2)	0.046 (2)	−0.0003 (17)	0.0084 (18)	0.0003 (18)
C9	0.046 (2)	0.030 (2)	0.038 (2)	−0.010 (2)	0.0198 (18)	−0.005 (2)
C4	0.039 (2)	0.041 (3)	0.039 (2)	−0.0078 (19)	0.0048 (18)	0.0057 (19)
C5	0.034 (2)	0.032 (3)	0.067 (3)	−0.0012 (18)	0.012 (2)	0.011 (2)
C14	0.043 (3)	0.042 (3)	0.053 (3)	0.000 (2)	0.008 (2)	−0.002 (2)
C21	0.041 (2)	0.035 (3)	0.051 (3)	0.0006 (19)	0.020 (2)	0.003 (2)
C20	0.036 (2)	0.047 (3)	0.059 (3)	0.002 (2)	0.007 (2)	0.005 (2)
C13	0.049 (3)	0.045 (3)	0.086 (4)	−0.008 (2)	0.038 (3)	−0.015 (3)
C10	0.042 (2)	0.033 (3)	0.048 (2)	−0.0031 (18)	0.0109 (19)	0.0041 (18)
C17	0.039 (2)	0.042 (3)	0.039 (2)	0.0072 (19)	0.0093 (18)	0.0051 (18)
C1	0.039 (2)	0.037 (3)	0.033 (2)	−0.0066 (19)	0.0087 (17)	0.0011 (17)
C16	0.033 (2)	0.036 (3)	0.041 (2)	−0.0009 (18)	0.0114 (17)	0.0069 (19)
C11	0.072 (3)	0.042 (3)	0.038 (2)	−0.021 (3)	0.014 (2)	−0.005 (2)
C18	0.060 (3)	0.042 (3)	0.045 (2)	0.002 (2)	0.019 (2)	−0.005 (2)
C8	0.063 (3)	0.037 (3)	0.043 (2)	0.014 (2)	0.022 (2)	0.010 (2)
C15	0.036 (2)	0.059 (3)	0.045 (2)	−0.002 (2)	0.0163 (19)	0.001 (2)
C7	0.044 (3)	0.038 (3)	0.048 (2)	−0.007 (2)	0.019 (2)	−0.0059 (19)
C19	0.055 (3)	0.047 (3)	0.039 (2)	−0.006 (2)	−0.003 (2)	0.001 (2)
C6	0.043 (3)	0.034 (3)	0.070 (3)	0.001 (2)	0.026 (2)	−0.001 (2)
C12	0.080 (4)	0.055 (4)	0.055 (3)	−0.022 (3)	0.038 (3)	−0.022 (3)

Geometric parameters (Å, º)

P1—O1	1.473 (3)	C20—C19	1.378 (7)
P1—O3	1.566 (3)	C20—H20	0.88 (5)
P1—O2	1.578 (3)	C13—C12	1.347 (8)
P1—C1	1.819 (4)	C13—H13	0.9500
Cl1—C4	1.732 (5)	C10—C11	1.394 (6)
O2—C8	1.463 (5)	C10—H10	0.9500
O4—C1	1.432 (5)	C17—C16	1.372 (6)
O4—H4	0.8400	C17—C18	1.389 (6)
O3—C15	1.472 (5)	C17—H17	0.94 (5)
C2—C3	1.389 (6)	C1—H1	1.0000
C2—C7	1.394 (6)	C16—C15	1.514 (6)
C2—C1	1.506 (6)	C11—C12	1.346 (8)

C3—C4	1.391 (6)	C11—H11	0.9500
C3—H3	0.92 (5)	C18—C19	1.379 (7)
C9—C14	1.393 (6)	C18—H18	0.97 (5)
C9—C10	1.393 (6)	C8—H8A	1.08 (4)
C9—C8	1.492 (6)	C8—H8B	1.08 (4)
C4—C5	1.386 (7)	C15—H15A	1.09 (4)
C5—C6	1.367 (7)	C15—H15B	1.09 (4)
C5—H5	0.94 (5)	C7—C6	1.386 (7)
C14—C13	1.395 (7)	C7—H7	0.9500
C14—H14	0.9500	C19—H19	0.92 (5)
C21—C20	1.374 (7)	C6—H6	1.04 (5)
C21—C16	1.377 (6)	C12—H12	0.9500
C21—H21	0.94 (5)		

O1—P1—O3	115.92 (18)	C18—C17—H17	119.9
O1—P1—O2	113.06 (17)	O4—C1—C2	113.3 (3)
O3—P1—O2	103.29 (17)	O4—C1—P1	104.0 (3)
O1—P1—C1	115.33 (19)	C2—C1—P1	110.9 (3)
O3—P1—C1	101.24 (19)	O4—C1—H1	109.5
O2—P1—C1	106.57 (18)	C2—C1—H1	109.5
C8—O2—P1	121.3 (3)	P1—C1—H1	109.5
C1—O4—H4	109.5	C17—C16—C21	119.6 (4)
C15—O3—P1	119.2 (3)	C17—C16—C15	121.2 (4)
C3—C2—C7	119.0 (4)	C21—C16—C15	119.2 (4)
C3—C2—C1	119.3 (4)	C12—C11—C10	120.4 (5)
C7—C2—C1	121.7 (4)	C12—C11—H11	119.8
C2—C3—C4	119.7 (4)	C10—C11—H11	119.8
C2—C3—H3	120.2	C19—C18—C17	119.9 (5)
C4—C3—H3	120.2	C19—C18—H18	120.0
C14—C9—C10	118.3 (4)	C17—C18—H18	120.0
C14—C9—C8	122.0 (4)	O2—C8—C9	109.5 (4)
C10—C9—C8	119.6 (4)	O2—C8—H8A	109.8
C5—C4—C3	121.2 (4)	C9—C8—H8A	109.8
C5—C4—Cl1	120.5 (4)	O2—C8—H8B	109.8
C3—C4—Cl1	118.3 (4)	C9—C8—H8B	109.8
C6—C5—C4	118.6 (5)	H8A—C8—H8B	108.2
C6—C5—H5	120.7	O3—C15—C16	109.7 (3)
C4—C5—H5	120.7	O3—C15—H15A	109.7
C9—C14—C13	119.3 (5)	C16—C15—H15A	109.7
C9—C14—H14	120.3	O3—C15—H15B	109.7
C13—C14—H14	120.3	C16—C15—H15B	109.7
C20—C21—C16	120.5 (4)	H15A—C15—H15B	108.2
C20—C21—H21	119.8	C6—C7—C2	120.0 (4)
C16—C21—H21	119.8	C6—C7—H7	120.0
C21—C20—C19	120.3 (4)	C2—C7—H7	120.0
C21—C20—H20	119.9	C20—C19—C18	119.5 (4)
C19—C20—H20	119.9	C20—C19—H19	120.2
C12—C13—C14	121.2 (5)	C18—C19—H19	120.2

C12—C13—H13	119.4	C5—C6—C7	121.5 (4)
C14—C13—H13	119.4	C5—C6—H6	119.2
C9—C10—C11	120.3 (5)	C7—C6—H6	119.2
C9—C10—H10	119.9	C11—C12—C13	120.5 (5)
C11—C10—H10	119.9	C11—C12—H12	119.7
C16—C17—C18	120.2 (4)	C13—C12—H12	119.7
C16—C17—H17	119.9		

O1—P1—O2—C8	17.5 (4)	O2—P1—C1—O4	−178.1 (3)
O3—P1—O2—C8	143.6 (3)	O1—P1—C1—C2	−66.5 (3)
C1—P1—O2—C8	−110.2 (3)	O3—P1—C1—C2	167.5 (3)
O1—P1—O3—C15	51.4 (4)	O2—P1—C1—C2	59.8 (3)
O2—P1—O3—C15	−72.8 (3)	C18—C17—C16—C21	−1.1 (7)
C1—P1—O3—C15	177.0 (3)	C18—C17—C16—C15	178.7 (4)
C7—C2—C3—C4	−1.3 (6)	C20—C21—C16—C17	2.4 (7)
C1—C2—C3—C4	179.3 (4)	C20—C21—C16—C15	−177.4 (5)
C2—C3—C4—C5	2.5 (6)	C9—C10—C11—C12	0.1 (7)
C2—C3—C4—Cl1	−178.7 (3)	C16—C17—C18—C19	−0.7 (7)
C3—C4—C5—C6	−2.3 (7)	P1—O2—C8—C9	−162.5 (3)
Cl1—C4—C5—C6	178.9 (3)	C14—C9—C8—O2	39.0 (6)
C10—C9—C14—C13	0.1 (7)	C10—C9—C8—O2	−144.8 (4)
C8—C9—C14—C13	176.4 (5)	P1—O3—C15—C16	−124.0 (4)
C16—C21—C20—C19	−2.0 (7)	C17—C16—C15—O3	37.6 (6)
C9—C14—C13—C12	−0.3 (8)	C21—C16—C15—O3	−142.6 (4)
C14—C9—C10—C11	0.0 (7)	C3—C2—C7—C6	−0.1 (6)
C8—C9—C10—C11	−176.4 (4)	C1—C2—C7—C6	179.4 (4)
C3—C2—C1—O4	164.9 (4)	C21—C20—C19—C18	0.2 (8)
C7—C2—C1—O4	−14.5 (6)	C17—C18—C19—C20	1.1 (8)
C3—C2—C1—P1	−78.6 (4)	C4—C5—C6—C7	0.9 (7)
C7—C2—C1—P1	102.0 (4)	C2—C7—C6—C5	0.2 (7)
O1—P1—C1—O4	55.6 (3)	C10—C11—C12—C13	−0.3 (8)
O3—P1—C1—O4	−70.4 (3)	C14—C13—C12—C11	0.4 (8)

Dibenzyl [hydroxy(2-nitrophenyl)methyl]phosphonate (3a)

Crystal data

$C_{21}H_{20}NO_6P$
$M_r = 413.35$
Triclinic, $P\overline{1}$
$a = 10.0795$ (3) Å
$b = 13.8530$ (6) Å
$c = 15.9354$ (5) Å
$\alpha = 111.110$ (4)°
$\beta = 90.852$ (3)°
$\gamma = 106.326$ (3)°
$V = 1975.23$ (13) Å^3

$Z = 4$
$F(000) = 864$
$D_x = 1.390$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8023 reflections
$\theta = 4.2$–31.4°
$\mu = 0.18$ mm^{-1}
$T = 133$ K
Block, colorless
0.43 × 0.30 × 0.25 mm

Data collection

Agilent Xcalibur Sapphire3 diffractometer	39828 measured reflections
Radiation source: Enhance (Mo) X-ray Source	11989 independent reflections
Detector resolution: 15.9809 pixels mm^{-1}	8512 reflections with $I > 2\sigma(I)$
ω scans	$R_{\rm int} = 0.038$
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)	$\theta_{\rm max} = 30.5°$, $\theta_{\rm min} = 4.2°$
	$h = -14 \rightarrow 14$
	$k = -19 \rightarrow 19$
$T_{\rm min} = 0.980$, $T_{\rm max} = 1.000$	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.046$	$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.5554P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.124$	$(\Delta/\sigma)_{\rm max} < 0.001$
$S = 1.03$	$\Delta\rho_{\rm max} = 0.60$ e Å^{-3}
11989 reflections	$\Delta\rho_{\rm min} = -0.30$ e Å^{-3}
565 parameters	
0 restraints	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 > 2σ(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.

An Xcalibur, Sapphire3 detector equipped diffractometer was used with an Enhance Mo Kα X-ray radiation to collect all the intensity data. The program CrysAlis PRO (CrysAlisPro, Agilent, 2014) was used for data collection, space group determination and all data reduction purposes including empirical absorption correction using spherical harmonics. The initial structure models were provided by direct methods using SHELXT (Sheldrick, 2015a) and refined using full-matrix least-squares on F^2 using SHELXL (Sheldrick, 2015b). All non-H atoms were refined anisotropically.

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

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
P1	0.34036 (4)	0.33610 (3)	0.24334 (2)	0.01798 (9)
H400	0.484 (2)	0.5613 (17)	0.3690 (13)	0.033 (5)*
P2	0.65755 (4)	0.70132 (3)	0.27149 (2)	0.01823 (9)
H100	0.496 (2)	0.4733 (18)	0.1433 (14)	0.049 (6)*
O9	0.81171 (10)	0.77607 (8)	0.30493 (7)	0.0215 (2)
O2	0.19137 (10)	0.25153 (8)	0.20799 (7)	0.0211 (2)
O8	0.59353 (10)	0.76486 (8)	0.22569 (7)	0.0227 (2)
O4	0.44813 (11)	0.50956 (9)	0.38479 (7)	0.0235 (2)
O3	0.41292 (10)	0.28115 (9)	0.29324 (8)	0.0236 (2)
C23	0.78247 (15)	0.60271 (11)	0.11945 (10)	0.0191 (3)
O10	0.53685 (11)	0.53214 (9)	0.12951 (7)	0.0246 (2)
O7	0.57636 (11)	0.67567 (9)	0.34107 (7)	0.0258 (2)
N1	−0.00314 (13)	0.38299 (11)	0.28147 (9)	0.0257 (3)
O5	0.06966 (12)	0.42184 (10)	0.23397 (8)	0.0307 (3)

C22	0.67239 (15)	0.58044 (11)	0.18032 (10)	0.0194 (3)
H22	0.6919 (4)	0.5306 (9)	0.2066 (5)	0.023*
N2	0.98969 (14)	0.62531 (11)	0.22338 (9)	0.0252 (3)
C24	0.92640 (15)	0.62283 (12)	0.13842 (10)	0.0212 (3)
C7	0.25435 (16)	0.42323 (12)	0.47355 (10)	0.0229 (3)
H7	0.3525 (19)	0.4450 (4)	0.4915 (4)	0.027*
C1	0.31458 (14)	0.45437 (11)	0.33225 (9)	0.0183 (3)
H1	0.2883 (5)	0.5001 (8)	0.3057 (5)	0.022*
C16	0.03692 (16)	0.07050 (12)	0.12503 (10)	0.0239 (3)
C2	0.20635 (14)	0.42283 (11)	0.39074 (9)	0.0184 (3)
C37	0.40708 (15)	0.77098 (13)	0.13515 (11)	0.0247 (3)
O1	0.41947 (11)	0.36438 (9)	0.17393 (7)	0.0252 (2)
C4	−0.03052 (17)	0.35731 (14)	0.42395 (11)	0.0271 (3)
H4	−0.126 (2)	0.3347 (5)	0.4066 (4)	0.033*
C10	0.59503 (17)	0.26396 (14)	0.44355 (12)	0.0303 (4)
H10	0.5792 (4)	0.3293 (14)	0.4789 (8)	0.036*
C3	0.06145 (15)	0.38843 (12)	0.36733 (10)	0.0207 (3)
C9	0.59567 (15)	0.23593 (13)	0.35077 (11)	0.0247 (3)
O11	0.91432 (13)	0.58963 (11)	0.27171 (8)	0.0348 (3)
O12	1.11618 (13)	0.66325 (12)	0.24296 (9)	0.0416 (3)
C17	−0.08745 (17)	0.08349 (13)	0.10044 (11)	0.0281 (3)
H17	−0.08650 (17)	0.1468 (13)	0.0867 (3)	0.034*
C25	1.01936 (17)	0.64088 (13)	0.07796 (11)	0.0275 (3)
H25	1.116 (2)	0.6549 (3)	0.0933 (3)	0.033*
C28	0.73746 (17)	0.60301 (12)	0.03646 (10)	0.0235 (3)
H28	0.6423 (19)	0.5915 (3)	0.0215 (3)	0.028*
C36	0.44344 (16)	0.74987 (15)	0.21718 (12)	0.0296 (4)
H36A	0.4195 (4)	0.8019 (7)	0.2729 (7)	0.036*
H36B	0.3898 (7)	0.6737 (10)	0.20999 (14)	0.036*
C14	0.62044 (16)	0.13931 (13)	0.29942 (11)	0.0278 (3)
H14	0.62187 (17)	0.1196 (4)	0.2354 (13)	0.033*
C31	1.00525 (19)	1.04519 (13)	0.37666 (11)	0.0303 (4)
H31	0.9248 (17)	1.0712 (6)	0.37619 (11)	0.036*
C8	0.56506 (16)	0.30702 (14)	0.30601 (13)	0.0307 (4)
H8A	0.6094 (6)	0.3856 (10)	0.3453 (5)	0.037*
H8B	0.6020 (5)	0.2920 (2)	0.2461 (8)	0.037*
C21	0.03337 (19)	−0.01984 (14)	0.14458 (11)	0.0311 (4)
H21	0.1159 (19)	−0.0290 (2)	0.1615 (4)	0.037*
C30	0.98821 (15)	0.94508 (12)	0.38278 (10)	0.0229 (3)
C26	0.97016 (18)	0.63830 (14)	−0.00458 (11)	0.0305 (4)
H26	1.0352 (13)	0.6495 (3)	−0.0487 (9)	0.037*
C35	1.10341 (17)	0.90917 (14)	0.38432 (11)	0.0292 (3)
H35	1.0927 (3)	0.8399 (15)	0.38963 (16)	0.035*
C29	0.84652 (17)	0.87533 (13)	0.38640 (11)	0.0305 (4)
H29A	0.84691 (17)	0.8581 (3)	0.4398 (8)	0.037*
H29B	0.7788 (10)	0.9130 (5)	0.38844 (12)	0.037*
C19	−0.21548 (19)	−0.08318 (14)	0.11459 (11)	0.0327 (4)
H19	−0.3023 (19)	−0.1358 (11)	0.11095 (14)	0.039*

C42	0.39673 (17)	0.69247 (14)	0.04910 (12)	0.0288 (3)
H42	0.4117 (3)	0.6234 (14)	0.04279 (17)	0.035*
O6	−0.12840 (13)	0.33932 (14)	0.26055 (10)	0.0544 (4)
C6	0.16325 (17)	0.39282 (14)	0.53056 (11)	0.0276 (3)
H6	0.1977 (8)	0.39435 (14)	0.5845 (12)	0.033*
C18	−0.21298 (18)	0.00679 (14)	0.09529 (12)	0.0321 (4)
H18	−0.3014 (19)	0.0165 (3)	0.0777 (4)	0.038*
C11	0.61763 (19)	0.19606 (16)	0.48406 (13)	0.0372 (4)
H11	0.61670 (19)	0.2154 (5)	0.5471 (14)	0.045*
C27	0.82926 (18)	0.61991 (14)	−0.02487 (11)	0.0286 (3)
H27	0.7955 (7)	0.61882 (14)	−0.0800 (12)	0.034*
C20	−0.0929 (2)	−0.09669 (14)	0.13900 (12)	0.0355 (4)
H20	−0.0943 (2)	−0.1560 (14)	0.1515 (3)	0.043*
C5	0.02075 (18)	0.36026 (14)	0.50618 (11)	0.0304 (4)
H5	−0.0428 (13)	0.3397 (4)	0.5464 (8)	0.036*
C38	0.38634 (18)	0.86858 (15)	0.14305 (12)	0.0330 (4)
H38	0.3931 (2)	0.9250 (12)	0.2036 (13)	0.040*
C15	0.17277 (18)	0.15174 (14)	0.12808 (12)	0.0358 (4)
H15A	0.2467 (11)	0.1232 (4)	0.13115 (12)	0.043*
H15B	0.17338 (19)	0.1671 (3)	0.0749 (8)	0.043*
C41	0.36579 (19)	0.71037 (16)	−0.02724 (12)	0.0358 (4)
H41	0.3578 (3)	0.6543 (12)	−0.0872 (13)	0.043*
C34	1.23371 (19)	0.97247 (17)	0.37825 (12)	0.0382 (4)
H34	1.3155 (18)	0.9466 (6)	0.37877 (12)	0.046*
C13	0.64307 (19)	0.07126 (15)	0.33998 (12)	0.0337 (4)
H13	0.6594 (4)	0.0058 (15)	0.3047 (8)	0.040*
C33	1.2494 (2)	1.07134 (17)	0.37148 (12)	0.0412 (5)
H33	1.337 (2)	1.1134 (10)	0.36705 (16)	0.049*
C12	0.64167 (19)	0.09951 (17)	0.43228 (13)	0.0368 (4)
H12	0.6571 (4)	0.0532 (11)	0.4601 (7)	0.044*
C39	0.3561 (2)	0.88701 (17)	0.06609 (13)	0.0415 (5)
H39	0.3421 (4)	0.9554 (16)	0.0719 (2)	0.050*
C40	0.3460 (2)	0.80819 (17)	−0.01888 (13)	0.0411 (5)
H40	0.3252 (5)	0.8212 (3)	−0.0722 (13)	0.049*
C32	1.1362 (2)	1.10841 (15)	0.37123 (12)	0.0387 (4)
H32	1.1473 (3)	1.1748 (16)	0.36747 (15)	0.046*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.01575 (17)	0.01667 (17)	0.02039 (18)	0.00240 (13)	0.00380 (13)	0.00764 (14)
P2	0.01637 (17)	0.01721 (17)	0.01916 (18)	0.00092 (13)	0.00155 (13)	0.00790 (14)
O9	0.0162 (5)	0.0184 (5)	0.0230 (5)	0.0006 (4)	−0.0003 (4)	0.0035 (4)
O2	0.0166 (5)	0.0184 (5)	0.0228 (5)	0.0021 (4)	0.0029 (4)	0.0040 (4)
O8	0.0172 (5)	0.0242 (5)	0.0291 (6)	0.0043 (4)	0.0033 (4)	0.0145 (5)
O4	0.0189 (5)	0.0210 (5)	0.0242 (5)	−0.0032 (4)	−0.0018 (4)	0.0086 (4)
O3	0.0146 (5)	0.0244 (5)	0.0361 (6)	0.0051 (4)	0.0053 (4)	0.0169 (5)
C23	0.0208 (7)	0.0149 (6)	0.0190 (7)	0.0026 (5)	0.0011 (5)	0.0058 (5)

O10	0.0203 (5)	0.0218 (5)	0.0253 (5)	−0.0033 (4)	−0.0036 (4)	0.0093 (5)
O7	0.0269 (6)	0.0245 (5)	0.0235 (5)	0.0020 (4)	0.0068 (4)	0.0106 (4)
N1	0.0200 (6)	0.0308 (7)	0.0273 (7)	0.0079 (5)	0.0010 (5)	0.0119 (6)
O5	0.0269 (6)	0.0434 (7)	0.0304 (6)	0.0131 (5)	0.0052 (5)	0.0219 (5)
C22	0.0190 (7)	0.0165 (6)	0.0196 (7)	0.0009 (5)	−0.0006 (5)	0.0071 (5)
N2	0.0247 (7)	0.0295 (7)	0.0239 (6)	0.0123 (6)	0.0016 (5)	0.0100 (6)
C24	0.0221 (7)	0.0208 (7)	0.0197 (7)	0.0064 (6)	0.0013 (5)	0.0067 (6)
C7	0.0212 (7)	0.0230 (7)	0.0212 (7)	0.0023 (6)	0.0008 (6)	0.0080 (6)
C1	0.0172 (6)	0.0167 (6)	0.0194 (7)	0.0019 (5)	0.0017 (5)	0.0075 (5)
C16	0.0235 (7)	0.0184 (7)	0.0208 (7)	0.0014 (6)	0.0047 (6)	0.0010 (6)
C2	0.0187 (7)	0.0161 (6)	0.0192 (7)	0.0039 (5)	0.0033 (5)	0.0066 (5)
C37	0.0167 (7)	0.0290 (8)	0.0304 (8)	0.0088 (6)	0.0044 (6)	0.0122 (7)
O1	0.0262 (6)	0.0236 (5)	0.0251 (5)	0.0040 (4)	0.0088 (4)	0.0110 (4)
C4	0.0183 (7)	0.0324 (8)	0.0281 (8)	0.0044 (6)	0.0058 (6)	0.0109 (7)
C10	0.0227 (8)	0.0283 (8)	0.0328 (9)	0.0087 (7)	0.0030 (6)	0.0031 (7)
C3	0.0190 (7)	0.0219 (7)	0.0195 (7)	0.0047 (6)	0.0011 (5)	0.0072 (6)
C9	0.0137 (6)	0.0247 (7)	0.0340 (8)	0.0043 (6)	0.0010 (6)	0.0106 (7)
O11	0.0323 (6)	0.0561 (8)	0.0299 (6)	0.0225 (6)	0.0096 (5)	0.0252 (6)
O12	0.0249 (6)	0.0562 (9)	0.0417 (7)	0.0060 (6)	−0.0060 (5)	0.0215 (7)
C17	0.0320 (9)	0.0220 (7)	0.0316 (8)	0.0091 (6)	0.0073 (7)	0.0109 (7)
C25	0.0222 (8)	0.0307 (8)	0.0276 (8)	0.0075 (6)	0.0055 (6)	0.0093 (7)
C28	0.0230 (7)	0.0239 (7)	0.0216 (7)	0.0028 (6)	0.0000 (6)	0.0097 (6)
C36	0.0200 (7)	0.0417 (10)	0.0339 (9)	0.0135 (7)	0.0076 (6)	0.0188 (8)
C14	0.0252 (8)	0.0303 (8)	0.0250 (8)	0.0107 (7)	0.0007 (6)	0.0056 (7)
C31	0.0330 (9)	0.0247 (8)	0.0271 (8)	0.0053 (7)	−0.0001 (7)	0.0059 (7)
C8	0.0143 (7)	0.0323 (9)	0.0500 (11)	0.0047 (6)	0.0049 (7)	0.0223 (8)
C21	0.0345 (9)	0.0292 (8)	0.0265 (8)	0.0112 (7)	−0.0011 (7)	0.0060 (7)
C30	0.0206 (7)	0.0213 (7)	0.0180 (7)	0.0000 (6)	0.0011 (5)	0.0025 (6)
C26	0.0301 (8)	0.0344 (9)	0.0251 (8)	0.0056 (7)	0.0079 (7)	0.0125 (7)
C35	0.0295 (8)	0.0281 (8)	0.0282 (8)	0.0079 (7)	0.0047 (7)	0.0091 (7)
C29	0.0236 (8)	0.0265 (8)	0.0243 (8)	−0.0039 (6)	0.0043 (6)	−0.0011 (6)
C19	0.0346 (9)	0.0247 (8)	0.0277 (8)	−0.0018 (7)	0.0076 (7)	0.0055 (7)
C42	0.0247 (8)	0.0255 (8)	0.0354 (9)	0.0107 (6)	0.0045 (7)	0.0085 (7)
O6	0.0215 (6)	0.0889 (12)	0.0506 (9)	−0.0042 (7)	−0.0089 (6)	0.0404 (9)
C6	0.0279 (8)	0.0330 (8)	0.0205 (7)	0.0042 (7)	0.0028 (6)	0.0127 (7)
C18	0.0260 (8)	0.0335 (9)	0.0319 (9)	0.0082 (7)	0.0036 (7)	0.0077 (7)
C11	0.0357 (10)	0.0486 (11)	0.0265 (9)	0.0158 (9)	0.0033 (7)	0.0113 (8)
C27	0.0320 (9)	0.0307 (8)	0.0216 (7)	0.0042 (7)	0.0017 (6)	0.0125 (7)
C20	0.0543 (12)	0.0212 (8)	0.0293 (9)	0.0062 (8)	0.0048 (8)	0.0119 (7)
C5	0.0277 (8)	0.0350 (9)	0.0264 (8)	0.0038 (7)	0.0095 (7)	0.0135 (7)
C38	0.0359 (9)	0.0319 (9)	0.0304 (9)	0.0171 (8)	0.0012 (7)	0.0062 (7)
C15	0.0307 (9)	0.0243 (8)	0.0328 (9)	−0.0021 (7)	0.0109 (7)	−0.0038 (7)
C41	0.0367 (10)	0.0427 (10)	0.0282 (9)	0.0221 (8)	0.0050 (7)	0.0061 (8)
C34	0.0230 (8)	0.0537 (12)	0.0311 (9)	0.0096 (8)	0.0042 (7)	0.0101 (8)
C13	0.0360 (9)	0.0317 (9)	0.0345 (9)	0.0186 (8)	0.0004 (7)	0.0076 (7)
C33	0.0300 (9)	0.0445 (11)	0.0302 (9)	−0.0106 (8)	0.0033 (7)	0.0095 (8)
C12	0.0356 (10)	0.0463 (11)	0.0381 (10)	0.0201 (9)	0.0009 (8)	0.0214 (9)
C39	0.0545 (12)	0.0402 (10)	0.0408 (10)	0.0311 (10)	0.0054 (9)	0.0155 (9)

C40	0.0489 (12)	0.0548 (12)	0.0339 (10)	0.0331 (10)	0.0084 (8)	0.0198 (9)
C32	0.0515 (12)	0.0240 (8)	0.0293 (9)	−0.0042 (8)	0.0022 (8)	0.0094 (7)

Geometric parameters (Å, º)

P1—O1	1.4749 (11)	C28—C27	1.391 (2)
P1—O2	1.5670 (10)	C28—H28	0.940 (18)
P1—O3	1.5743 (11)	C36—H36A	1.005 (13)
P1—C1	1.8269 (14)	C36—H36B	1.005 (13)
P2—O7	1.4739 (11)	C14—C13	1.383 (2)
P2—O9	1.5634 (10)	C14—H14	0.958 (19)
P2—O8	1.5785 (11)	C31—C32	1.387 (2)
P2—C22	1.8255 (15)	C31—C30	1.388 (2)
O9—C29	1.4590 (18)	C31—H31	0.98 (2)
O2—C15	1.4653 (18)	C8—H8A	1.002 (13)
O8—C36	1.4654 (18)	C8—H8B	1.002 (13)
O4—C1	1.4228 (17)	C21—C20	1.388 (2)
O4—H400	0.83 (2)	C21—H21	0.93 (2)
O3—C8	1.4665 (18)	C30—C35	1.389 (2)
C23—C28	1.394 (2)	C30—C29	1.498 (2)
C23—C24	1.405 (2)	C26—C27	1.382 (2)
C23—C22	1.5238 (19)	C26—H26	0.992 (19)
O10—C22	1.4257 (17)	C35—C34	1.386 (2)
O10—H100	0.91 (2)	C35—H35	0.97 (2)
N1—O6	1.2182 (17)	C29—H29A	0.963 (13)
N1—O5	1.2202 (17)	C29—H29B	0.963 (13)
N1—C3	1.4740 (19)	C19—C20	1.372 (3)
C22—H22	0.987 (17)	C19—C18	1.381 (3)
N2—O12	1.2216 (17)	C19—H19	0.95 (2)
N2—O11	1.2229 (17)	C42—C41	1.374 (2)
N2—C24	1.4729 (19)	C42—H42	0.98 (2)
C24—C25	1.392 (2)	C6—C5	1.382 (2)
C7—C6	1.389 (2)	C6—H6	0.913 (19)
C7—C2	1.396 (2)	C18—H18	0.99 (2)
C7—H7	0.955 (18)	C11—C12	1.386 (3)
C1—C2	1.5183 (19)	C11—H11	0.94 (2)
C1—H1	0.968 (17)	C27—H27	0.93 (2)
C16—C17	1.386 (2)	C20—H20	0.91 (2)
C16—C21	1.386 (2)	C5—H5	0.971 (19)
C16—C15	1.495 (2)	C38—C39	1.386 (3)
C2—C3	1.401 (2)	C38—H38	0.99 (2)
C37—C38	1.387 (2)	C15—H15A	0.945 (14)
C37—C42	1.390 (2)	C15—H15B	0.945 (14)
C37—C36	1.500 (2)	C41—C40	1.384 (3)
C4—C5	1.384 (2)	C41—H41	0.98 (2)
C4—C3	1.393 (2)	C34—C33	1.377 (3)
C4—H4	0.926 (19)	C34—H34	0.99 (2)
C10—C11	1.381 (3)	C13—C12	1.380 (3)

C10—C9	1.387 (2)	C13—H13	0.94 (2)
C10—H10	0.94 (2)	C33—C32	1.378 (3)
C9—C14	1.389 (2)	C33—H33	0.93 (2)
C9—C8	1.498 (2)	C12—H12	0.94 (2)
C17—C18	1.384 (2)	C39—C40	1.380 (3)
C17—H17	0.98 (2)	C39—H39	0.97 (2)
C25—C26	1.383 (2)	C40—H40	0.96 (2)
C25—H25	0.948 (19)	C32—H32	0.92 (2)

O1—P1—O2	115.93 (6)	C32—C31—C30	120.22 (17)
O1—P1—O3	113.27 (6)	C32—C31—H31	119.9
O2—P1—O3	102.41 (6)	C30—C31—H31	119.9
O1—P1—C1	112.69 (6)	O3—C8—C9	106.44 (12)
O2—P1—C1	105.42 (6)	O3—C8—H8A	110.4
O3—P1—C1	106.07 (6)	C9—C8—H8A	110.4
O7—P2—O9	116.27 (6)	O3—C8—H8B	110.4
O7—P2—O8	112.73 (6)	C9—C8—H8B	110.4
O9—P2—O8	102.91 (6)	H8A—C8—H8B	108.6
O7—P2—C22	112.87 (6)	C16—C21—C20	120.52 (17)
O9—P2—C22	104.04 (6)	C16—C21—H21	119.7
O8—P2—C22	107.00 (6)	C20—C21—H21	119.7
C29—O9—P2	121.07 (9)	C31—C30—C35	119.51 (15)
C15—O2—P1	119.34 (9)	C31—C30—C29	120.41 (15)
C36—O8—P2	121.24 (9)	C35—C30—C29	120.07 (15)
C1—O4—H400	106.0 (14)	C27—C26—C25	119.23 (15)
C8—O3—P1	121.25 (9)	C27—C26—H26	120.4
C28—C23—C24	116.06 (13)	C25—C26—H26	120.4
C28—C23—C22	117.55 (13)	C34—C35—C30	119.92 (17)
C24—C23—C22	126.39 (13)	C34—C35—H35	120.0
C22—O10—H100	105.9 (14)	C30—C35—H35	120.0
O6—N1—O5	122.33 (14)	O9—C29—C30	107.49 (12)
O6—N1—C3	118.26 (13)	O9—C29—H29A	110.2
O5—N1—C3	119.42 (12)	C30—C29—H29A	110.2
O10—C22—C23	110.48 (11)	O9—C29—H29B	110.2
O10—C22—P2	103.59 (9)	C30—C29—H29B	110.2
C23—C22—P2	114.88 (10)	H29A—C29—H29B	108.5
O10—C22—H22	109.2	C20—C19—C18	119.87 (16)
C23—C22—H22	109.2	C20—C19—H19	120.1
P2—C22—H22	109.2	C18—C19—H19	120.1
O12—N2—O11	122.37 (14)	C41—C42—C37	120.89 (16)
O12—N2—C24	118.50 (13)	C41—C42—H42	119.6
O11—N2—C24	119.13 (13)	C37—C42—H42	119.6
C25—C24—C23	122.44 (14)	C5—C6—C7	120.42 (15)
C25—C24—N2	115.16 (13)	C5—C6—H6	119.8
C23—C24—N2	122.40 (13)	C7—C6—H6	119.8
C6—C7—C2	121.76 (14)	C19—C18—C17	120.38 (17)
C6—C7—H7	119.1	C19—C18—H18	119.8
C2—C7—H7	119.1	C17—C18—H18	119.8

O4—C1—C2	110.39 (11)	C10—C11—C12	120.18 (17)
O4—C1—P1	103.70 (9)	C10—C11—H11	119.9
C2—C1—P1	112.43 (9)	C12—C11—H11	119.9
O4—C1—H1	110.1	C26—C27—C28	120.53 (15)
C2—C1—H1	110.1	C26—C27—H27	119.7
P1—C1—H1	110.1	C28—C27—H27	119.7
C17—C16—C21	119.06 (15)	C19—C20—C21	120.02 (17)
C17—C16—C15	120.16 (16)	C19—C20—H20	120.0
C21—C16—C15	120.76 (16)	C21—C20—H20	120.0
C7—C2—C3	116.59 (13)	C6—C5—C4	119.38 (15)
C7—C2—C1	117.57 (13)	C6—C5—H5	120.3
C3—C2—C1	125.77 (13)	C4—C5—H5	120.3
C38—C37—C42	118.93 (16)	C39—C38—C37	120.22 (17)
C38—C37—C36	121.39 (15)	C39—C38—H38	119.9
C42—C37—C36	119.67 (15)	C37—C38—H38	119.9
C5—C4—C3	119.88 (15)	O2—C15—C16	109.09 (12)
C5—C4—H4	120.1	O2—C15—H15A	109.9
C3—C4—H4	120.1	C16—C15—H15A	109.9
C11—C10—C9	120.30 (16)	O2—C15—H15B	109.9
C11—C10—H10	119.9	C16—C15—H15B	109.9
C9—C10—H10	119.9	H15A—C15—H15B	108.3
C4—C3—C2	121.95 (14)	C42—C41—C40	119.88 (17)
C4—C3—N1	115.85 (13)	C42—C41—H41	120.1
C2—C3—N1	122.20 (13)	C40—C41—H41	120.1
C10—C9—C14	119.18 (16)	C33—C34—C35	120.16 (18)
C10—C9—C8	120.42 (15)	C33—C34—H34	119.9
C14—C9—C8	120.37 (15)	C35—C34—H34	119.9
C18—C17—C16	120.15 (16)	C12—C13—C14	119.93 (17)
C18—C17—H17	119.9	C12—C13—H13	120.0
C16—C17—H17	119.9	C14—C13—H13	120.0
C26—C25—C24	119.74 (15)	C34—C33—C32	120.37 (17)
C26—C25—H25	120.1	C34—C33—H33	119.8
C24—C25—H25	120.1	C32—C33—H33	119.8
C27—C28—C23	121.98 (15)	C13—C12—C11	119.87 (18)
C27—C28—H28	119.0	C13—C12—H12	120.1
C23—C28—H28	119.0	C11—C12—H12	120.1
O8—C36—C37	107.48 (12)	C40—C39—C38	120.17 (18)
O8—C36—H36A	110.2	C40—C39—H39	119.9
C37—C36—H36A	110.2	C38—C39—H39	119.9
O8—C36—H36B	110.2	C39—C40—C41	119.91 (18)
C37—C36—H36B	110.2	C39—C40—H40	120.0
H36A—C36—H36B	108.5	C41—C40—H40	120.0
C13—C14—C9	120.53 (16)	C33—C32—C31	119.81 (18)
C13—C14—H14	119.7	C33—C32—H32	120.1
C9—C14—H14	119.7	C31—C32—H32	120.1

O7—P2—O9—C29	−46.67 (14)	C11—C10—C9—C8	177.34 (15)
O8—P2—O9—C29	77.05 (13)	C21—C16—C17—C18	−0.2 (2)

C22—P2—O9—C29	−171.44 (12)	C15—C16—C17—C18	178.28 (15)
O1—P1—O2—C15	47.15 (14)	C23—C24—C25—C26	−0.6 (2)
O3—P1—O2—C15	−76.68 (13)	N2—C24—C25—C26	178.85 (15)
C1—P1—O2—C15	172.54 (12)	C24—C23—C28—C27	1.3 (2)
O7—P2—O8—C36	−29.37 (13)	C22—C23—C28—C27	−178.43 (14)
O9—P2—O8—C36	−155.41 (11)	P2—O8—C36—C37	−151.53 (11)
C22—P2—O8—C36	95.30 (12)	C38—C37—C36—O8	−101.89 (17)
O1—P1—O3—C8	30.14 (14)	C42—C37—C36—O8	76.69 (18)
O2—P1—O3—C8	155.73 (12)	C10—C9—C14—C13	0.5 (2)
C1—P1—O3—C8	−93.98 (12)	C8—C9—C14—C13	−177.33 (15)
C28—C23—C22—O10	17.28 (18)	P1—O3—C8—C9	−176.94 (10)
C24—C23—C22—O10	−162.46 (13)	C10—C9—C8—O3	−80.39 (18)
C28—C23—C22—P2	−99.44 (14)	C14—C9—C8—O3	97.46 (16)
C24—C23—C22—P2	80.82 (17)	C17—C16—C21—C20	0.5 (2)
O7—P2—C22—O10	73.45 (10)	C15—C16—C21—C20	−178.07 (15)
O9—P2—C22—O10	−159.63 (9)	C32—C31—C30—C35	0.6 (2)
O8—P2—C22—O10	−51.13 (10)	C32—C31—C30—C29	−178.51 (15)
O7—P2—C22—C23	−165.96 (10)	C24—C25—C26—C27	1.3 (3)
O9—P2—C22—C23	−39.04 (12)	C31—C30—C35—C34	−1.1 (2)
O8—P2—C22—C23	69.46 (11)	C29—C30—C35—C34	178.09 (15)
C28—C23—C24—C25	−0.7 (2)	P2—O9—C29—C30	−161.51 (11)
C22—C23—C24—C25	179.04 (14)	C31—C30—C29—O9	115.86 (16)
C28—C23—C24—N2	179.89 (13)	C35—C30—C29—O9	−63.28 (19)
C22—C23—C24—N2	−0.4 (2)	C38—C37—C42—C41	−0.3 (2)
O12—N2—C24—C25	14.3 (2)	C36—C37—C42—C41	−178.94 (15)
O11—N2—C24—C25	−165.73 (14)	C2—C7—C6—C5	0.4 (2)
O12—N2—C24—C23	−166.23 (14)	C20—C19—C18—C17	0.0 (3)
O11—N2—C24—C23	13.7 (2)	C16—C17—C18—C19	0.0 (2)
O1—P1—C1—O4	−74.02 (10)	C9—C10—C11—C12	0.3 (3)
O2—P1—C1—O4	158.60 (9)	C25—C26—C27—C28	−0.7 (3)
O3—P1—C1—O4	50.46 (10)	C23—C28—C27—C26	−0.7 (2)
O1—P1—C1—C2	166.73 (10)	C18—C19—C20—C21	0.2 (3)
O2—P1—C1—C2	39.35 (12)	C16—C21—C20—C19	−0.4 (3)
O3—P1—C1—C2	−68.79 (11)	C7—C6—C5—C4	0.6 (3)
C6—C7—C2—C3	−1.0 (2)	C3—C4—C5—C6	−0.9 (3)
C6—C7—C2—C1	−178.26 (14)	C42—C37—C38—C39	−0.1 (3)
O4—C1—C2—C7	−17.19 (18)	C36—C37—C38—C39	178.44 (16)
P1—C1—C2—C7	98.08 (14)	P1—O2—C15—C16	162.34 (11)
O4—C1—C2—C3	165.85 (13)	C17—C16—C15—O2	73.8 (2)
P1—C1—C2—C3	−78.88 (16)	C21—C16—C15—O2	−107.72 (17)
C5—C4—C3—C2	0.2 (2)	C37—C42—C41—C40	0.7 (3)
C5—C4—C3—N1	−179.72 (15)	C30—C35—C34—C33	0.6 (3)
C7—C2—C3—C4	0.7 (2)	C9—C14—C13—C12	−0.3 (3)
C1—C2—C3—C4	177.68 (14)	C35—C34—C33—C32	0.4 (3)
C7—C2—C3—N1	−179.35 (13)	C14—C13—C12—C11	0.0 (3)
C1—C2—C3—N1	−2.4 (2)	C10—C11—C12—C13	0.0 (3)
O6—N1—C3—C4	−9.3 (2)	C37—C38—C39—C40	0.3 (3)
O5—N1—C3—C4	170.73 (14)	C38—C39—C40—C41	0.1 (3)

O6—N1—C3—C2	170.71 (16)	C42—C41—C40—C39	−0.6 (3)
O5—N1—C3—C2	−9.2 (2)	C34—C33—C32—C31	−0.8 (3)
C11—C10—C9—C14	−0.5 (2)	C30—C31—C32—C33	0.3 (3)

Dimethyl [1-hydroxy-1-(4-nitrophenyl)ethyl]phosphonate (2b)

Crystal data

$C_{10}H_{14}NO_6P$	$Z = 2$
$M_r = 275.19$	$F(000) = 288$
Triclinic, $P\overline{1}$	$D_x = 1.450$ Mg m^{-3}
$a = 8.1800$ (4) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 8.4006$ (6) Å	Cell parameters from 3426 reflections
$c = 9.9661$ (4) Å	$\theta = 4.6$–$31.3°$
$\alpha = 102.173$ (5)°	$\mu = 0.24$ mm^{-1}
$\beta = 94.897$ (4)°	$T = 173$ K
$\gamma = 107.504$ (5)°	Block, colorless
$V = 630.26$ (6) Å^3	0.40 × 0.35 × 0.20 mm

Data collection

Agilent Xcalibur Sapphire3 diffractometer	12564 measured reflections
Radiation source: Enhance (Mo) X-ray Source	3827 independent reflections
Detector resolution: 15.9809 pixels mm^{-1}	3070 reflections with $I > 2\sigma(I)$
ω scans	$R_{\rm int} = 0.028$
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)	$\theta_{\rm max} = 30.5°$, $\theta_{\rm min} = 4.2°$
$T_{\rm min} = 0.948$, $T_{\rm max} = 1.000$	$h = -11 \rightarrow 11$
	$k = -11 \rightarrow 11$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.041$	$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2 + 0.1729P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.114$	$(\Delta/\sigma)_{\rm max} < 0.001$
$S = 1.03$	$\Delta\rho_{\rm max} = 0.34$ e Å^{-3}
3827 reflections	$\Delta\rho_{\rm min} = -0.28$ e Å^{-3}
176 parameters	
0 restraints	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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.

An Xcalibur, Sapphire3 detector equipped diffractometer was used with an Enhance Mo $K\alpha$ X-ray radiation to collect all the intensity data. The program CrysAlis PRO (CrysAlisPro, Agilent, 2014) was used for data collection, space group determination and all data reduction purposes including empirical absorption correction using spherical harmonics. The initial structure models were provided by direct methods using SHELXT (Sheldrick, 2015a) and refined using full-matrix least-squares on F^2 using SHELXL (Sheldrick, 2015b). All non-H atoms were refined anisotropically.

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

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
P1	0.25993 (4)	0.15887 (5)	0.41073 (4)	0.02383 (11)
O4	−0.01562 (13)	0.24691 (13)	0.42662 (11)	0.0275 (2)
C3	0.12907 (16)	0.32849 (17)	0.24037 (13)	0.0214 (2)
O2	0.37141 (13)	0.12800 (15)	0.29430 (11)	0.0336 (3)
C5	0.07201 (16)	0.18886 (17)	0.31853 (13)	0.0207 (2)
O1	0.21030 (13)	0.02257 (14)	0.48551 (11)	0.0315 (2)
O3	0.37375 (14)	0.33881 (14)	0.50550 (11)	0.0367 (3)
C8	0.22597 (19)	0.57705 (19)	0.09385 (15)	0.0274 (3)
C9	0.10946 (19)	0.48879 (18)	0.28755 (15)	0.0279 (3)
H9	0.0657 (9)	0.5115 (5)	0.3667 (17)	0.033*
C10	−0.04346 (18)	0.01791 (18)	0.22095 (15)	0.0272 (3)
H10A	−0.0811 (12)	−0.0655 (10)	0.2735 (6)	0.041*
H10B	0.0208 (8)	−0.0219 (9)	0.1534 (10)	0.041*
H10C	−0.1422 (13)	0.0343 (4)	0.1749 (10)	0.041*
C11	0.20148 (18)	0.29652 (18)	0.11999 (14)	0.0258 (3)
H11	0.2176 (3)	0.185 (2)	0.0872 (6)	0.031*
N1	0.27623 (19)	0.70781 (18)	0.01358 (14)	0.0357 (3)
C13	0.25077 (19)	0.42079 (19)	0.04627 (15)	0.0282 (3)
H13	0.2968 (10)	0.4007 (5)	−0.0291 (16)	0.034*
O6	0.2299 (2)	0.83360 (17)	0.04140 (15)	0.0505 (3)
C15	0.1568 (2)	0.6144 (2)	0.21369 (16)	0.0312 (3)
H15	0.1421 (4)	0.723 (2)	0.2447 (7)	0.037*
O5	0.3616 (3)	0.6835 (2)	−0.07774 (19)	0.0765 (6)
C17	0.5299 (2)	0.0903 (3)	0.3215 (2)	0.0542 (6)
H17A	0.6078 (14)	0.1807 (16)	0.3884 (15)	0.081*
H17B	0.5770 (13)	0.075 (2)	0.2408 (12)	0.081*
H17C	0.5063 (5)	−0.0089 (18)	0.3526 (17)	0.081*
C18	0.3562 (3)	0.3990 (3)	0.64670 (19)	0.0507 (5)
H18A	0.2565 (18)	0.429 (2)	0.64949 (19)	0.076*
H18B	0.4518 (17)	0.4942 (18)	0.6898 (8)	0.076*
H18C	0.349 (2)	0.3126 (14)	0.6924 (8)	0.076*
H1A	−0.069 (3)	0.159 (3)	0.456 (3)	0.061*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.01850 (16)	0.02768 (19)	0.02616 (18)	0.00507 (13)	0.00364 (12)	0.01212 (14)
O4	0.0301 (5)	0.0268 (5)	0.0299 (5)	0.0110 (4)	0.0150 (4)	0.0100 (4)
C3	0.0201 (6)	0.0243 (6)	0.0213 (6)	0.0088 (5)	0.0027 (4)	0.0072 (5)
O2	0.0254 (5)	0.0518 (7)	0.0353 (6)	0.0211 (5)	0.0108 (4)	0.0208 (5)
C5	0.0190 (5)	0.0221 (6)	0.0225 (6)	0.0075 (5)	0.0058 (4)	0.0065 (5)
O1	0.0246 (5)	0.0351 (6)	0.0406 (6)	0.0087 (4)	0.0068 (4)	0.0225 (5)
O3	0.0315 (6)	0.0364 (6)	0.0300 (5)	−0.0065 (5)	−0.0012 (4)	0.0105 (5)
C8	0.0290 (7)	0.0301 (7)	0.0275 (7)	0.0110 (6)	0.0065 (5)	0.0137 (6)
C9	0.0340 (7)	0.0280 (7)	0.0276 (7)	0.0147 (6)	0.0130 (6)	0.0097 (5)

C10	0.0236 (6)	0.0252 (7)	0.0293 (7)	0.0048 (5)	0.0022 (5)	0.0051 (5)
C11	0.0311 (7)	0.0252 (6)	0.0231 (6)	0.0119 (5)	0.0063 (5)	0.0058 (5)
N1	0.0443 (8)	0.0364 (7)	0.0346 (7)	0.0165 (6)	0.0127 (6)	0.0189 (6)
C13	0.0345 (7)	0.0333 (7)	0.0216 (6)	0.0149 (6)	0.0096 (5)	0.0090 (5)
O6	0.0756 (10)	0.0413 (7)	0.0533 (8)	0.0321 (7)	0.0246 (7)	0.0267 (6)
C15	0.0400 (8)	0.0279 (7)	0.0333 (7)	0.0170 (6)	0.0134 (6)	0.0120 (6)
O5	0.1234 (15)	0.0685 (10)	0.0812 (11)	0.0551 (11)	0.0753 (11)	0.0527 (9)
C17	0.0344 (9)	0.0907 (16)	0.0652 (13)	0.0394 (10)	0.0210 (9)	0.0448 (12)
C18	0.0494 (11)	0.0493 (11)	0.0326 (9)	−0.0051 (8)	0.0025 (8)	−0.0009 (8)

Geometric parameters (Å, º)

P1—O1	1.4708 (10)	C9—H9	0.902 (18)
P1—O2	1.5625 (11)	C10—H10A	0.955 (10)
P1—O3	1.5636 (11)	C10—H10B	0.955 (10)
P1—C5	1.8330 (13)	C10—H10C	0.955 (10)
O4—C5	1.4258 (15)	C11—C13	1.3831 (19)
O4—H1A	0.86 (3)	C11—H11	0.979 (17)
C3—C9	1.3914 (19)	N1—O6	1.2135 (18)
C3—C11	1.3940 (18)	N1—O5	1.2137 (19)
C3—C5	1.5228 (18)	C13—H13	0.876 (19)
O2—C17	1.4414 (18)	C15—H15	0.944 (19)
C5—C10	1.5292 (19)	C17—H17A	0.922 (13)
O3—C18	1.426 (2)	C17—H17B	0.922 (13)
C8—C13	1.380 (2)	C17—H17C	0.922 (13)
C8—C15	1.382 (2)	C18—H18A	0.926 (13)
C8—N1	1.4732 (18)	C18—H18B	0.926 (13)
C9—C15	1.3916 (19)	C18—H18C	0.926 (13)
O1—P1—O2	115.61 (6)	C5—C10—H10C	109.5
O1—P1—O3	114.01 (6)	H10A—C10—H10C	109.5
O2—P1—O3	102.79 (6)	H10B—C10—H10C	109.5
O1—P1—C5	112.77 (6)	C13—C11—C3	120.80 (13)
O2—P1—C5	103.31 (6)	C13—C11—H11	119.6
O3—P1—C5	107.26 (6)	C3—C11—H11	119.6
C5—O4—H1A	107.4 (16)	O6—N1—O5	123.31 (14)
C9—C3—C11	119.21 (12)	O6—N1—C8	118.61 (13)
C9—C3—C5	120.69 (12)	O5—N1—C8	118.08 (13)
C11—C3—C5	120.10 (12)	C8—C13—C11	118.65 (13)
C17—O2—P1	121.67 (11)	C8—C13—H13	120.7
O4—C5—C3	108.65 (10)	C11—C13—H13	120.7
O4—C5—C10	111.20 (10)	C8—C15—C9	118.46 (13)
C3—C5—C10	111.47 (11)	C8—C15—H15	120.8
O4—C5—P1	104.11 (8)	C9—C15—H15	120.8
C3—C5—P1	111.08 (8)	O2—C17—H17A	109.5
C10—C5—P1	110.10 (9)	O2—C17—H17B	109.5
C18—O3—P1	123.59 (11)	H17A—C17—H17B	109.5
C13—C8—C15	122.26 (13)	O2—C17—H17C	109.5

C13—C8—N1	118.35 (13)	H17A—C17—H17C	109.5
C15—C8—N1	119.39 (13)	H17B—C17—H17C	109.5
C3—C9—C15	120.60 (13)	O3—C18—H18A	109.5
C3—C9—H9	119.7	O3—C18—H18B	109.5
C15—C9—H9	119.7	H18A—C18—H18B	109.5
C5—C10—H10A	109.5	O3—C18—H18C	109.5
C5—C10—H10B	109.5	H18A—C18—H18C	109.5
H10A—C10—H10B	109.5	H18B—C18—H18C	109.5

O1—P1—O2—C17	−53.42 (16)	O1—P1—O3—C18	−33.54 (16)
O3—P1—O2—C17	71.43 (15)	O2—P1—O3—C18	−159.44 (14)
C5—P1—O2—C17	−177.09 (14)	C5—P1—O3—C18	92.04 (15)
C9—C3—C5—O4	6.74 (17)	C11—C3—C9—C15	1.8 (2)
C11—C3—C5—O4	−173.11 (11)	C5—C3—C9—C15	−178.05 (13)
C9—C3—C5—C10	129.61 (13)	C9—C3—C11—C13	−1.1 (2)
C11—C3—C5—C10	−50.23 (16)	C5—C3—C11—C13	178.70 (12)
C9—C3—C5—P1	−107.20 (13)	C13—C8—N1—O6	168.34 (15)
C11—C3—C5—P1	72.95 (14)	C15—C8—N1—O6	−12.0 (2)
O1—P1—C5—O4	64.33 (10)	C13—C8—N1—O5	−11.3 (2)
O2—P1—C5—O4	−170.16 (8)	C15—C8—N1—O5	168.37 (18)
O3—P1—C5—O4	−62.00 (10)	C15—C8—C13—C11	1.3 (2)
O1—P1—C5—C3	−178.91 (9)	N1—C8—C13—C11	−179.05 (13)
O2—P1—C5—C3	−53.40 (10)	C3—C11—C13—C8	−0.4 (2)
O3—P1—C5—C3	54.76 (10)	C13—C8—C15—C9	−0.6 (2)
O1—P1—C5—C10	−54.94 (11)	N1—C8—C15—C9	179.69 (13)
O2—P1—C5—C10	70.57 (10)	C3—C9—C15—C8	−0.9 (2)
O3—P1—C5—C10	178.73 (9)		

Dimethyl (1-hydroxy-1-phenylethyl)phosphonate (2a)

Crystal data

$C_{10}H_{15}O_4P$
$M_r = 230.19$
Monoclinic, $P2_1/c$
$a = 8.4780\ (3)$ Å
$b = 17.2370\ (6)$ Å
$c = 8.1357\ (3)$ Å
$\beta = 106.484\ (4)°$
$V = 1140.05\ (7)$ Å^3
$Z = 4$

$F(000) = 488$
$D_x = 1.341$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8846 reflections
$\theta = 4.4–32.3°$
$\mu = 0.23$ mm^{-1}
$T = 173$ K
Block, colorless
0.40 × 0.35 × 0.25 mm

Data collection

Agilent Xcalibur Sapphire3 diffractometer
Radiation source: Enhance (Mo) X-ray Source
Detector resolution: 15.9809 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)
$T_{min} = 0.933$, $T_{max} = 1.000$

22954 measured reflections
3450 independent reflections
3080 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 30.5°$, $\theta_{min} = 4.3°$
$h = -12 \rightarrow 12$
$k = -24 \rightarrow 24$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.089$
$S = 1.04$
3450 reflections
150 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2 + 0.2717P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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.
An Xcalibur, Sapphire3 detector equipped diffractometer was used with an Enhance Mo Kα X-ray radiation to collect all the intensity data. The program CrysAlis PRO (CrysAlisPro, Agilent, 2014) was used for data collection, space group determination and all data reduction purposes including empirical absorption correction using spherical harmonics. The initial structure models were provided by direct methods using SHELXT (Sheldrick, 2015a) and refined using full-matrix least-squares on F^2 using SHELXL (Sheldrick, 2015b). All non-H atoms were refined anisotropically.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
P1	0.81342 (3)	0.05200 (2)	0.72375 (3)	0.01989 (8)
O4	0.74312 (9)	0.04889 (5)	1.01317 (9)	0.02685 (16)
O3	0.66366 (9)	0.00078 (4)	0.62661 (10)	0.02942 (17)
O2	0.81828 (10)	0.11643 (4)	0.58901 (9)	0.02953 (17)
C1	0.75367 (11)	0.10611 (5)	0.89008 (11)	0.02041 (17)
C3	0.58302 (11)	0.14067 (5)	0.81672 (12)	0.02116 (17)
C2	0.88556 (13)	0.16627 (7)	0.97005 (14)	0.0311 (2)
H2A	0.8507 (6)	0.1966 (5)	1.0536 (12)	0.047*
H2B	0.9018 (9)	0.2002 (5)	0.8813 (9)	0.047*
H2C	0.9878 (10)	0.1401 (3)	1.0259 (12)	0.047*
C8	0.44531 (12)	0.10121 (6)	0.83454 (13)	0.0263 (2)
H8	0.4588 (2)	0.0529 (7)	0.8961 (9)	0.032*
C7	0.28845 (13)	0.13134 (7)	0.76373 (16)	0.0346 (2)
H7	0.1968 (16)	0.1046 (5)	0.7770 (3)	0.042*
C6	0.26717 (15)	0.20044 (7)	0.67392 (17)	0.0387 (3)
H6	0.1594 (19)	0.2211 (4)	0.6262 (8)	0.046*
C5	0.40312 (16)	0.23950 (7)	0.65363 (16)	0.0375 (3)
H5	0.3892 (3)	0.2861 (8)	0.5917 (11)	0.045*
C4	0.55997 (14)	0.20979 (6)	0.72474 (14)	0.0300 (2)
H4	0.6522 (15)	0.2369 (4)	0.7105 (3)	0.036*
C10	0.64171 (17)	−0.07743 (7)	0.67685 (18)	0.0402 (3)
H10A	0.7407 (11)	−0.1029 (3)	0.7034 (14)	0.060*

H10B	0.5680 (13)	−0.1025 (3)	0.5883 (11)	0.060*
H10C	0.6025 (14)	−0.07680 (7)	0.7709 (14)	0.060*
C9	0.8454 (2)	0.09599 (9)	0.42782 (16)	0.0458 (3)
H9A	0.9519 (13)	0.0810 (7)	0.4456 (3)	0.069*
H9B	0.8243 (14)	0.1378 (5)	0.3565 (10)	0.069*
H9C	0.7773 (13)	0.0563 (6)	0.3793 (9)	0.069*
O1	0.96698 (9)	0.00774 (5)	0.79093 (9)	0.02834 (16)
H1A	0.834 (2)	0.0365 (9)	1.059 (2)	0.034*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.01892 (12)	0.02348 (13)	0.01659 (12)	0.00242 (8)	0.00395 (8)	−0.00086 (7)
O4	0.0205 (3)	0.0382 (4)	0.0223 (3)	0.0058 (3)	0.0068 (3)	0.0099 (3)
O3	0.0266 (3)	0.0256 (4)	0.0292 (4)	0.0006 (3)	−0.0032 (3)	−0.0042 (3)
O2	0.0403 (4)	0.0299 (4)	0.0225 (3)	0.0049 (3)	0.0154 (3)	0.0024 (3)
C1	0.0182 (4)	0.0251 (4)	0.0184 (4)	−0.0002 (3)	0.0060 (3)	−0.0005 (3)
C3	0.0218 (4)	0.0218 (4)	0.0202 (4)	0.0020 (3)	0.0064 (3)	−0.0010 (3)
C2	0.0264 (5)	0.0357 (5)	0.0301 (5)	−0.0071 (4)	0.0061 (4)	−0.0110 (4)
C8	0.0220 (4)	0.0273 (5)	0.0297 (5)	0.0022 (3)	0.0077 (4)	0.0032 (4)
C7	0.0207 (5)	0.0405 (6)	0.0416 (6)	0.0033 (4)	0.0070 (4)	0.0007 (5)
C6	0.0316 (5)	0.0393 (6)	0.0400 (6)	0.0145 (5)	0.0018 (5)	0.0007 (5)
C5	0.0462 (7)	0.0269 (5)	0.0361 (6)	0.0116 (5)	0.0065 (5)	0.0058 (4)
C4	0.0346 (5)	0.0237 (4)	0.0325 (5)	0.0007 (4)	0.0106 (4)	0.0031 (4)
C10	0.0422 (6)	0.0278 (5)	0.0454 (7)	−0.0065 (5)	0.0040 (5)	−0.0034 (5)
C9	0.0717 (9)	0.0474 (7)	0.0268 (5)	0.0092 (6)	0.0277 (6)	0.0031 (5)
O1	0.0212 (3)	0.0388 (4)	0.0240 (3)	0.0085 (3)	0.0048 (3)	−0.0004 (3)

Geometric parameters (Å, º)

P1—O1	1.4738 (7)	C8—C7	1.3911 (14)
P1—O3	1.5641 (8)	C8—H8	0.962 (14)
P1—O2	1.5692 (8)	C7—C6	1.3821 (18)
P1—C1	1.8294 (9)	C7—H7	0.936 (16)
O4—C1	1.4265 (11)	C6—C5	1.385 (2)
O4—H1A	0.787 (16)	C6—H6	0.955 (16)
O3—C10	1.4362 (14)	C5—C4	1.3887 (16)
O2—C9	1.4381 (13)	C5—H5	0.938 (17)
C1—C3	1.5212 (13)	C4—H4	0.946 (15)
C1—C2	1.5284 (13)	C10—H10A	0.917 (10)
C3—C4	1.3910 (14)	C10—H10B	0.917 (10)
C3—C8	1.3938 (13)	C10—H10C	0.917 (10)
C2—H2A	0.968 (9)	C9—H9A	0.910 (11)
C2—H2B	0.968 (9)	C9—H9B	0.910 (11)
C2—H2C	0.968 (9)	C9—H9C	0.910 (11)
O1—P1—O3	113.59 (5)	C3—C8—H8	119.8
O1—P1—O2	115.46 (4)	C6—C7—C8	120.44 (11)

O3—P1—O2	103.00 (4)	C6—C7—H7	119.8
O1—P1—C1	112.98 (4)	C8—C7—H7	119.8
O3—P1—C1	107.82 (4)	C7—C6—C5	119.60 (11)
O2—P1—C1	102.92 (4)	C7—C6—H6	120.2
C1—O4—H1A	105.5 (11)	C5—C6—H6	120.2
C10—O3—P1	122.56 (7)	C6—C5—C4	120.14 (11)
C9—O2—P1	120.42 (8)	C6—C5—H5	119.9
O4—C1—C3	107.70 (7)	C4—C5—H5	119.9
O4—C1—C2	110.75 (8)	C5—C4—C3	120.78 (10)
C3—C1—C2	113.63 (8)	C5—C4—H4	119.6
O4—C1—P1	104.62 (6)	C3—C4—H4	119.6
C3—C1—P1	109.97 (6)	O3—C10—H10A	109.5
C2—C1—P1	109.76 (7)	O3—C10—H10B	109.5
C4—C3—C8	118.68 (9)	H10A—C10—H10B	109.5
C4—C3—C1	121.28 (9)	O3—C10—H10C	109.5
C8—C3—C1	119.97 (8)	H10A—C10—H10C	109.5
C1—C2—H2A	109.5	H10B—C10—H10C	109.5
C1—C2—H2B	109.5	O2—C9—H9A	109.5
H2A—C2—H2B	109.5	O2—C9—H9B	109.5
C1—C2—H2C	109.5	H9A—C9—H9B	109.5
H2A—C2—H2C	109.5	O2—C9—H9C	109.5
H2B—C2—H2C	109.5	H9A—C9—H9C	109.5
C7—C8—C3	120.35 (10)	H9B—C9—H9C	109.5
C7—C8—H8	119.8		

O1—P1—O3—C10	34.73 (11)	O4—C1—C3—C4	164.60 (9)
O2—P1—O3—C10	160.34 (9)	C2—C1—C3—C4	41.53 (12)
C1—P1—O3—C10	−91.28 (10)	P1—C1—C3—C4	−81.95 (10)
O1—P1—O2—C9	62.50 (11)	O4—C1—C3—C8	−18.28 (11)
O3—P1—O2—C9	−61.89 (10)	C2—C1—C3—C8	−141.34 (9)
C1—P1—O2—C9	−173.93 (10)	P1—C1—C3—C8	95.17 (9)
O1—P1—C1—O4	−56.46 (7)	C4—C3—C8—C7	−1.01 (15)
O3—P1—C1—O4	69.91 (6)	C1—C3—C8—C7	−178.21 (9)
O2—P1—C1—O4	178.34 (6)	C3—C8—C7—C6	0.44 (17)
O1—P1—C1—C3	−171.88 (6)	C8—C7—C6—C5	0.42 (19)
O3—P1—C1—C3	−45.51 (7)	C7—C6—C5—C4	−0.70 (19)
O2—P1—C1—C3	62.92 (7)	C6—C5—C4—C3	0.12 (18)
O1—P1—C1—C2	62.41 (8)	C8—C3—C4—C5	0.73 (15)
O3—P1—C1—C2	−171.22 (7)	C1—C3—C4—C5	177.90 (10)
O2—P1—C1—C2	−62.79 (8)		

Dimethyl [(3,4-dimethoxyphenyl)(hydroxy)methyl]phosphonate (1b)

Crystal data

$C_{11}H_{17}O_6P$
$M_r = 276.21$
Monoclinic, $C2/c$
$a = 39.464\ (3)$ Å
$b = 8.5132\ (4)$ Å
$c = 8.0044\ (3)$ Å
$\beta = 100.620\ (5)°$
$V = 2643.2\ (2)$ Å^3
$Z = 8$
$F(000) = 1168$

$D_x = 1.388$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2697 reflections
$\theta = 4.9$–$30.5°$
$\mu = 0.23$ mm^{-1}
$T = 173$ K
Block, colorless
0.30 × 0.20 × 0.05 mm

Data collection

Agilent Xcalibur Sapphire3 diffractometer
Radiation source: Enhance (Mo) X-ray Source
Detector resolution: 15.9809 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)
$T_{\min} = 0.956$, $T_{\max} = 1.000$
13696 measured reflections
4023 independent reflections
2812 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.049$
$\theta_{\max} = 30.5°$, $\theta_{\min} = 4.2°$
$h = -56 \rightarrow 52$
$k = -9 \rightarrow 12$
$l = -8 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.126$
$S = 1.03$
4023 reflections
178 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2 + 1.0539P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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.
An Xcalibur, Sapphire3 detector equipped diffractometer was used with an Enhance Mo Kα X-ray radiation to collect all the intensity data. The program CrysAlis PRO (CrysAlisPro, Agilent, 2014) was used for data collection, space group determination and all data reduction purposes including empirical absorption correction using spherical harmonics. The initial structure models were provided by direct methods using SHELXT (Sheldrick, 2015a) and refined using full-matrix least-squares on F^2 using SHELXL (Sheldrick, 2015b). All non-H atoms were refined anisotropically.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
P1	0.56049 (2)	0.22453 (5)	0.55325 (5)	0.02391 (13)
O5	0.69582 (3)	0.23316 (15)	0.89486 (15)	0.0296 (3)
O3	0.56238 (3)	0.39780 (15)	0.48490 (15)	0.0307 (3)
O2	0.52552 (3)	0.16331 (17)	0.44805 (17)	0.0345 (3)
C1	0.59193 (5)	0.1112 (2)	0.4634 (2)	0.0250 (3)
H1	0.58536 (13)	0.1140 (2)	0.334 (2)	0.030*
O6	0.72468 (3)	0.37616 (17)	0.67767 (17)	0.0361 (3)
C5	0.69270 (5)	0.3178 (2)	0.6143 (2)	0.0263 (4)
C2	0.62749 (4)	0.1814 (2)	0.5161 (2)	0.0240 (3)
O4	0.59076 (4)	−0.04869 (15)	0.51955 (17)	0.0326 (3)

C6	0.67557 (5)	0.3291 (2)	0.4488 (2)	0.0309 (4)
H6	0.6857 (2)	0.3837 (13)	0.3684 (18)	0.037*
C4	0.67689 (5)	0.23697 (19)	0.7345 (2)	0.0235 (3)
C7	0.64311 (5)	0.2601 (2)	0.3991 (2)	0.0280 (4)
H7	0.6329 (3)	0.2664 (3)	0.296 (3)	0.034*
C3	0.64461 (4)	0.1704 (2)	0.6854 (2)	0.0229 (3)
H3	0.6339 (2)	0.1161 (11)	0.7680 (17)	0.028*
C11	0.49302 (6)	0.2215 (3)	0.4808 (3)	0.0526 (6)
H11A	0.4912 (2)	0.200 (2)	0.592 (2)	0.079*
H11B	0.4751 (3)	0.1731 (18)	0.408 (2)	0.079*
H11C	0.4918 (2)	0.3290 (18)	0.463 (2)	0.079*
C10	0.58384 (6)	0.5159 (2)	0.5824 (3)	0.0385 (5)
H10A	0.5758 (3)	0.5353 (13)	0.6871 (17)	0.058*
H10B	0.5827 (3)	0.6118 (15)	0.5174 (11)	0.058*
H10C	0.6074 (3)	0.4793 (9)	0.6075 (16)	0.058*
C9	0.74214 (5)	0.4591 (3)	0.5627 (3)	0.0408 (5)
H9A	0.7451 (4)	0.3913 (11)	0.4715 (17)	0.061*
H9B	0.7642 (4)	0.4929 (17)	0.6217 (10)	0.061*
H9C	0.7288 (3)	0.5483 (16)	0.5184 (17)	0.061*
C8	0.68164 (6)	0.1518 (3)	1.0207 (2)	0.0416 (5)
H8A	0.6591 (4)	0.1996 (13)	1.0309 (14)	0.062*
H8B	0.6977 (3)	0.1593 (16)	1.1319 (16)	0.062*
H8C	0.6782 (4)	0.0395 (16)	0.9877 (11)	0.062*
O1	0.56403 (3)	0.21578 (15)	0.73921 (16)	0.0307 (3)
H1A	0.5808 (6)	−0.101 (3)	0.434 (3)	0.037*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0241 (2)	0.0244 (2)	0.0232 (2)	0.00164 (18)	0.00415 (16)	0.00097 (17)
O5	0.0308 (7)	0.0330 (7)	0.0233 (6)	−0.0076 (6)	0.0009 (5)	0.0031 (5)
O3	0.0371 (7)	0.0265 (6)	0.0277 (6)	0.0023 (6)	0.0042 (5)	0.0041 (5)
O2	0.0236 (6)	0.0410 (8)	0.0383 (7)	−0.0003 (6)	0.0043 (6)	−0.0048 (6)
C1	0.0261 (8)	0.0247 (8)	0.0236 (8)	0.0011 (7)	0.0034 (7)	−0.0020 (6)
O6	0.0300 (7)	0.0413 (8)	0.0373 (7)	−0.0113 (6)	0.0071 (6)	0.0067 (6)
C5	0.0259 (8)	0.0237 (8)	0.0302 (9)	−0.0010 (7)	0.0078 (7)	0.0013 (7)
C2	0.0236 (8)	0.0238 (8)	0.0249 (8)	0.0029 (7)	0.0054 (6)	−0.0031 (6)
O4	0.0377 (8)	0.0238 (6)	0.0343 (7)	−0.0005 (6)	0.0010 (6)	−0.0050 (5)
C6	0.0328 (10)	0.0323 (9)	0.0299 (9)	0.0021 (8)	0.0114 (8)	0.0065 (8)
C4	0.0269 (8)	0.0208 (7)	0.0233 (8)	0.0007 (7)	0.0057 (6)	−0.0004 (6)
C7	0.0282 (9)	0.0344 (10)	0.0216 (8)	0.0045 (8)	0.0049 (7)	0.0015 (7)
C3	0.0248 (8)	0.0214 (7)	0.0237 (8)	0.0006 (7)	0.0075 (7)	−0.0003 (6)
C11	0.0258 (10)	0.0718 (17)	0.0603 (15)	0.0026 (11)	0.0086 (10)	−0.0110 (12)
C10	0.0515 (12)	0.0224 (9)	0.0418 (11)	−0.0006 (9)	0.0089 (10)	−0.0023 (8)
C9	0.0329 (10)	0.0377 (11)	0.0538 (12)	−0.0058 (9)	0.0131 (9)	0.0176 (10)
C8	0.0386 (11)	0.0609 (14)	0.0251 (9)	−0.0103 (10)	0.0053 (8)	0.0068 (9)
O1	0.0356 (7)	0.0311 (7)	0.0267 (6)	0.0046 (6)	0.0088 (5)	0.0039 (5)

Geometric parameters (Å, º)

P1—O1	1.4711 (13)	C6—C7	1.399 (3)
P1—O2	1.5676 (14)	C6—H6	0.94 (2)
P1—O3	1.5797 (13)	C4—C3	1.383 (2)
P1—C1	1.8213 (18)	C7—H7	0.85 (2)
O5—C4	1.362 (2)	C3—H3	0.967 (19)
O5—C8	1.420 (2)	C11—H11A	0.926 (15)
O3—C10	1.447 (2)	C11—H11B	0.926 (15)
O2—C11	1.443 (2)	C11—H11C	0.926 (15)
C1—O4	1.437 (2)	C10—H10A	0.965 (13)
C1—C2	1.512 (2)	C10—H10B	0.965 (13)
C1—H1	1.018 (19)	C10—H10C	0.965 (13)
O6—C5	1.364 (2)	C9—H9A	0.954 (13)
O6—C9	1.433 (2)	C9—H9B	0.954 (14)
C5—C6	1.375 (3)	C9—H9C	0.954 (13)
C5—C4	1.417 (2)	C8—H8A	0.995 (13)
C2—C7	1.385 (2)	C8—H8B	0.995 (13)
C2—C3	1.401 (2)	C8—H8C	0.995 (13)
O4—H1A	0.85 (2)		

O1—P1—O2	115.90 (8)	C2—C7—H7	119.7
O1—P1—O3	113.32 (7)	C6—C7—H7	119.7
O2—P1—O3	102.56 (8)	C4—C3—C2	120.14 (15)
O1—P1—C1	115.36 (8)	C4—C3—H3	119.9
O2—P1—C1	102.01 (8)	C2—C3—H3	119.9
O3—P1—C1	106.20 (8)	O2—C11—H11A	109.5
C4—O5—C8	117.46 (14)	O2—C11—H11B	109.5
C10—O3—P1	121.49 (12)	H11A—C11—H11B	109.5
C11—O2—P1	120.82 (14)	O2—C11—H11C	109.5
O4—C1—C2	111.66 (14)	H11A—C11—H11C	109.5
O4—C1—P1	108.34 (11)	H11B—C11—H11C	109.5
C2—C1—P1	110.16 (11)	O3—C10—H10A	109.5
O4—C1—H1	108.9	O3—C10—H10B	109.5
C2—C1—H1	108.9	H10A—C10—H10B	109.5
P1—C1—H1	108.9	O3—C10—H10C	109.5
C5—O6—C9	117.53 (15)	H10A—C10—H10C	109.5
O6—C5—C6	126.12 (16)	H10B—C10—H10C	109.5
O6—C5—C4	114.67 (16)	O6—C9—H9A	109.5
C6—C5—C4	119.21 (17)	O6—C9—H9B	109.5
C7—C2—C3	119.39 (16)	H9A—C9—H9B	109.5
C7—C2—C1	120.54 (16)	O6—C9—H9C	109.5
C3—C2—C1	120.05 (15)	H9A—C9—H9C	109.5
C1—O4—H1A	106.1 (15)	H9B—C9—H9C	109.5
C5—C6—C7	120.41 (17)	O5—C8—H8A	109.5
C5—C6—H6	119.8	O5—C8—H8B	109.5
C7—C6—H6	119.8	H8A—C8—H8B	109.5
O5—C4—C3	125.08 (15)	O5—C8—H8C	109.5

O5—C4—C5	114.69 (15)	H8A—C8—H8C	109.5
C3—C4—C5	120.23 (16)	H8B—C8—H8C	109.5
C2—C7—C6	120.61 (17)		

O1—P1—O3—C10	33.33 (16)	P1—C1—C2—C3	70.10 (18)
O2—P1—O3—C10	159.02 (14)	O6—C5—C6—C7	178.26 (17)
C1—P1—O3—C10	−94.32 (15)	C4—C5—C6—C7	−0.8 (3)
O1—P1—O2—C11	52.68 (19)	C8—O5—C4—C3	1.3 (3)
O3—P1—O2—C11	−71.31 (18)	C8—O5—C4—C5	−179.03 (17)
C1—P1—O2—C11	178.83 (17)	O6—C5—C4—O5	1.2 (2)
O1—P1—C1—O4	54.60 (14)	C6—C5—C4—O5	−179.60 (16)
O2—P1—C1—O4	−71.91 (13)	O6—C5—C4—C3	−179.11 (15)
O3—P1—C1—O4	−178.97 (11)	C6—C5—C4—C3	0.0 (3)
O1—P1—C1—C2	−67.82 (14)	C3—C2—C7—C6	−0.5 (3)
O2—P1—C1—C2	165.67 (12)	C1—C2—C7—C6	178.12 (16)
O3—P1—C1—C2	58.62 (13)	C5—C6—C7—C2	1.0 (3)
C9—O6—C5—C6	0.8 (3)	O5—C4—C3—C2	−179.91 (16)
C9—O6—C5—C4	179.93 (16)	C5—C4—C3—C2	0.5 (3)
O4—C1—C2—C7	131.07 (17)	C7—C2—C3—C4	−0.3 (3)
P1—C1—C2—C7	−108.49 (16)	C1—C2—C3—C4	−178.88 (15)
O4—C1—C2—C3	−50.3 (2)		

Dimethyl [(hydroxy)(phenyl)methyl]phosphonate (1a)

Crystal data

$C_9H_{13}O_4P$
$M_r = 216.16$
Monoclinic, $P2_1/n$
$a = 8.4039$ (5) Å
$b = 7.7007$ (3) Å
$c = 16.6012$ (7) Å
$\beta = 99.149$ (4)°
$V = 1060.69$ (9) Å^3
$Z = 4$

$F(000) = 456$
$D_x = 1.354$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4166 reflections
$\theta = 4.6$–30.9°
$\mu = 0.25$ mm^{-1}
$T = 173$ K
Block, colorless
0.40 × 0.20 × 0.04 mm

Data collection

Agilent Xcalibur Sapphire3 diffractometer
Radiation source: Enhance (Mo) X-ray Source
Detector resolution: 15.9809 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)
$T_{\min} = 0.846$, $T_{\max} = 1.000$

20344 measured reflections
3209 independent reflections
2491 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.041$
$\theta_{\max} = 30.5°$, $\theta_{\min} = 4.1°$
$h = -12 \rightarrow 12$
$k = -10 \rightarrow 10$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.108$
$S = 1.02$
3209 reflections

139 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 0.2064P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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.
An Xcalibur, Sapphire3 detector equipped diffractometer was used with an Enhance Mo K*α* X-ray radiation to collect all the intensity data. The program CrysAlis PRO (CrysAlisPro, Agilent, 2014) was used for data collection, space group determination and all data reduction purposes including empirical absorption correction using spherical harmonics. The initial structure models were provided by direct methods using SHELXT (Sheldrick, 2015a) and refined using full-matrix least-squares on F^2 using SHELXL (Sheldrick, 2015b). All non-H atoms were refined anisotropically.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
P1	0.88836 (4)	0.22015 (5)	0.36890 (2)	0.02690 (11)
O4	0.69794 (12)	0.26302 (13)	0.23287 (6)	0.0324 (2)
O2	0.74859 (13)	0.27837 (13)	0.41599 (6)	0.0360 (2)
O1	0.90892 (11)	0.03033 (13)	0.36664 (5)	0.0307 (2)
O3	1.03594 (13)	0.32532 (14)	0.41315 (6)	0.0371 (2)
C1	0.85171 (16)	0.32552 (17)	0.26993 (8)	0.0278 (3)
H1	0.8441 (2)	0.451 (2)	0.27822 (17)	0.033*
C2	0.98395 (16)	0.29140 (17)	0.22002 (8)	0.0278 (3)
C3	0.97089 (19)	0.1600 (2)	0.16223 (8)	0.0349 (3)
H3	0.8787 (18)	0.0862 (14)	0.15465 (17)	0.042*
C8	0.6006 (2)	0.1790 (2)	0.40829 (11)	0.0458 (4)
H8A	0.5292	0.2134	0.3583	0.069*
H8B	0.5471	0.2013	0.4556	0.069*
H8C	0.6254	0.0549	0.4058	0.069*
C4	1.0920 (2)	0.1360 (3)	0.11544 (10)	0.0473 (4)
H4	1.0819 (3)	0.047 (2)	0.0756 (9)	0.057*
C7	1.12124 (19)	0.3953 (2)	0.23104 (10)	0.0408 (3)
H7	1.1322 (3)	0.4860 (19)	0.2714 (8)	0.049*
C9	1.1277 (2)	0.2684 (3)	0.48861 (11)	0.0541 (5)
H9A	1.0634 (10)	0.2545 (19)	0.5249 (6)	0.081*
H9B	1.2013 (16)	0.3464 (15)	0.5061 (6)	0.081*
H9C	1.1747 (16)	0.1692 (18)	0.4810 (2)	0.081*
C6	1.2420 (2)	0.3695 (3)	0.18461 (11)	0.0515 (5)
H6	1.333 (2)	0.4388 (17)	0.1927 (2)	0.062*
C5	1.2269 (2)	0.2405 (3)	0.12611 (11)	0.0523 (5)
H5	1.313 (2)	0.2229 (5)	0.0918 (8)	0.063*
H1A	0.653 (3)	0.334 (3)	0.1967 (13)	0.063*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.03003 (18)	0.02395 (17)	0.02590 (17)	−0.00095 (12)	0.00192 (12)	−0.00101 (12)
O4	0.0263 (5)	0.0321 (5)	0.0364 (5)	−0.0014 (4)	−0.0027 (4)	0.0061 (4)
O2	0.0401 (6)	0.0332 (5)	0.0364 (5)	−0.0027 (4)	0.0116 (4)	−0.0085 (4)
O1	0.0361 (5)	0.0253 (5)	0.0297 (5)	0.0015 (4)	0.0020 (4)	0.0011 (4)
O3	0.0405 (6)	0.0364 (5)	0.0310 (5)	−0.0091 (4)	−0.0049 (4)	0.0013 (4)
C1	0.0286 (6)	0.0221 (6)	0.0310 (6)	−0.0013 (5)	−0.0005 (5)	0.0013 (5)
C2	0.0288 (6)	0.0267 (6)	0.0261 (6)	−0.0014 (5)	−0.0010 (5)	0.0071 (5)
C3	0.0392 (8)	0.0368 (7)	0.0285 (6)	−0.0040 (6)	0.0046 (5)	0.0017 (5)
C8	0.0396 (8)	0.0516 (10)	0.0493 (9)	−0.0081 (7)	0.0172 (7)	−0.0115 (7)
C4	0.0526 (10)	0.0572 (11)	0.0341 (8)	0.0033 (8)	0.0129 (7)	0.0006 (7)
C7	0.0357 (8)	0.0413 (8)	0.0434 (8)	−0.0100 (6)	0.0001 (6)	0.0031 (7)
C9	0.0508 (10)	0.0636 (12)	0.0408 (9)	−0.0117 (9)	−0.0145 (8)	0.0096 (8)
C6	0.0335 (8)	0.0672 (12)	0.0531 (10)	−0.0107 (8)	0.0050 (7)	0.0173 (9)
C5	0.0421 (9)	0.0774 (13)	0.0404 (8)	0.0057 (9)	0.0159 (7)	0.0189 (9)

Geometric parameters (Å, º)

P1—O1	1.4731 (10)	C8—H8A	0.9800
P1—O3	1.5633 (10)	C8—H8B	0.9800
P1—O2	1.5760 (11)	C8—H8C	0.9800
P1—C1	1.8144 (14)	C4—C5	1.378 (3)
O4—C1	1.4238 (16)	C4—H4	0.95 (2)
O4—H1A	0.85 (2)	C7—C6	1.383 (2)
O2—C8	1.4485 (19)	C7—H7	0.962 (19)
O3—C9	1.4315 (19)	C9—H9A	0.878 (13)
C1—C2	1.5111 (19)	C9—H9B	0.878 (13)
C1—H1	0.977 (17)	C9—H9C	0.878 (13)
C2—C3	1.386 (2)	C6—C5	1.381 (3)
C2—C7	1.3918 (19)	C6—H6	0.92 (2)
C3—C4	1.388 (2)	C5—H5	1.00 (2)
C3—H3	0.953 (18)		

O1—P1—O3	116.01 (6)	H8A—C8—H8B	109.5
O1—P1—O2	113.24 (6)	O2—C8—H8C	109.5
O3—P1—O2	102.58 (6)	H8A—C8—H8C	109.5
O1—P1—C1	115.11 (6)	H8B—C8—H8C	109.5
O3—P1—C1	101.63 (6)	C5—C4—C3	120.78 (17)
O2—P1—C1	106.82 (6)	C5—C4—H4	119.6
C1—O4—H1A	110.7 (15)	C3—C4—H4	119.6
C8—O2—P1	120.21 (10)	C6—C7—C2	120.72 (16)
C9—O3—P1	121.95 (10)	C6—C7—H7	119.6
O4—C1—C2	113.60 (11)	C2—C7—H7	119.6
O4—C1—P1	104.58 (9)	O3—C9—H9A	109.5
C2—C1—P1	112.65 (9)	O3—C9—H9B	109.5
O4—C1—H1	108.6	H9A—C9—H9B	109.5

C2—C1—H1	108.6	O3—C9—H9C	109.5
P1—C1—H1	108.6	H9A—C9—H9C	109.5
C3—C2—C7	118.89 (14)	H9B—C9—H9C	109.5
C3—C2—C1	121.47 (12)	C5—C6—C7	120.09 (17)
C7—C2—C1	119.63 (13)	C5—C6—H6	120.0
C2—C3—C4	120.01 (15)	C7—C6—H6	120.0
C2—C3—H3	120.0	C4—C5—C6	119.50 (17)
C4—C3—H3	120.0	C4—C5—H5	120.2
O2—C8—H8A	109.5	C6—C5—H5	120.2
O2—C8—H8B	109.5		

O1—P1—O2—C8	−38.37 (13)	O4—C1—C2—C3	−22.67 (17)
O3—P1—O2—C8	−164.16 (12)	P1—C1—C2—C3	96.02 (13)
C1—P1—O2—C8	89.38 (13)	O4—C1—C2—C7	156.34 (12)
O1—P1—O3—C9	−42.43 (15)	P1—C1—C2—C7	−84.97 (14)
O2—P1—O3—C9	81.54 (14)	C7—C2—C3—C4	−1.3 (2)
C1—P1—O3—C9	−168.06 (14)	C1—C2—C3—C4	177.76 (13)
O1—P1—C1—O4	66.37 (10)	C2—C3—C4—C5	0.6 (2)
O3—P1—C1—O4	−167.41 (9)	C3—C2—C7—C6	0.7 (2)
O2—P1—C1—O4	−60.28 (10)	C1—C2—C7—C6	−178.31 (14)
O1—P1—C1—C2	−57.47 (11)	C2—C7—C6—C5	0.5 (3)
O3—P1—C1—C2	68.76 (10)	C3—C4—C5—C6	0.6 (3)
O2—P1—C1—C2	175.88 (9)	C7—C6—C5—C4	−1.1 (3)