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Acidic and anionic forms of 1,3-cyclic dihydroxyacetone phosphate (cDHAP) dimethyl acetal

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The six-membered cyclic phosphate diester, 5,5-dimethoxy-2-hydroxy-1,3,2-dioxaphosphorinan-2-one, $C_5H_{11}O_6P$ or $(MeO)_2$cDHAP, which is the dimethyl acetal of cyclic dihydroxyacetone phosphate (cDHAP), has been obtained in the form of two new cyclohexylammonium (cha) salts, cyclohexylammonium 5,5-dimethoxy-2-oxo-1,3,2-dioxaphosphorinan-2-olate monohydrate, (cha)[$(MeO)_2$cDHAP]·H_2O or $C_6H_{14}N^+\cdot C_5H_{10}O_6P^-\cdot H_2O$, and cyclohexylammonium 5,5-dimethoxy-2-oxo-1,3,2-dioxaphosphorinan-2-olate, (cha)[$(MeO)_2$cDHAP] or $C_6H_{14}N^+\cdot C_5H_{10}O_6P^-$, as well as in the form of the anhydrous free acid, $(MeO)_2$cDHAP. It is shown that protonation of the cyclic phosphate group influences the chair conformation of the P/O/C/C/C/O 1,3,2-dioxaphosphorinane ring, and that differences in the ring conformation correlate with different deformations observed in the ionized and protonated phosphate groups. The ring is more evenly puckered in the anions, in contrast with the flattening observed in the structure of the free acid.

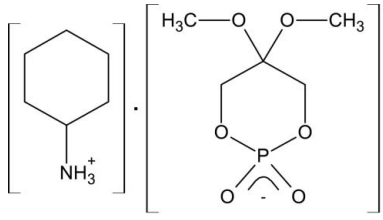
Comment

Six-membered cyclic phosphate esters are constituents of a number of biologically important molecules, such as 3′:5′-cyclic nucleotides, *e.g.* cAMP. Dihydroxyacetone phosphate (DHAP), the linear form of cDHAP, is one of the most important biochemical intermediates and of great importance for all living cells [for a review, see Ślepokura & Lis (2010)]. The cyclic form, cDHAP, has aroused interest recently as a new molecule of biological importance (Goswami & Adak, 2002). Occurring in living organisms, small cyclic phosphates of cDHAP-like structure began to attract attention when their biological activity as signalling molecules was suggested (Shinitzky *et al.*, 2000). Cyclic glycerophosphates can be formed by enzymatic degradation of phospholipids, *e.g.* 1,3-cyclic glycerophosphate is naturally formed by the action of phospholipase C on phosphatidyl glycerol.

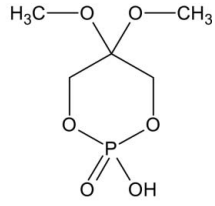
Only five of more than 160 hits for cyclic phosphates with six-membered rings deposited in the Cambridge Structural Database (CSD, Version 5.32; Allen, 2002) bear the H atom at the exocyclic O atom. We will discuss just three of the reported protonated cyclic phosphates [CSD refcodes ETPHOS (Gerlt *et al.*, 1980), KADPUA (Johnson *et al.*, 1989) and SEZRUL (Samas *et al.*, 2007)], because the remaining two have high *R* factors and low bond precision, and the positions of the H atoms were not determined.

Previously, we have reported the synthesis and structural investigations of nine different salts of $(MeO)_2$cDHAP with both organic and inorganic cations [(5*a*)–(5*e*) and (5*e*′)–(5*h*); Ślepokura, 2008], along with its phenyl derivative, $(MeO)_2$cDHAP(Ph) [(4); Ślepokura & Lis, 2004*b*]. Among these, the structures of two cyclohexylammonium (cha) salts and the acid in the form of an oxonium salt were presented: (cha)[$(MeO)_2$cDHAP]·3H_2O, (5*a*), (cha)[$(MeO)_2$cDHAP]·H_2O, (5*b*), and (H_5O_2)[$(MeO)_2$cDHAP], (5*c*).

The present paper concerns the synthesis and crystal structure of 5,5-dimethoxy-2-hydroxy-1,3,2-dioxaphosphorinan-2-one, the dimethyl acetal of cyclic dihydroxyacetone phosphate, $(MeO)_2$cDHAP, in the form of two crystalline cha salts, (cha)[$(MeO)_2$cDHAP]·H_2O, (5*i*) [polymorphous form of (5*b*)], and anhydrous (cha)[$(MeO)_2$cDHAP], (5*j*), as well as in the form of the free acid, $(MeO)_2$cDHAP, (5*k*).



(5*i*) monohydrate
(5*j*) anhydrous



(5*k*)

The overall structures of the $(MeO)_2$cDHAP anions in compounds (5*i*) and (5*j*) bear great similarities with each other and with the previously reported anions in (5*a*)–(5*h*) (Ślepokura, 2008). The six-membered 1,3,2-dioxaphosphorinane ring adopts a chair (*C*) conformation only slightly distorted towards an envelope (*E*), which is reflected in the values of the dihedral angles between the least-squares plane through the four central atoms of the ring (O1/O3/C1/C3) and the O1/P/O3 and C1/C2/C3 planes (φ_1 and φ_2), as well as in the Cremer–Pople puckering parameters (Cremer & Pople, 1975; see Table 1). The values of $|\varphi_2 - \varphi_1|$ for (5*a*), (5*b*), (5*i*) and (5*j*) clearly show that the flattening of the dioxaphosphorinane ring at the P atom is negligible in the $(MeO)_2$cDHAP anions and that the conformation of the rings is close to an ideal chair.

Selected geometric parameters for (5*i*)–(5*k*) are given in Table 2. The deformation of the phosphate group from the ideal tetrahedral shape, which was observed previously in (5*a*)–(5*h*), is also observed in (5*i*) and (5*j*). The deformation of the ionized cyclic phosphate is seen particularly in the endocyclic O1—P1—O3 and exocyclic O4—P1—O5 bond angles, which are, respectively, the smallest [101.73 (11)° on average

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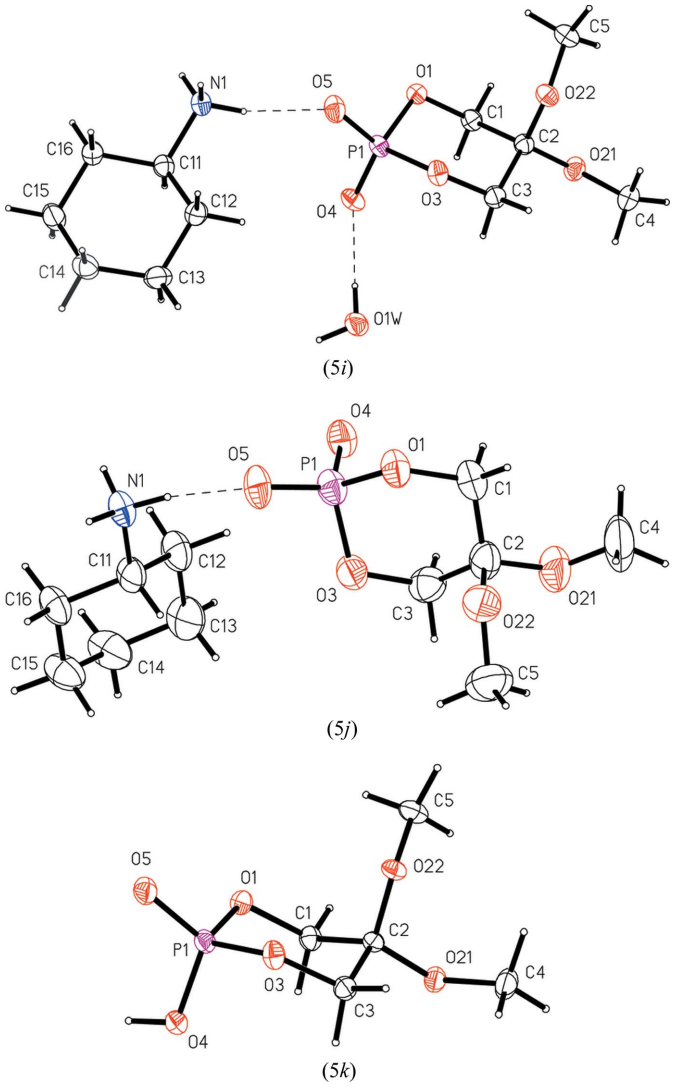


Figure 1
Views of (5*i*) (top), (5*j*) (middle) and (5*k*) (bottom), showing the atom-numbering schemes and the symmetry-independent $N^+—H\cdots O^-$ and $O—H\cdots O^-$ hydrogen bonds (dashed lines). Displacement ellipsoids are drawn at the 50% probability level.

for (5*a*)–(5*j*)] and the largest [119.24 (12)° on average]. The values of the endo- and exocyclic O—P—O angles correlate with the respective P—O bond lengths. In all the known $(MeO)_2$cDHAP anions, the $P—O_{endo}$ bonds are all approximately 1.60 Å and more than 0.1 Å longer than the $P—O_{exo}$ bonds.

A completely different deformation is present in the protonated phosphate group of the $(MeO)_2$cDHAP molecule in (5*k*). The hydroxy group in (5*k*) adopts an axial position similar to the previously reported structures ETPHOS, KADPUA and SEZRUL. As can be seen by the $P—O_{endo}$, P—O(H) and P═O distances (Table 2), the protonation of the phosphate group affects to a larger extent the length of the $P—O_{endo}$ bonds (becoming, on average, 0.03 Å shorter than in the anion) than that of the exocyclic equatorially oriented P1═O5 bond [becoming formally double, but only slightly shortened compared with the $P—O_{exo}$ bonds in the

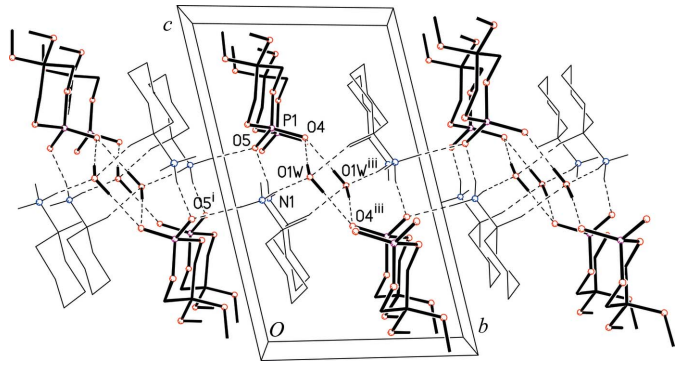
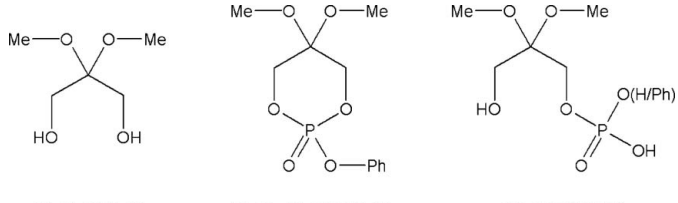


Figure 2
The double layer parallel to the (001) plane in (5*i*), built up from $(MeO)_2$cDHAP anions (solid lines), cha cations (thin lines) and water molecules joined by N—H···O and O—H···O hydrogen bonds and C—H···O contacts (dashed lines). H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $-x$, $-y$, $-z+1$; (iii) $-x+1$, $-y+1$, $-z+1$.]

$(MeO)_2$cDHAP anions]. Within the O—P—O angles in (5*k*), the exocyclic O4—P1—O5 angle is the largest [115.13 (6)°], although none of them is distinctly smaller than the others. Instead, in the protonated phosphate group, three lower values for the angles involving endocyclic O atoms and three higher values for the angles involving P═O bonds are observed. It may be noted that the geometry of the phosphate group in (5*k*) is similar to that observed in the phenyl derivative, (4). These differences in the deformations observed in the ionized and protonated phosphate groups are accompanied by different distortions of the P/O/C/C/C/O rings. In contrast with the almost ideal chair conformation in the $(MeO)_2$cDHAP anions of (5*a*)–(5*j*), the ring in acidic (5*k*) is significantly flattened at the P atom (see Table 1), which is comparable with the conformations observed in phenyl derivative (4) and the acidic cyclic phosphates ETPHOS and SEZRUL.



$(MeO)_2$DHA (3) $(MeO)_2$cDHAP(Ph) (4) $(MeO)_2$DHAP (6) $(MeO)_2$DHAP(Ph) (6*e*)

It has been shown that the acetal group in the analogous linear compounds, different salts of $(MeO)_2$DHAP and $(MeO)_2$DHAP(Ph) [(6*a*)–(6*e*); Ślepokura & Lis, 2006], and in the unphosphorylated species $(MeO)_2$DHA [(3); Ślepokura & Lis, 2004*a*] seems to be very rigid, and its conformation is independent of phosphorylation, the ionization state of the inserted phosphate group, or additional substitution. It is likely that such a conformation is determined and stabilized by the generalized anomeric effect. The acetal group in the cyclic compounds (5*i*)–(5*k*), as in (4) and (5*a*)–(5*h*), reveals some

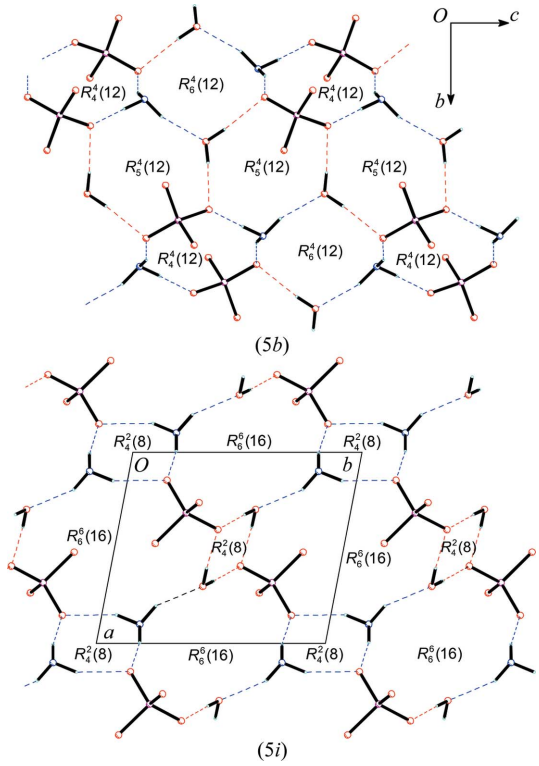


Figure 3
A comparison of the layer constructions observed in two polymorphous forms of (cha)[$(MeO)_2$cDHAP]·H_2O, *viz.* monoclinic (5*b*) (top; Ślepokura, 2008) and triclinic (5*i*) (bottom; this work). Phosphate and ammonium groups represent the anions and cations, respectively. N^+—H···O^-/O*W* and O*W*—H···O^- hydrogen bonds are shown as dashed lines (blue and red, respectively, in the electronic version of the paper).

common features with linear (3) and (6*a*)–(6*e*) (see scheme above): the relevant C4—O21—C2—O22 and C5—O22—C2—O21 torsion angles show a synclinal orientation of the methyl groups (C4 and C5) in relation to the acetal atoms O22 and O21. Similarly, as was observed in the structures of (3), (4), (5*a*)–(5*h*) and (6*a*)–(6*e*), two of the angles with their vertex on acetal atom C2 are much smaller than the others (Table 2).

The cations and anions in (5*i*) and (5*j*) are arranged in a way that leads to the aggregation of their hydrophilic and hydrophobic groups into distinct regions in the crystals. The packing schemes of (5*i*) and (5*j*) are dominated by N^+—H···O^- hydrogen bonds, but in the hydrated salt (5*i*), as in (5*a*) and (5*b*) (Ślepokura, 2008), an additional important role is played by contacts of the N^+—H···O*W* and O*W*—H···O^- type (O*W* is the water O atom). Geometric parameters of hydrogen bonds and close contacts are given in Table 3.

The crystal structure of the monohydrated salt (5*i*) has a layered architecture (Fig. 2), similar to that observed in the other hydrated cha salts, (5*a*) and (5*b*). Each cha cation is directly linked by two charge–assisted N—H···O hydrogen bonds to two adjacent $(MeO)_2$cDHAP anions, resulting in centrosymmetric $R_4^2(8)$ motifs (Fig. 3) [see Bernstein *et al.* (1995) for graph-set notation]. The same cation is linked to two additional anions *via* water-mediated hydrogen bonds. Thus, another type of ring is formed, $R_6^6(16)$, this time also

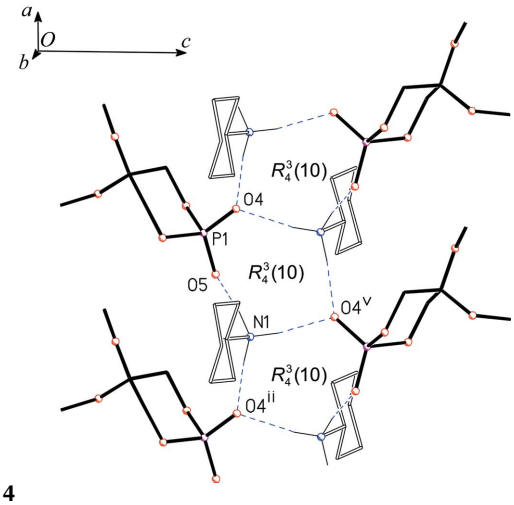


Figure 4
The polymeric ribbons with ladder-type hydrogen bonding formed in (5*j*) by the $(MeO)_2$cDHAP anions (solid lines) and cha cations (open lines) along the *a* axis. N^+—H···O^- hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (ii) $x-1, y, z$; (v) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$.]

involving water molecules in addition to cha cations and $(MeO)_2$cDHAP anions. Another $R_4^2(8)$ ring results from the centrosymmetric O*W*—H···O^- bonds between two water molecules and two anions. The sequence of these three rings generates double layers parallel to the (001) plane, as shown in Figs. 2 and 3. The same types of interaction, namely cation···anion, cation···H_2O···anion and anion···H_2O··· anion, were also observed in the polymorphous salt (5*b*). However, as shown in Fig. 3, the construction of the layers observed in (5*b*) is different: three unique rings generate the layer, $R_4^4(12)$ involving two cations and two anions, $R_5^4(12)$ involving one cation, two anions and two water molecules, and $R_6^4(12)$ involving two cations, two anions and two water molecules.

The arrangement of organic ions in the crystal structure of the anhydrous salt (5*j*) is different. Each cha cation is linked directly by three N^+—H···O^- hydrogen bonds to three adjacent $(MeO)_2$cDHAP anions. These interactions generate $R_4^3(10)$ rings forming ribbons with ladder-type hydrogen bonding along the *a* axis, as shown in Fig. 4.

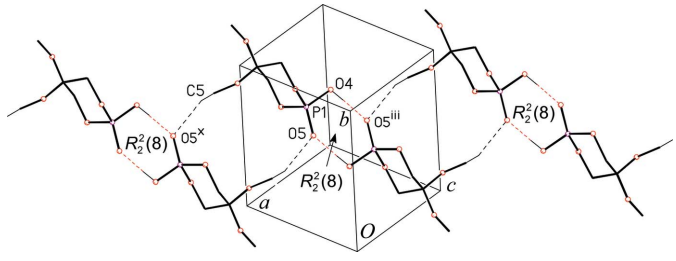


Figure 5
The ribbons in (5*k*) resulting from centrosymmetric molecular dimers [with $R_2^2(8)$ rings formed by the $(MeO)_2$cDHAP molecules joined *via* strong O—H···O hydrogen bonds; dashed lines (red in the electronic version of the paper)] linked through C—H···O contacts (black dashed lines). H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (iii) $-x+1, -y+1, -z+1$; (x) $-x+2, -y+1, -z$.]

The crystal packing of (5*k*) is determined by the strong centrosymmetric almost linear O—H···O hydrogen bonds formed by the phosphate groups of two adjacent $(MeO)_2$-cDHAP molecules. In this way, centrosymmetric molecular dimers are formed (Fig. 5), giving rise to $R_2^2(8)$ rings. Adjacent dimers interact with each other *via* weak C—H···O contacts, as shown in Fig. 5, resulting in ribbons along $[10\bar{1}]$.

In conclusion, we have shown that protonation of the cyclic phosphate group influences the conformation of the 1,3,2-dioxaphosphorinane ring, causing its flattening, *i.e.* deformation from the ideal chair towards an envelope. In other words, the ring is more evenly puckered in compounds with an ionized phosphate group than in the acid molecule. We have also demonstrated that differences in the ring conformation correlate with different deformations observed in the ionized and protonated phosphate groups. Some common features for analogous protonated and esterified compounds have been revealed. In addition, we have shown that the arrangement of the ions in the crystal structures of four different (cha)-[$(MeO)_2$cDHAP] salts results in different crystal architectures, depending on water content, and gives rise to layers in hydrated (5*a*), (5*b*) and (5*i*) and to ribbons in anhydrous (5*j*).

Experimental

The cyclohexylammonium salt of $(MeO)_2$cDHAP was obtained by isolation of an intermediate in the basic hydrolysis of the cyclic triester derivative, using a method described previously (Ślepokura, 2008). Excess cyclohexylamine was removed by washing the crude product with diethyl ether. Concentration of the resulting mixture under vacuum and then under a nitrogen stream at room temperature gave two kinds of crystals, *viz.* small plates of (5*j*) and needles of the monohydrated monoclinic form described previously, (5*b*). Recrystallization of (5*b*) from water at room temperature resulted in large plates of its triclinic form, (5*i*).

Crystals of $(MeO)_2$cDHAP, (5*k*), were grown from an acidic solution prepared as follows. The cyclohexylammonium salt of $(MeO)_2$cDHAP (250 mg dissolved in a minimum quantity of water) was passed through an ion-exchange column (Dowex 50-H^+). The acidic solution was stirred at 313 K for 3.5 h. Subsequent evaporation of the solvent under a nitrogen stream yielded large blocks of (5*k*).

Table 1
Values of φ_1 and φ_2, and the Cremer–Pople puckering parameters Q, θ and φ for the P/O1/C1/C2/C3/O3 rings in the $(MeO)_2$cDHAP anions in (5*i*) and (5*j*) and in the molecule of (5*k*), along with the relevant values for the previously reported compounds (4), (5*a*) and (5*b*).

Compound	φ_1 (°)	φ_2 (°)	$\lvert\varphi_2-\varphi_1\rvert$ (°)	Q (Å)	θ (°)	φ (°)
(5*i*)	46.9 (1)	52.4 (1)	5.5	0.580 (1)	176.4 (1)	280 (2)
(5*j*)	47.4 (2)	48.0 (3)	0.6	0.558 (2)	176.0 (2)	189 (4)
(5*k*)	40.4 (1)	53.0 (1)	12.6	0.541 (1)	171.1 (1)	342 (1)
(5*a*)[a]	47.3 (1)	50.8 (1)	3.6	0.573 (1)	178.4 (1)	234 (4)
(5*b*)[a]	48.2 (1)	50.3 (1)	2.1	0.577 (1)	177.5 (1)	199 (2)
(4)[b]	35.9 (1)	51.8 (2)	15.9	0.514 (2)	167.5 (2)	349 (1)

References: (*a*) Ślepokura (2008) {(5*a*) is (cha)[$(MeO)_2$cDHAP]·3H_2O and (5*b*) is monoclinic (cha)[$(MeO)_2$cDHAP]·H_2O}; (*b*) Ślepokura & Lis (2004*b*) [(4) is $(MeO)_2$cDHAP(Ph)].

Compound (5*i*)

Crystal data

$C_6H_{14}N^+\cdot C_5H_{10}O_6P^-\cdot H_2O$
M_r = 315.30
Triclinic, $P\bar{1}$
a = 7.064 (2) Å
b = 8.475 (4) Å
c = 13.966 (6) Å
α = 102.48 (3)°
β = 92.58 (3)°
γ = 99.96 (3)°
V = 801.1 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.20 mm^{-1}
T = 100 K
0.37 × 0.23 × 0.04 mm

Data collection

Kuma KM-4 CCD κ-geometry diffractometer with a Sapphire CCD camera
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)
T_{min} = 0.913, T_{max} = 1.000
13552 measured reflections
4519 independent reflections
3579 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.094
S = 1.03
4519 reflections
190 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Compound (5*j*)

Crystal data

$C_6H_{14}N^+\cdot C_5H_{10}O_6P^-$
M_r = 297.28
Orthorhombic, $P2_12_12_1$
a = 6.678 (2) Å
b = 8.877 (2) Å
c = 24.930 (6) Å
V = 1477.9 (7) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 1.86 mm^{-1}
T = 120 K
0.13 × 0.08 × 0.01 mm

Data collection

Oxford Diffraction Xcalibur PX κ-geometry diffractometer with an Onyx CCD camera
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2009)
T_{min} = 0.832, T_{max} = 0.978
11210 measured reflections
2803 independent reflections
1876 reflections with $I > 2\sigma(I)$
R_{int} = 0.062

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.060
S = 1.02
2803 reflections
175 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Absolute structure: Flack (1983), with 988 Friedel pairs
Flack parameter: −0.03 (3)

Compound (5*k*)

Crystal data

$C_5H_{11}O_6P$
M_r = 198.11
Triclinic, $P\bar{1}$
a = 6.859 (2) Å
b = 7.114 (3) Å
c = 8.939 (3) Å
α = 89.13 (3)°
β = 76.00 (3)°
γ = 81.18 (3)°
V = 418.1 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.32 mm^{-1}
T = 100 K
0.41 × 0.22 × 0.06 mm

Table 2
Selected geometric parameters (Å, °) for (5*i*)–(5*k*).

	(5*i*)	(5*j*)	(5*k*)
P1—O1	1.6061 (10)	1.5929 (18)	1.5721 (10)
P1—O3	1.6004 (10)	1.6013 (18)	1.5614 (11)
P1—O4	1.4866 (10)	1.4846 (18)	1.5453 (11)
P1—O5	1.4784 (11)	1.4753 (18)	1.4727 (10)
O1—C1	1.4343 (14)	1.445 (3)	1.4488 (14)
O21—C2	1.4118 (13)	1.415 (3)	1.4071 (14)
O21—C4	1.4328 (15)	1.436 (4)	1.4304 (16)
O22—C2	1.4080 (13)	1.417 (3)	1.3999 (13)
O22—C5	1.4229 (15)	1.431 (3)	1.4319 (14)
O3—C3	1.4304 (14)	1.425 (3)	1.4543 (15)
C1—C2	1.5270 (15)	1.510 (4)	1.5253 (16)
C2—C3	1.5297 (16)	1.515 (4)	1.5267 (16)
O1—P1—O3	102.13 (5)	101.74 (10)	105.77 (5)
O1—P1—O4	109.24 (5)	109.49 (9)	107.67 (6)
O1—P1—O5	107.69 (5)	109.15 (10)	110.23 (6)
O3—P1—O4	109.74 (5)	109.33 (10)	105.76 (6)
O3—P1—O5	106.58 (6)	108.30 (11)	111.75 (6)
O4—P1—O5	119.97 (5)	117.64 (11)	115.13 (6)
P1—O1—C1	114.57 (7)	115.64 (17)	116.69 (7)
C2—O21—C4	114.41 (9)	114.8 (3)	116.04 (9)
C2—O22—C5	115.66 (9)	115.2 (2)	115.71 (9)
P1—O3—C3	116.69 (7)	115.64 (17)	118.21 (7)
O1—C1—C2	109.64 (9)	111.5 (2)	109.72 (9)
O21—C2—O22	111.81 (9)	111.8 (2)	113.39 (9)
O21—C2—C1	104.21 (9)	111.8 (2)	102.94 (9)
O22—C2—C1	113.65 (9)	105.7 (3)	113.94 (9)
O21—C2—C3	112.14 (9)	103.7 (2)	111.50 (9)
O22—C2—C3	105.01 (9)	112.7 (2)	104.92 (9)
C1—C2—C3	110.21 (9)	111.3 (2)	110.33 (10)
O3—C3—C2	110.72 (9)	112.2 (2)	110.28 (9)
O3—P1—O1—C1	55.31 (8)	54.88 (18)	47.93 (9)
O4—P1—O1—C1	−60.85 (8)	−60.73 (19)	−64.78 (9)
O5—P1—O1—C1	167.33 (7)	169.19 (17)	168.89 (7)
O1—P1—O3—C3	−52.80 (8)	−54.61 (19)	−45.92 (9)
O4—P1—O3—C3	63.00 (9)	61.1 (2)	68.13 (9)
O5—P1—O3—C3	−165.65 (7)	−169.55 (18)	−165.89 (7)
P1—O1—C1—C2	−62.20 (9)	−58.2 (3)	−57.28 (11)
P1—O3—C3—C2	56.68 (10)	57.6 (3)	53.06 (11)
C4—O21—C2—O22	60.27 (12)	−63.4 (3)	50.07 (12)
C4—O21—C2—C1	−176.57 (8)	54.9 (4)	173.64 (9)
C4—O21—C2—C3	−57.38 (12)	174.9 (3)	−68.09 (13)
C5—O22—C2—O21	67.92 (11)	−60.9 (3)	65.74 (12)
C5—O22—C2—C1	−49.72 (12)	177.2 (2)	−51.58 (13)
C5—O22—C2—C3	−170.24 (9)	55.4 (3)	−172.36 (9)
O1—C1—C2—O21	179.58 (7)	168.6 (2)	178.45 (8)
O1—C1—C2—O22	−58.46 (11)	−69.6 (3)	−58.34 (12)
O1—C1—C2—C3	59.08 (11)	53.1 (3)	59.37 (11)
O21—C2—C3—O3	−171.66 (8)	−173.6 (2)	−170.68 (8)
O22—C2—C3—O3	66.71 (11)	65.3 (3)	66.19 (11)
C1—C2—C3—O3	−56.06 (11)	−53.2 (3)	−56.94 (12)

Table 3
Hydrogen-bond geometry (Å, °) for (5*i*)–(5*k*).

Compound	*D*—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
(5*i*)	N1—H1N···O5	0.91	1.87	2.758 (2)	166
	N1—H2N···O5^{i}	0.91	1.96	2.817 (2)	157
	N1—H3N···O1*W*^{ii}	0.91	1.87	2.719 (2)	154
	O1*W*—H1*W*···O4	0.83 (2)	1.92 (2)	2.749 (2)	176 (2)
	O1*W*—H2*W*···O4^{iii}	0.83 (2)	1.93 (2)	2.758 (2)	176 (2)
	C4—H4*A*···O1^{iv}	0.98	2.60	3.534 (2)	159
	C11—H11···O1*W*^{iii}	1.00	2.52	3.416 (2)	149
(5*j*)	N1—H1N···O5	0.91	1.81	2.718 (3)	172
	N1—H2N···O4^{ii}	0.91	1.90	2.809 (3)	174
	N1—H3N···O4^{v}	0.91	1.90	2.799 (3)	169
	C3—H3*B*···O22^{vi}	0.99	2.60	3.495 (3)	150
	C14—H14*A*···O5^{vii}	0.99	2.50	3.396 (3)	150
(5*k*)	O4—H4···O5^{iii}	0.84	1.70	2.533 (2)	175
	C1—H1*A*···O21^{viii}	0.99	2.57	3.544 (2)	169
	C3—H3*B*···O22^{ix}	0.99	2.61	3.560 (2)	161
	C5—H5*B*···O5^{x}	0.98	2.49	3.423 (2)	159

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

Data collection

Kuma KM-4 CCD κ-geometry diffractometer with a Sapphire CCD camera
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)
T_{min} = 0.970, T_{max} = 1.000
5919 measured reflections
2274 independent reflections
1985 reflections with $I > 2\sigma(I)$
R_{int} = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.086
S = 1.08
2274 reflections
112 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

All H atoms were found in difference Fourier maps. In the final refinement cycles, water H atoms in (5*i*) were refined with U_{iso}(H) = 1.5U_{eq}(O). All remaining H atoms were treated as riding atoms in geometrically optimized positions, with C—H = 0.98–1.00 Å, N—H = 0.91 Å and O—H = 0.84 Å, and with U_{iso}(H) = 1.2U_{eq}(C) for CH and CH_2, or 1.5U_{eq}(C,N,O) for CH_3, NH_3 and OH.

For all compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Bruker, 1998); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MX3045). Services for accessing these data are described at the back of the journal.

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