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5,5-Dimethoxy-2-phenoxy-1,3,2-dioxaphosphorinane 2-oxide

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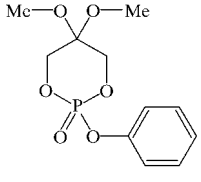
In the title compound, $C_{11}H_{15}O_6P$, the six-membered dioxaphosphorinane ring of the cyclic phosphate triester exists in a distorted chair conformation, with the phenoxy group in an axial position. The phenyl ring and both methoxy groups are in a *trans–gauche* orientation with respect to the 1,3,2-dioxaphosphorinane ring. In the phosphate group, a significant deformation from the ideal tetrahedral shape is observed. The crystal structure is stabilized by a three-dimensional network of C—H···O interactions.

Comment

The title compound, (4), the phenyl ester of cyclic dihydroxyacetone phosphate dimethyl acetal, is one of the intermediates in the chemical pathway leading from dihydroxyacetone (DHA) to dihydroxyacetone phosphate (DHAP), as described by Ferroni *et al.* (1999). The present paper is the second of a series of crystal structure investigations of this chemical pathway, which we have undertaken as a completion of our research on DHAP, its precursors and analogues (Mazurek & Lis, 1999; Ślepokura *et al.*, 2003). The other compounds, namely DHA in the monomeric and three dimeric forms, and two complexes of DHA with calcium chloride and dihydroxyacetone dimethyl acetal, have been reported elsewhere (Ślepokura & Lis, 2004). In general, six-membered cyclic phosphate esters are present in a number of biologically important molecules, *e.g.* cyclic adenosine monophosphate.



(4)

The molecular structure and atom-numbering scheme of (4) are shown in Fig. 1. In one of the methyl groups (C52), the H atoms are disordered over two sites. Excellent agreement is observed between the geometric features of the O1/P2/O3/C4–C6 ring of the title compound and those of the structurally related 2-oxo-1,3,2-dioxaphosphorinanes and their derivatives [*e.g.* 2-hydroxy-5-methyl-5-nitro derivatives (Johnson *et al.*, 1989), several 2-OAr derivatives (Jones *et al.*, 1984), and a 5-hydroxy-2-methoxy derivative (Hamor, 1986)]. The dioxaphosphorinane ring in (4) adopts a distorted chair conformation, with the phenoxy group in an axial position. The dihedral angles between the least-squares plane through the four central atoms of the ring (O1, O3, C4 and C6) and the O1/P2/O3 and C4/C5/C6 planes are 35.86 (10) and 51.84 (15)°, respectively. The flattening of the ring at the P atom and the deformation of the chair conformation towards an envelope have been observed in similar cyclic structures (Jones *et al.*, 1984). The seemingly energetically unfavourable location of the large phenoxy substituent in the axial position may be explained by the anomeric effect that has been noted previously in a cyclic phosphate (van Nuffel *et al.*, 1980) and is commonly observed in structures such as that reported here. A similar location of the P-bonded substituents in the axial position was also observed in the case of alkyloxy groups, *e.g.* methoxy groups in methyl esters (Hamor, 1986) or in bicyclic organic pyro- and thiopyrophosphates, in which two cyclic thiophosphates are linked by an O atom (Bukowska-Strzyżewska & Dobrowolska, 1978, 1980; Jones *et al.*, 1985). However, when the substituent is $-NMe_2$, its position is found to be equatorial (Cameron & Karolak-Wojciechowska, 1977, and references therein).

The orientation of the aromatic substituent with respect to the dioxaphosphorinane ring may be described as *trans–gauche* (*tg*), the C11—O22—P2—O1 and C11—O22—P2—O3 torsion angles being 176.70 (12) and 65.65 (13)°, respectively. Similarly, the locations of the two methoxy groups are found to be *tg* and *gt* with respect to the dioxaphosphorinane ring (Table 1).

In the phosphate group, a deformation from the ideal tetrahedral shape is observed, especially in the O1—P2—O22 and O21—P2—O22 bond angles. On the whole, the largest O—P—O angles (Table 1) are those associated with atom O21

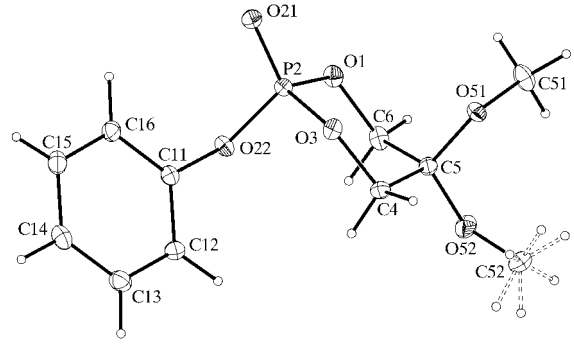


Figure 1
The molecular structure and atom-numbering scheme of (4), showing the disorder of the H atoms at methyl atom C52. Displacement ellipsoids are drawn at the 40% probability level.

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of the P2═O21 double bond. Additionally, there are significant differences in the three ester P—O distances. The endocyclic P2—O1 distance is significantly shorter than the exocyclic P2—O22 distance. A similar situation was reported for the structures of five 2-oxo-2-aryloxy-1,3,2-dioxaphosphorinanes (Jones *et al.*, 1984). As expected, the P2═O21 double bond is the shortest of the P—O bonds in (4).

The crystal structure of (4) is stabilized by a three-dimensional network of C—H···O intermolecular hydrogen bonds linking adjacent molecules (Table 2). As shown in Fig. 2, sheets of molecules are generated in the *bc* plane by means of C—H···O interactions linking the aromatic C14—H14 and methyl C51—H51*C* groups to adjacent O atoms of molecules related by the actions of 2_1 screw axes; these interactions give rise to $R_4^4(30)$ rings. A direct *a*-axis translation (Fig. 3) generates an infinite chain of molecules *via* C—H···O interactions linking the C4—H4*A* and C12—H12 groups with an adjacent O21 atom (Table 2), and the C52—H52*A* group with an adjacent ether atom (O51). In this way, $R_2^1(9)$ and $R_2^2(12)$ rings are generated, and the sheets shown in Fig. 2 are linked into a three-dimensional network. One characteristic of the crystal packing in (4) (also shown in Fig. 2) is an alternate occurrence of aliphatic and aromatic layers parallel to (001), with the aromatic rings at $z = 0, 1, 2, \ldots$ and the aliphatic rings at $z = \frac{1}{2}, \frac{3}{2}, \ldots$.

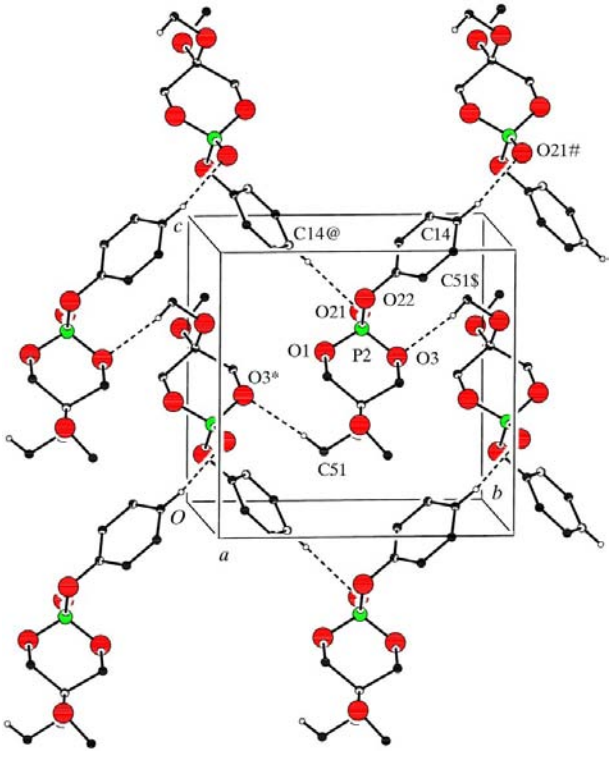

Figure 2
A view of the two-dimensional network of molecules in the *bc* plane. Atoms marked with an asterisk (*), dollar sign ($), at sign (@) or hash (#) are at equivalent positions $(1-x, y-\frac{1}{2}, 1-z)$, $(1-x, \frac{1}{2}+y, 1-z)$, $(1-x, y-\frac{1}{2}, 2-z)$ and $(1-x, \frac{1}{2}+y, 2-z)$, respectively. Dashed lines indicate C—H···O contacts and H atoms not involved in these contacts are not shown.

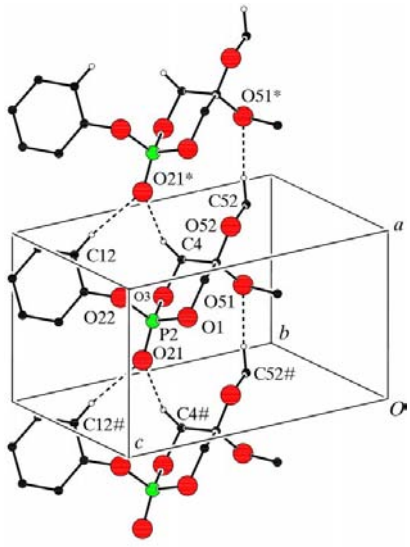

Figure 3
A view showing the linking of molecules by *a*-axis translation. Atoms marked with an asterisk (*) or a hash (#) are at the equivalent positions $(1+x, y, z)$ and $(-1+x, y, z)$, respectively. Dashed lines indicate C—H···O contacts and H atoms not involved in these contacts are not shown.

Experimental

The crystalline dimethyl acetal of cyclic dihydroxyacetone phosphate was obtained by phosphorylation of both hydroxy groups of dihydroxyacetone dimethyl acetal with $PhOP(O)Cl_2$ in anhydrous pyridine (Ferroni *et al.*, 1999). Recrystallization of the crude product by slow evaporation of its benzene solution at room temperature gave large well formed colourless plates. NMR analysis (300 MHz, benzene-d_6, 297 K) reveals that the title compound also exists as a single conformer in solution at room temperature. ^{1}H NMR (p.p.m.): 7.30 (*d*, J_{HH} = 8.4 Hz, 2H), 6.99 (*t*, J_{HH} = 7.8 Hz, 2H), 6.83 (*t*, J_{HH} = 7.4 Hz, 1H), 3.94–3.85 (*m*, 4H, CH_2 ring), 2.81 and 2.62 (2*s*, 2 × 3H, OCH_3 ax, eq); ^{13}C NMR (p.p.m.): 130.05, 125.14, 119.92 (*d*, *J* = 5.1 Hz, CH), 93.20 (*d*, J_{CCOP} = 6.1 Hz, C), 69.62 (*d*, J_{COP} = 7.1 Hz, CH_2 ring), 48.53 and 48.46 (2*s*, OCH_3 ax, eq) (not all of the Ph signals could be observed in the ^{13}C NMR spectrum because of the large solvent signal); ^{31}P NMR (p.p.m.): −12.91.

Crystal data

$C_{11}H_{15}O_6P$
M_r = 274.20
Monoclinic, $P2_1$
a = 6.024 (2) Å
b = 10.371 (3) Å
c = 9.917 (3) Å
β = 97.53 (3)°
V = 614.2 (3) Å^3
Z = 2
D_x = 1.483 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 6408 reflections
θ = 3.8–37.4°
μ = 0.24 mm^{-1}
T = 100 (2) K
Plate, colourless
0.65 × 0.35 × 0.04 mm

Data collection

Kuma KM-4 CCD diffractometer
ω scans
10 758 measured reflections
4632 independent reflections
4232 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 37.4°
h = −7 → 10
k = −13 → 17
l = −16 → 16

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.082$
$S = 1.06$
2908 reflections
166 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 0.1259P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.015 (4)
Absolute structure: Flack (1983), 1282 Friedel pairs
Flack parameter = −0.10 (8)

Table 1
Selected geometric parameters (Å, °).

P2—O1	1.5713 (14)	O51—C5	1.409 (2)
P2—O3	1.5733 (14)	O51—C51	1.431 (2)
P2—O21	1.4579 (13)	O52—C5	1.407 (2)
P2—O22	1.5986 (12)	O52—C52	1.440 (2)
O1—C6	1.454 (2)	C4—C5	1.530 (2)
O3—C4	1.462 (2)	C5—C6	1.531 (2)
O22—C11	1.408 (2)		
O1—P2—O21	114.89 (8)	C5—O52—C52	115.31 (14)
O1—P2—O3	106.57 (7)	O3—C4—C5	110.12 (13)
O1—P2—O22	100.98 (7)	O52—C5—O51	112.46 (13)
O3—P2—O21	112.00 (8)	O52—C5—C4	111.78 (14)
O3—P2—O22	106.24 (7)	O51—C5—C4	105.13 (13)
O21—P2—O22	115.13 (7)	O52—C5—C6	103.03 (13)
C6—O1—P2	117.91 (11)	O51—C5—C6	113.77 (13)
C4—O3—P2	120.04 (11)	C4—C5—C6	110.87 (14)
C11—O22—P2	120.64 (11)	O1—C6—C5	110.88 (13)
C5—O51—C51	115.20 (13)		
O1—P2—O3—C4	−41.4 (2)	O21—P2—O1—C6	167.3 (1)
P2—O3—C4—C5	50.1 (2)	O22—P2—O1—C6	−68.1 (2)
O3—C4—C5—C6	−55.7 (2)	O21—P2—O3—C4	−167.8 (2)
C4—C5—C6—O1	58.5 (2)	O22—P2—O3—C4	65.7 (2)
C5—C6—O1—P2	−53.9 (2)	O21—P2—O22—C11	−58.9 (2)
C6—O1—P2—O3	42.7 (2)	O3—C4—C5—O52	−170.1 (2)
C51—O51—C5—C4	−176.4 (2)	O3—C4—C5—O51	67.6 (2)
C51—O51—C5—C6	−54.9 (2)	O52—C5—C6—O1	178.2 (2)
C52—O52—C5—C4	−64.5 (2)	O51—C5—C6—O1	−59.8 (2)
C52—O52—C5—C6	176.4 (2)		

All H atoms were found in difference Fourier maps, which showed that the methyl H atoms on atom C52 were disordered equally over two sites. In the final refinement cycles, all H atoms were treated as riding atoms, with C—H distances of 0.93–0.97 Å, and with U_{iso}(H) values of $1.2U_{eq}$(C) for aromatic and CH_2 group H atoms, and $1.5U_{eq}$(C) for methyl H atoms.

Data collection: *KM*-4 *CCD Software* (Oxford Diffraction, 1995–2003); cell refinement: *KM*-4 *CCD Software*; data reduction: *KM*-4 *CCD Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXL*97.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14···O21^{i}	0.93	2.52	3.368 (2)	151
C51—H51*C*···O3^{ii}	0.96	2.52	3.414 (3)	155
C4—H4*A*···O21^{iii}	0.97	2.49	3.384 (2)	153
C12—H12···O21^{iii}	0.93	2.52	3.415 (2)	162
C52—H52*A*···O51^{iii}	0.96	2.40	3.332 (2)	165

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1743). Services for accessing these data are described at the back of the journal.

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