

Dimorphism in 4,4,6,6-tetrachloro-2,2-(2,2-dimethylpropane-1,3-dioxy)-cyclotriphosphazene and 6,6-dichloro-2,2:4,4-bis(2,2-dimethylpropane-1,3-dioxy)cyclotriphosphazene

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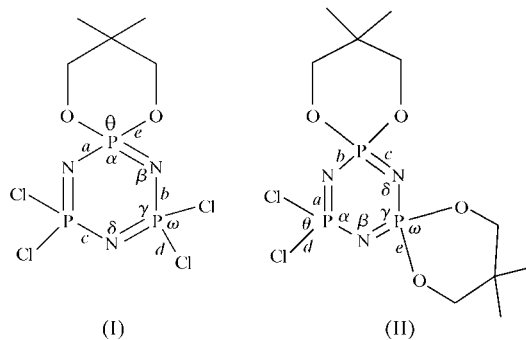
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A second, polymorphic, form of the previously reported compound 4,4,6,6-tetrachloro-2,2-(2,2-dimethylpropane-1,3-dioxy)cyclotriphosphazene, C₅H₁₀Cl₄N₃O₂P₃, is now reported. The molecular structures of these two compounds are similar, aside from minor conformational differences. However, the compounds crystallize in two different space groups and exhibit quite different crystal structure assemblies. Additionally, 6,6-dichloro-2,2:4,4-bis(2,2-dimethylpropane-1,3-dioxy)-cyclotriphosphazene, C₁₀H₂₀Cl₂N₃O₄P₃, is shown to exhibit two different conformational polymorphs when crystallized from different solvent mixtures. The α form crystallizes in the space group *Pnma* with the molecular structure lying on a mirror plane (symmetry code: $x, -y + \frac{1}{2}, z$), whilst the β form is in the space group *C2/c* with the molecular structure lying on a twofold axis (symmetry code: $-x, y, -z + \frac{3}{2}$). The difference between the two molecular structures is in the conformation of the spiro-ring substituents with respect to the phosphazene ring. The resulting crystal structures give rise to differing packing motifs.

Comment

The reaction of hexachlorocyclotriphosphazene, N₃P₃Cl₆, with 2,2-dimethylpropane-1,3-diol in tetrahydrofuran (THF) gives a mixture of the known mono-spiro compound 4,4,6,6-tetrachloro-2,2-(2,2-dimethylpropane-1,3-dioxy)cyclotriphosphazene and the known dispiro compound 6,6-dichloro-2,2:4,4-bis(2,2-dimethylpropane-1,3-dioxy)cyclotriphosphazene *via* a different synthetic route from that in the literature (Al-Madfa *et al.*, 1990).

The crystal structure of 4,4,6,6-tetrachloro-2,2-(2,2-dimethylpropane-1,3-dioxy)cyclotriphosphazene has previously



been determined and reported (Satish Kumar & Kumara Swamy, 2001) and is available in the Cambridge Structural Database (refcode MEVVEO; Allen, 2002). The present paper reports a new crystal structure of this compound, (I) (Fig. 1), arising from different crystallization conditions, *viz.* MEVVEO was crystallized from dichloromethane–hexane (1:4) and (I) from THF–*n*-hexane (1:6). Whilst the molecular connectivities of the two structures are identical, the crystal packing differs somewhat, as do some other parameters. The melting point measured for (I) is 430–431 K and is identical to that reported for MEVVEO (427–428 K).

MEVVEO crystallizes in the space group *P2₁/n*, whilst (I) is in *P1̄*. The phosphazene N₃P₃ ring is nearly planar [the maximum deviation from the mean ring plane in (I) is 0.061 Å for atom N3]. Neither structure exhibits any classical hydrogen bonding, but an inspection of the close contacts (*i.e.* the closest non-bonded separations in the solid state that are less than the sum of the van der Waals radii) reveals the differences between the two.

MEVVEO only forms one close contact, between a bridge-head methyl H atom and an O atom in the 1,3,2-dioxaphosphorinane ring [C4–H5...O1ⁱ = 2.530 Å; symmetry

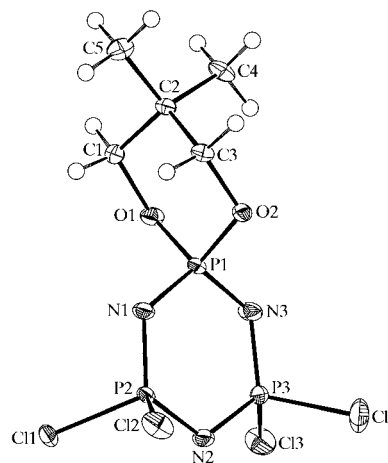


Figure 1
A view of the molecule of (I), shown with 50% probability displacement ellipsoids.

code: (i) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$], which gives rise to a two-dimensional ribbon-like motif (Fig. 2). The polymorph reported here forms a slightly more complex crystal structure, again a two-dimensional ribbon-like motif. This motif arises from an alternation of head-to-tail interactions between Cl atoms [Cl1 \cdots Cl3ⁱⁱ = 3.433 (7) Å; symmetry code: (ii) $-x, 2 - y, -z$] and between a different Cl atom and an O atom in the 1,3,2-dioxaphosphorinane ring [Cl4 \cdots O2ⁱⁱⁱ = 3.1051 (12) Å; symmetry code: (iii) $-x, 1 - y, 1 - z$; Fig. 3].

To highlight similarities and contrasts between these two polymorphic structures some equivalent bond lengths and angles are tabulated in Table 1. These show remarkable similarities. Crucially, the parameter $\Delta(\text{P}-\text{N})$ [for definition, see Bešli *et al.* (2002)], a measure of the electron-releasing power of the spiro group, is gratifyingly virtually the same. We can see, however, significant differences in the torsion angles of these two structures (Table 2). This shows clearly that, whilst both spiro rings are in a chair conformation, the spiro ring in (I) is much more distorted than that in MEVVEO. The differences in the chemically related segments of the spiro group are vastly greater in (I) than in MEVVEO.

We now also report the new crystal structure and polymorphic behaviour of the dispiro compound (II) when crystallized from different solvent mixtures. The α form results from crystallization with THF-*n*-hexane (1:6), whilst the β form arises from crystallization with THF-*n*-hexane-dichloromethane (1:6:5).

The molecular structures of the α and β forms exhibit the same connectivities and geometric parameters and are in

accordance with those expected (Chandrasekhar & Thomas, 1993). The phosphazene rings in both structures are planar as a result of crystallographic symmetry and the main molecular geometric parameters are given in Table 5. These are very similar, except that θ , the bond angle of the Cl-P-Cl group, is somewhat larger in the β form [101.38 (3)°] than in the α form [99.85 (3)°], whilst the reverse is the case for $\Delta(\text{P}-\text{N})$ (defined as $b - a$; 0.0220 *versus* 0.0122 Å), which is a measure of the transfer of the electron-density from the spiro groups towards the PCl₂ group.

The 1,3,2-dioxaphosphorinane rings adopt chair conformations in both structures. However, when viewed perpendi-

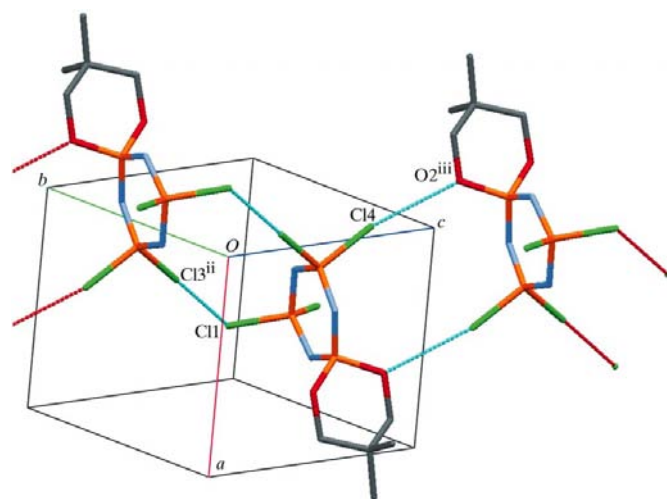


Figure 3

The crystal structure of (I). [Symmetry codes: (ii) $-x, 2 - y, -z$; (iii) $-x, 1 - y, 1 - z$.]

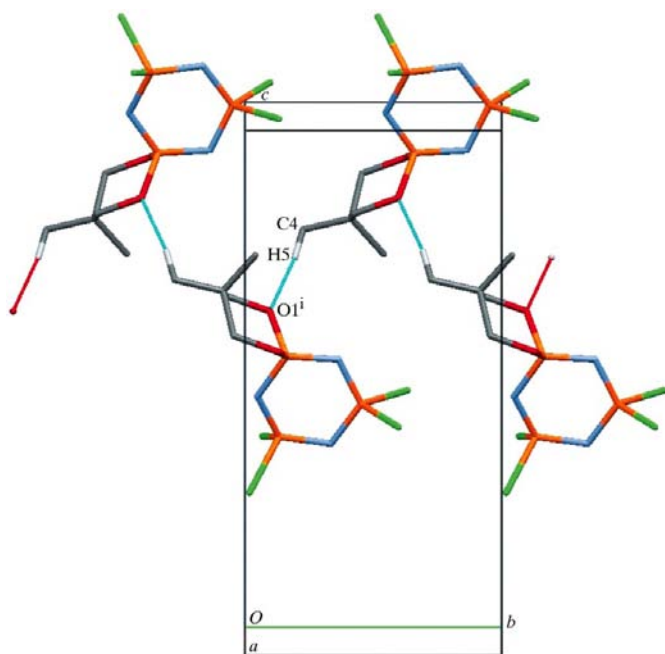


Figure 2

The crystal structure of MEVVEO. [Symmetry code: (i) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$.]

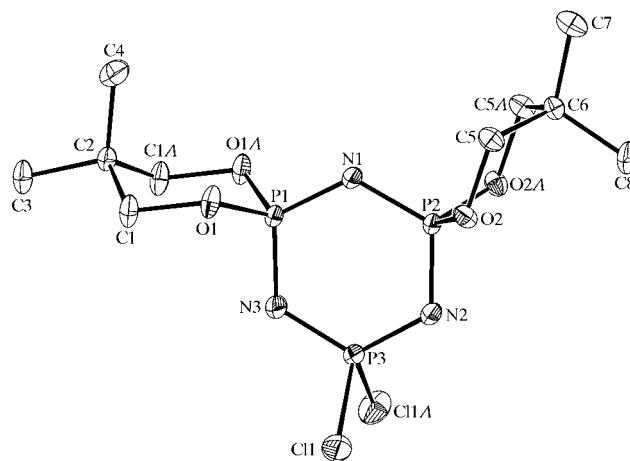


Figure 4

A view of the molecule of the α form of (II), shown with 50% probability displacement ellipsoids.

cular to the phosphazene ring (Figs. 4 and 5), it can be seen that there are differences in the molecular structure in that the 1,3,2-dioxaphosphorinane rings can adopt different conformations with respect to the N_3P_3 ring. This conformation may be simply described as either 'up' or 'down', where in the α form the ring attached to atom P1 is 'down' and that attached to P2 is 'up', whilst both rings in the β form may be described as 'up'. Quantitatively, this can be described by the dihedral angle between a plane perpendicularly bisecting the phosphazene ring (as defined by the N, P and Cl atoms) and a plane

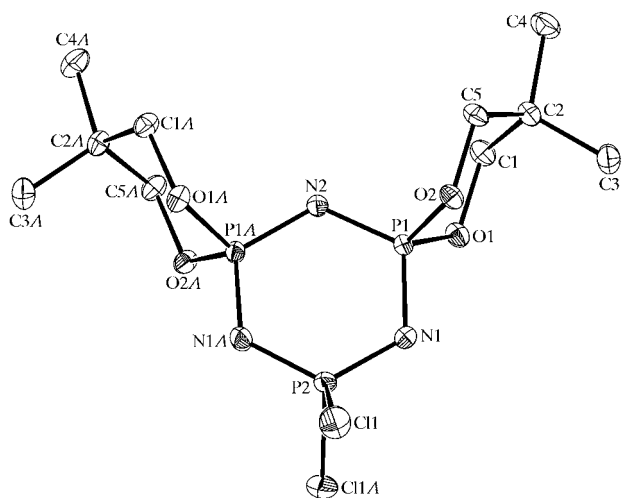


Figure 5
A view of the molecule of the β form of (II), shown with 50% probability displacement ellipsoids.

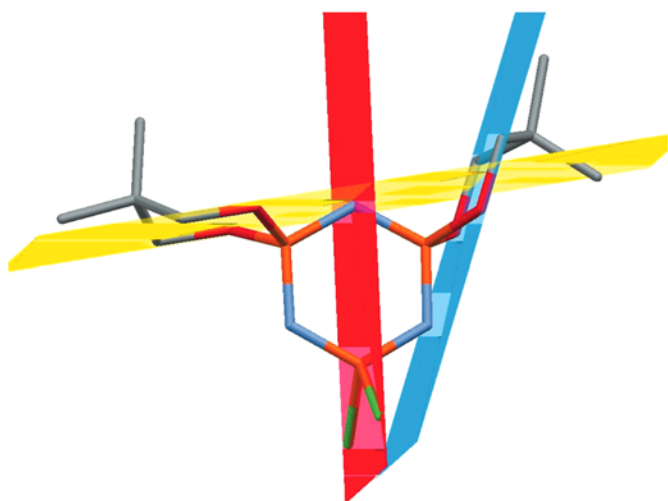


Figure 6
A description of the planes used in calculating the relative conformation of the dioxaphosphorinane rings. The rings are defined by the inclined ('up' conformation) and near horizontal ('down' conformation) planes and their conformation calculated relative to the $N \cdots PCl_2$ plane (the near vertical band).

formed by the O atom and connected C atoms of the dioxaphosphorinane ring, as shown in Fig. 6. In the α form, the 'down' conformation has a value of $70.67(6)^\circ$, whilst the 'up' conformation has the value $23.47(5)^\circ$. In the β form, as a result of crystallographic symmetry, both rings are in the 'up' configuration and have a value of $19.58(4)^\circ$. As with the pair of polymorphs of the related monospiro derivative, $N_3P_3Cl_4[(OCH_2)_2CMe_2]$, we have analysed the torsion angles of the spiro substituents of both polymorphs (Tables 3 and 4). As in the case of the monospiro derivatives, there are differences between these two polymorphs, but here they are less marked.

The compound crystallizes with a rod morphology in the space group $Pnma$ and a block morphology in the space group $C2/c$ for the α and β forms, respectively. The melting point of both forms is 484–485 K.

There are no classical intermolecular hydrogen bonds present in either structure and hence the differences in the crystal structure assemblies is influenced by close packing considerations. Figs. 7 and 8 depict projections down the unit-

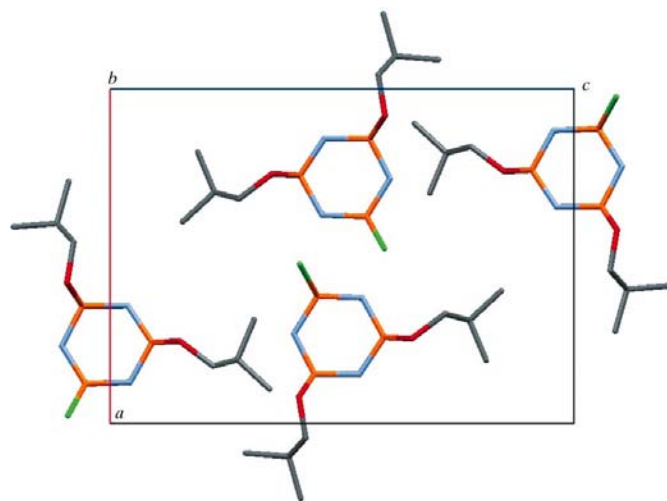


Figure 7
A projection down the b axis of the close packing of the α form of (II).

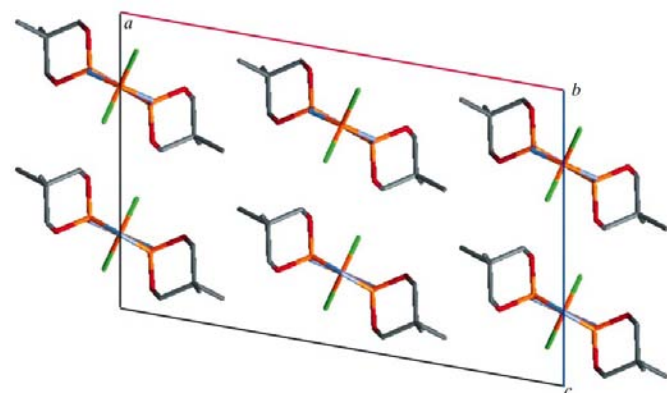


Figure 8
A projection down the b axis of the close packing of the β form of (II).

cell *b* axis of the α and β forms, respectively. This clearly shows that the symmetric nature of the molecular structure of the β form allows for correspondingly symmetric packing and hence the molecules align in sheet-like motifs, which then stack on top of each other. The crystal structure of the α form is also composed of stacked sheets; however, its asymmetric molecular structure gives rise to less symmetric packing than that of the β form. Despite this observation, the percentages of space occupied in the unit cell (Spek, 2003; Kitaigorodski, 1973) are 66 and 66.6% for α and β forms, respectively, and hence the packing efficiencies are effectively equal.

Experimental

A solution of $\text{N}_3\text{P}_3\text{Cl}_6$ (9 g, 25.86 mmol) in dry THF (25 ml) was added dropwise to a stirred solution of pyridine (8.2 g, 103.66 mmol) in dry THF (5 ml) under argon pressure in a 100 ml three-necked round-bottomed flask, and then 2,2-dimethylpropane-1,3-diol (5.4 g, 51.84 mmol) in dry THF (30 ml) was added. The reaction mixture was stirred under an atmosphere of argon at room temperature for a further 21 h and then refluxed for 2 h. Pyridine hydrochloride was filtered off and the solvent removed under reduced pressure at 303 K. Two compounds were detected ($R_F = 0.52$ and 0.25) by thin-layer chromatography using THF-*n*-hexane (1:6) as the mobile phase. The crude product was subjected to column chromatography using THF-*n*-hexane (1:6) as eluant. Compound (I) (1.5 g, yield 15.36%) was separated ($R_F = 0.52$) and crystallized from THF-*n*-hexane (1:6). Analysis found: C 15.03, H 2.78, N 10.95%; $(M + H)^+ = 378$; $\text{C}_5\text{H}_{10}\text{Cl}_4\text{N}_3\text{O}_2\text{P}_3$ requires: C 15.85, H 2.66, N 11.09%; $M^+ = 377$. The second fraction ($R_F = 0.25$) gave the dispiro compound (II). Analysis found: C 29.10, H 5.01, N 10.13%; $(M + H)^+ = 410$; $\text{C}_{10}\text{H}_{20}\text{Cl}_2\text{N}_3\text{O}_4\text{P}_3$ requires: C 29.29, H 4.92, N 10.25%; $M^+ = 409$. The α form was initially crystallized from THF-*n*-hexane (1:6) and the β form was subsequently crystallized from THF-*n*-hexane-dichloromethane (1:6:5).

Compound (I)

Crystal data

$\text{C}_5\text{H}_{10}\text{Cl}_4\text{N}_3\text{O}_2\text{P}_3$	$V = 716.62$ (2) \AA^3
$M_r = 378.87$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.756$ Mg m^{-3}
$a = 7.9063$ (1) \AA	Mo $K\alpha$ radiation
$b = 9.6543$ (2) \AA	$\mu = 1.15$ mm^{-1}
$c = 10.7025$ (2) \AA	$T = 120$ (2) K
$\alpha = 70.771$ (1) $^\circ$	Lath, colourless
$\beta = 71.470$ (1) $^\circ$	$0.40 \times 0.20 \times 0.12$ mm
$\gamma = 73.531$ (1) $^\circ$	

Data collection

Bruker-Nonius KappaCCD area-detector diffractometer	12367 measured reflections
φ and ω scans	3244 independent reflections
Absorption correction: multi-scan (SORTAV; Blessing, 1997)	3094 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.656$, $T_{\max} = 0.874$	$R_{\text{int}} = 0.051$
	$\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.4854P]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.069$	$(\Delta/\sigma)_{\text{max}} = 0.004$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.47$ e \AA^{-3}
3244 reflections	$\Delta\rho_{\text{min}} = -0.39$ e \AA^{-3}
157 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.039 (3)

Table 1

Selected bond lengths (\AA) and angles ($^\circ$) for (I) and MEVVEO.

	(I)	MEVVEO
<i>a</i>	1.5935 (13)	1.589 (2)
<i>b</i>	1.5683 (13)	1.563 (2)
<i>c</i>	1.5847 (13)	1.581 (2)
<i>d</i>	1.9992 (6)	1.9938 (11)
<i>e</i>	1.5706 (11)	1.5635 (18)
α	116.62 (7)	116.26 (11)
β	122.01 (8)	121.59 (13)
γ	119.29 (7)	118.85 (11)
δ	119.88 (8)	119.42 (13)
θ	104.75 (6)	104.57 (9)
ω	100.74 (3)	100.85 (5)
$\Delta(P-N)$ (<i>b</i> - <i>a</i>)	0.0252 (13)	0.026 (2)

Table 2

Selected torsion angles ($^\circ$) for (I) and MEVVEO.

	(I)	Δ	MEVVEO	Δ
N1-P1-O1-C1	70.23 (11)	1.79 (11)	69.24 (7)	0.13 (7)
N1-P1-O2-C3	-68.44 (11)	-	-69.37 (7)	-
N3-P1-O1-C1	-162.09 (10)	1.41 (10)	-	-
N3-P1-O2-C3	163.49 (10)	-	-	-
P1-O1-C1-C2	53.52 (15)	5.38 (15)	56.71 (9)	0.26 (11)
P1-O2-C3-C2	-58.79 (14)	-	-56.45 (11)	-
O1-C1-C2-C3	-55.57 (16)	2.67 (16)	-57.91 (10)	0.23 (12)
O2-C3-C2-C1	58.23 (16)	-	57.68 (12)	-

Compound (II), α form

Crystal data

$\text{C}_{10}\text{H}_{20}\text{Cl}_2\text{N}_3\text{O}_4\text{P}_3$	$Z = 4$
$M_r = 410.1$	$D_x = 1.538$ Mg m^{-3}
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
$a = 11.7673$ (2) \AA	$\mu = 0.66$ mm^{-1}
$b = 9.2325$ (1) \AA	$T = 120$ (2) K
$c = 16.3007$ (3) \AA	Block, colourless
$V = 1770.93$ (5) \AA^3	$0.40 \times 0.12 \times 0.12$ mm

Data collection

Bruker-Nonius KappaCCD area-detector diffractometer	20492 measured reflections
φ and ω scans	2143 independent reflections
Absorption correction: multi-scan (SORTAV; Blessing, 1997)	1974 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.780$, $T_{\max} = 0.926$	$R_{\text{int}} = 0.057$
	$\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2 + 1.1012P]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.078$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.10$	$\Delta\rho_{\text{max}} = 0.43$ e \AA^{-3}
2143 reflections	$\Delta\rho_{\text{min}} = -0.47$ e \AA^{-3}
139 parameters	Extinction correction: SHELXL97
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0182 (14)

Table 3

Selected torsion angles ($^\circ$) for the α form of (II).

O1-C1-C2-C1 ^{iv}	57.7 (2)	C1-O1-P1-N1	161.68 (11)
O2-C5-C6-C5 ^{iv}	56.99 (19)	C1-O1-P1-N3	-69.48 (12)
C2-C1-O1-P1	-56.47 (16)	C5-O2-P2-N2	163.58 (10)
C6-C5-O2-P2	-57.34 (14)	C5-O2-P2-N1	-67.60 (11)

Symmetry code: (iv) $x, -y + \frac{1}{2}, z$.

Compound (II), β form

Crystal data

$C_{10}H_{20}Cl_2N_3O_4P_3$	$Z = 4$
$M_r = 410.1$	$D_x = 1.553 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 18.0604 (4) \text{ \AA}$	$\mu = 0.66 \text{ mm}^{-1}$
$b = 8.3210 (1) \text{ \AA}$	$T = 120 (2) \text{ K}$
$c = 11.8528 (3) \text{ \AA}$	Block, colourless
$\beta = 99.955 (1)^\circ$	$0.40 \times 0.26 \times 0.08 \text{ mm}$
$V = 1754.43 (6) \text{ \AA}^3$	

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer	12671 measured reflections
φ and ω scans	2002 independent reflections
Absorption correction: multi-scan (SORTAV; Blessing, 1997)	1862 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.778, T_{\max} = 0.949$	$R_{\text{int}} = 0.081$
	$\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0235P)^2 + 1.7002P]$
$R[F^2 > 2\sigma(F^2)] = 0.027$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.068$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
2002 reflections	$\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$
104 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.0094 (7)

Table 4

Selected torsion angles ($^\circ$) for the β form of (II).

O1–C1–C2–C5	–57.07 (14)	C5–O2–P1–N2	–66.90 (10)
C1–C2–C5–O2	57.56 (14)	C5–O2–P1–N1	164.05 (9)
C2–C1–O1–P1	57.38 (13)	C1–O1–P1–N2	68.35 (10)
C2–C5–O2–P1	–58.62 (13)	C1–O1–P1–N1	–163.16 (9)

Table 5

Selected bond lengths (\AA) and angles ($^\circ$) for the α and β forms of (II).

	Form α	Form β
a	1.5671 (18)	1.5704 (12)
b	1.5891 (18)	1.5826 (12)
c	1.5748 (17)	1.5796 (8)
d	1.9985 (5)	2.0017 (5)
e	1.5739 (11)	1.5766 (10)
α	120.10 (10)	120.61 (9)
β	120.97 (12)	120.21 (8)
γ	117.33 (10)	117.23 (7)
δ	123.32 (11)	123.07 (10)
θ	99.85 (3)	101.38 (3)
ω	103.66 (8)	103.44 (5)
$\Delta(P-N) (b-a)$	0.0220 (18)	0.0122 (12)

For (I) and the β form of (II), all H atoms were fixed in idealized positions [C–H = 0.98 (CH₃) or 0.99 \AA (CH₂)] and refined using a riding model, with $U_{\text{iso}}(\text{H})$ values set at either $1.2U_{\text{eq}}(\text{C})$ (methylene groups) or $1.5U_{\text{eq}}(\text{C})$ (methyl groups). The H atoms of the α form of (II) were treated in the same manner, apart from those situated about the mirror plane, which were selected from a difference map, restrained to idealized bond lengths (C–H = 0.98 \AA) and their isotropic displacement parameters allowed to refine freely.

For all compounds, data collection: COLLECT (Hooft, 1998); cell refinement: DENZO (Otwinowski & Minor, 1997) and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003) and WinGX (Farrugia, 1999); software used to prepare material for publication: publCIF (Westrip, 2007).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3078). Services for accessing these data are described at the back of the journal.

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