organic compounds

4,4,5,5-Tetramethyl-1,3,2λ^5-dioxaphospholan-2-one

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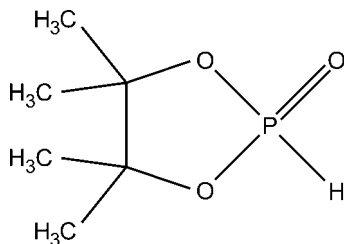
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The five-membered ring in the title compound, $C_6H_{13}O_3P$, exists in an envelope conformation with one of the ring C atoms at the flap position. The coordination geometry around the P atom is a distorted tetrahedron. The crystal structure is stabilized by several weak C—H···O and P—H···O hydrogen bonds, forming a three-dimensional network.

Related literature

For a discussion of 1,3,2-dioxaphospholane chemistry, see: Maffei & Buono (2003); Zwierzak (1967) and for the Heck reaction, see: Beletskaya & Cheprakov (2000); Skarżyńska *et al.* (2011). For hydrogen-bond interactions, see: Desiraju & Steiner (1999). For bond lengths in organic compounds, see: Allen *et al.* (1987). For details of the temperature control applied during data collection, see: Cosier & Glazer (1986) and for specifications of the analytical numeric absorption correction, see: Clark & Reid (1995).

Experimental

Crystal data

$C_6H_{13}O_3P$	a = 7.144 (2) Å
M_r = 164.13	b = 7.570 (2) Å
Monoclinic, $P2_1/c$	c = 15.064 (4) Å
β = 90.98 (2)°	μ = 0.29 mm^{-1}
V = 814.5 (4) Å^3	T = 100 K
Z = 4	$0.33 \times 0.27 \times 0.26$ mm
Mo $K\alpha$ radiation	

Data collection

Kuma KM-4 diffractometer with CCD detector	7254 measured reflections
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2010) T_{min} = 0.910, T_{max} = 0.952	1869 independent reflections
	1673 reflections with $I > 2\sigma(I)$
	R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035	143 parameters
$wR(F^2)$ = 0.096	All H-atom parameters refined
S = 1.10	$\Delta\rho_{max}$ = 0.49 e Å^{-3}
1869 reflections	$\Delta\rho_{min}$ = −0.30 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C11—H113···O^i	0.98 (2)	2.70 (2)	3.583 (2)	150 (2)
C12—H123···O^i	1.00 (2)	2.60 (2)	3.499 (2)	150 (2)
C21—H213···O^i	0.96 (2)	2.68 (2)	3.544 (2)	148 (2)
C22—H222···O1^{ii}	0.98 (2)	2.64 (2)	3.515 (2)	148 (2)
P—H···O1^{iii}	1.28 (2)	2.58 (2)	3.4713 (12)	124 (1)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2010); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2010); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5583).

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supporting information

4,4,5,5-Tetramethyl-1,3,2λ^5-dioxaphospholan-2-one

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S1. Comment

Carbon-carbon bond-forming catalytic reactions are very important fundamental processes in synthetic chemistry. Among them, one of the commonly recognized is the Heck reaction employing as the catalyst precursors palladium compounds with phosphorus ligands (Beletskaya & Cheprakov, 2000). Complexes incorporating in their structure 1,3,2-dioxa-phospholane heterocyclic rings have been recently found to be efficient catalysts of the Heck reaction carried out under mild conditions (Skarżyńska *et al.*, 2011). In this paper we report the synthesis and crystallization of tetramethyl dioxa-phospholane, the title compound.

The geometric parameters around the four-coordinate phosphorus atom (Fig. 1) indicate a deformation of the ideal tetrahedron towards a trigonal pyramid. The O—P—O1 and O—P—O2 angles differ considerably from the ideal value of 109.5° and approach 120°, while O1—P—O2 is close to 90°. Such deformations might be explained by the effect of different substituents and bond types. Bond lengths P—O1, P—O2, P—O, and P—H are typical (Allen *et al.*, 1987). The heterocyclic five-membered ring P/O1/C1/C2/O2 adopts an envelope conformation with the C1 atom deviating from the four-atom plane by about 0.55 Å.

The crystal structure is stabilized by a few hydrogen bonds of the C—H⋯O and P—H⋯O types (Desiraju & Steiner, 1999). Consequently, a three-dimensional network of such interactions is formed in the crystal. The C11, C12 and C21 atoms act as hydrogen-bond donors, *via* H113, H123 and H213, respectively, to the O^{i} atom [symmetry code: (i) *x*, −*y* + 1/2, *z* + 1/2] as an acceptor (Table 1). As a result, chains running parallel to the [001] direction are formed. The adjacent chains of the molecules are further linked by C22—H222⋯O1^{ii} and P—H⋯O1^{iii} hydrogen interactions [symmetry codes: (ii) −*x*, *y* − 1/2, −*z* + 1/2; (iii) −*x* + 1, *y* − 1/2, −*z* + 1/2].

S2. Experimental

The title compound may be prepared according to the known procedures: utilizing pinacol and phosphorus trichloride, followed by hydrolysis (Zwierzak, 1967) or involving a transesterification process between pinacol and diethyl phosphite (Maffei & Buono, 2003). Here we report an alternative route. Crystallization of 2,2,3,3,7,7,8,8-octamethyl-1,4,6,9–5λ^5-phosphaspiro[4.4]nonane in non-dried diethyl ether leads to hydrolysis of the tetraoxaspirophosphorane. As a result, 4,4,5,5-teramethyl-1,3,2-dioxaphospholane 2-oxide is formed as single crystals.

S3. Refinement

All H atoms were found in a difference Fourier map and refined isotropically. The measured C—H distances in methyl groups are in range 0.92 (2)–1.00 (2)Å and P—H bond length is 1.28 (2) Å. The highest residual peak and the deepest hole in the final difference map are located 0.77 and 0.76Å from the C1 and P atom, respectively.
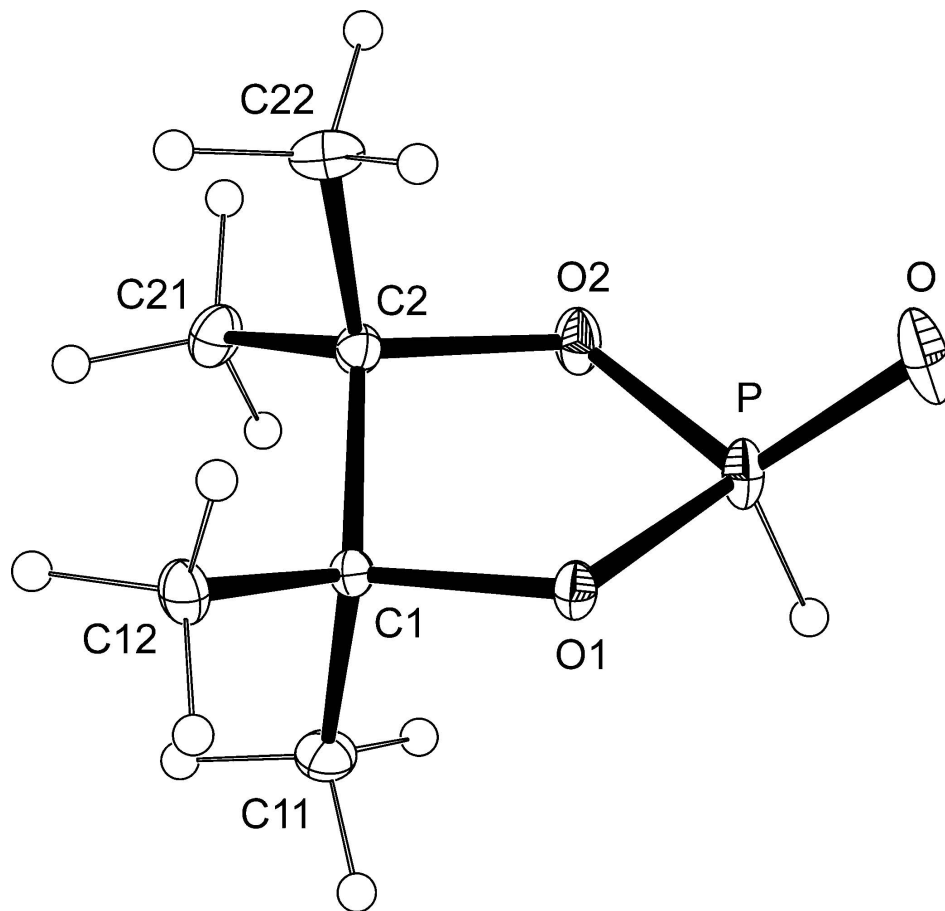
Figure 1

The molecular structure and atom numbering scheme of the title compound. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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Crystal data

$C_6H_{13}O_3P$	$F(000) = 352$
$M_r = 164.13$	$D_x = 1.338$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 4820 reflections
$a = 7.144$ (2) Å	$\theta = 3.0$–27.5°
$b = 7.570$ (2) Å	$\mu = 0.29$ mm^{-1}
$c = 15.064$ (4) Å	$T = 100$ K
$\beta = 90.98$ (2)°	Block, colorless
$V = 814.5$ (4) Å^3	$0.33 \times 0.27 \times 0.26$ mm
$Z = 4$	

Data collection

Kuma KM-4	Absorption correction: analytical
diffractometer with CCD detector	(*CrysAlis RED*; Oxford Diffraction, 2010)
Radiation source: fine-focus sealed tube	$T_{min} = 0.910$, $T_{max} = 0.952$
Graphite monochromator	7254 measured reflections
ω scans	1869 independent reflections

1673 reflections with $I > 2\sigma(I)$	$h = -9 \rightarrow 9$	
$R_{int} = 0.021$	$k = -9 \rightarrow 9$	
$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$	$l = -19 \rightarrow 13$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.035$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.096$	All H-atom parameters refined
$S = 1.10$	$w = 1/[\sigma^2(F_o^2) + (0.0645P)^2 + 0.1298P]$
1869 reflections	where $P = (F_o^2 + 2F_c^2)/3$
143 parameters	$(\Delta/\sigma)_{max} < 0.001$
0 restraints	$\Delta\rho_{max} = 0.49$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.30$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100 K. Analytical numeric absorption correction was carried out with *CrysAlis RED* (Oxford Diffraction, 2010) using a multifaceted crystal model (Clark & Reid, 1995).

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F and R- factors based on ALL data will be even larger.

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

	x	y	z	$U_{iso}*/U_{eq}$
P	0.35196 (5)	0.22996 (4)	0.21158 (2)	0.02085 (14)
H	0.528 (2)	0.199 (2)	0.2076 (11)	0.028 (4)*
O	0.26815 (19)	0.25962 (13)	0.12379 (7)	0.0376 (3)
O1	0.32677 (12)	0.38610 (11)	0.28007 (5)	0.0172 (2)
C1	0.29786 (16)	0.31569 (15)	0.37050 (8)	0.0152 (2)
C11	0.48914 (18)	0.28153 (19)	0.41307 (10)	0.0236 (3)
H111	0.553 (2)	0.190 (2)	0.3832 (12)	0.030 (4)*
H112	0.563 (3)	0.389 (3)	0.4098 (12)	0.044 (5)*
H113	0.476 (3)	0.251 (2)	0.4759 (14)	0.037 (5)*
C12	0.19155 (18)	0.45553 (17)	0.42081 (8)	0.0213 (3)
H121	0.076 (2)	0.494 (2)	0.3871 (11)	0.031 (4)*
H122	0.265 (2)	0.555 (2)	0.4267 (10)	0.026 (4)*
H123	0.163 (2)	0.408 (2)	0.4813 (11)	0.033 (4)*
O2	0.27159 (13)	0.07451 (11)	0.26996 (6)	0.0224 (2)
C2	0.18549 (16)	0.14270 (16)	0.35218 (8)	0.0168 (3)
C21	0.21170 (19)	0.00213 (17)	0.42256 (9)	0.0235 (3)
H211	0.339 (2)	−0.037 (2)	0.4228 (10)	0.028 (4)*
H212	0.131 (3)	−0.095 (3)	0.4074 (12)	0.037 (5)*
H213	0.179 (2)	0.044 (3)	0.4806 (12)	0.040 (5)*

C22	−0.02050 (19)	0.1768 (2)	0.33204 (11)	0.0278 (3)
H221	−0.039 (3)	0.273 (2)	0.2898 (13)	0.034 (5)*
H222	−0.069 (2)	0.063 (3)	0.3105 (11)	0.040 (5)*
H223	−0.082 (3)	0.215 (2)	0.3860 (13)	0.029 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P	0.0308 (2)	0.0184 (2)	0.0136 (2)	0.00484 (12)	0.00665 (14)	0.00041 (11)
O	0.0656 (8)	0.0339 (6)	0.0132 (5)	0.0071 (5)	0.0000 (5)	−0.0014 (4)
O1	0.0224 (4)	0.0161 (4)	0.0131 (4)	0.0004 (3)	0.0037 (3)	0.0011 (3)
C1	0.0160 (5)	0.0173 (5)	0.0123 (5)	−0.0012 (4)	0.0002 (4)	0.0012 (4)
C11	0.0167 (6)	0.0305 (7)	0.0235 (7)	−0.0014 (5)	−0.0050 (5)	0.0027 (5)
C12	0.0271 (6)	0.0195 (6)	0.0175 (6)	0.0021 (5)	0.0032 (5)	−0.0034 (5)
O2	0.0343 (5)	0.0159 (4)	0.0171 (4)	0.0007 (4)	0.0071 (4)	−0.0023 (3)
C2	0.0175 (5)	0.0169 (5)	0.0162 (5)	−0.0005 (4)	0.0027 (4)	−0.0012 (4)
C21	0.0282 (6)	0.0194 (6)	0.0232 (7)	−0.0016 (5)	0.0061 (5)	0.0051 (5)
C22	0.0173 (6)	0.0290 (7)	0.0368 (8)	−0.0047 (5)	−0.0031 (5)	−0.0009 (6)

Geometric parameters (Å, º)

P—O	1.4596 (12)	C12—H123	1.00 (2)
P—H	1.28 (2)	C1—C2	1.5582 (16)
P—O1	1.5812 (10)	O2—C2	1.4850 (14)
P—O2	1.5827 (10)	C2—C21	1.5115 (16)
O1—C1	1.4806 (14)	C2—C22	1.5196 (16)
C1—C12	1.5137 (16)	C21—H211	0.96 (2)
C1—C11	1.5216 (16)	C21—H212	0.96 (2)
C11—H111	0.95 (2)	C21—H213	0.96 (2)
C11—H112	0.98 (2)	C22—H221	0.98 (2)
C11—H113	0.98 (2)	C22—H222	0.98 (2)
C12—H121	1.00 (2)	C22—H223	0.97 (2)
C12—H122	0.92 (2)		
O—P—O1	115.26 (6)	H121—C12—H122	106 (2)
O—P—O2	118.08 (6)	H121—C12—H123	113 (2)
O—P—H	112.0 (8)	H122—C12—H123	109 (2)
O1—P—O2	98.44 (6)	C2—O2—P	111.37 (7)
O1—P—H	106.9 (8)	O2—C2—C21	106.99 (10)
O2—P—H	104.7 (8)	O2—C2—C22	107.82 (10)
C1—O1—P	110.52 (7)	C21—C2—C22	111.57 (10)
O1—C1—C11	108.09 (10)	O2—C2—C1	102.73 (9)
O1—C1—C12	106.74 (10)	C21—C2—C1	114.22 (10)
C12—C1—C11	111.25 (10)	C22—C2—C1	112.75 (10)
O1—C1—C2	102.66 (9)	C2—C21—H211	109.1 (12)
C11—C1—C2	112.83 (10)	C2—C21—H212	107.7 (12)
C12—C1—C2	114.52 (10)	C2—C21—H213	112.1 (12)
C1—C11—H111	111.0 (12)	H211—C21—H212	109 (2)

C1—C11—H112	108.7 (12)	H211—C21—H213	110 (2)
C1—C11—H113	110.5 (12)	H212—C21—H213	109 (2)
H111—C11—H112	109 (2)	C2—C22—H221	112.1 (12)
H111—C11—H113	110 (2)	C2—C22—H222	104.5 (12)
H112—C11—H113	108 (2)	C2—C22—H223	109.4 (12)
C1—C12—H121	111.4 (12)	H221—C22—H222	113 (2)
C1—C12—H122	109.0 (12)	H221—C22—H223	105 (2)
C1—C12—H123	108.5 (12)	H222—C22—H223	112 (2)
O—P—O1—C1	143.16 (9)	O1—C1—C2—O2	37.31 (10)
O2—P—O1—C1	16.56 (8)	C11—C1—C2—O2	−78.79 (12)
P—O1—C1—C11	85.34 (8)	C12—C1—C2—O2	152.58 (12)
P—O1—C1—C12	−154.89 (10)	O1—C1—C2—C21	152.79 (10)
P—O1—C1—C2	−34.11 (10)	C11—C1—C2—C21	36.69 (12)
O—P—O2—C2	−116.09 (9)	C12—C1—C2—C21	−91.94 (12)
O1—P—O2—C2	8.52 (8)	O1—C1—C2—C22	−78.47 (10)
P—O2—C2—C21	−149.19 (8)	C11—C1—C2—C22	165.44 (12)
P—O2—C2—C22	90.67 (10)	C12—C1—C2—C22	36.80 (12)
P—O2—C2—C1	−28.61 (10)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C11—H113···O[i]	0.98 (2)	2.70 (2)	3.583 (2)	150 (2)
C12—H123···O[i]	1.00 (2)	2.60 (2)	3.499 (2)	150 (2)
C21—H213···O[i]	0.96 (2)	2.68 (2)	3.544 (2)	148 (2)
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P—H···O1[iii]	1.28 (2)	2.58 (2)	3.4713 (12)	124 (1)

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