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cis-6-Methoxycarbonyl-2,10-dioxa-1-phosphabicyclo[4.4.0]d 1-Oxide

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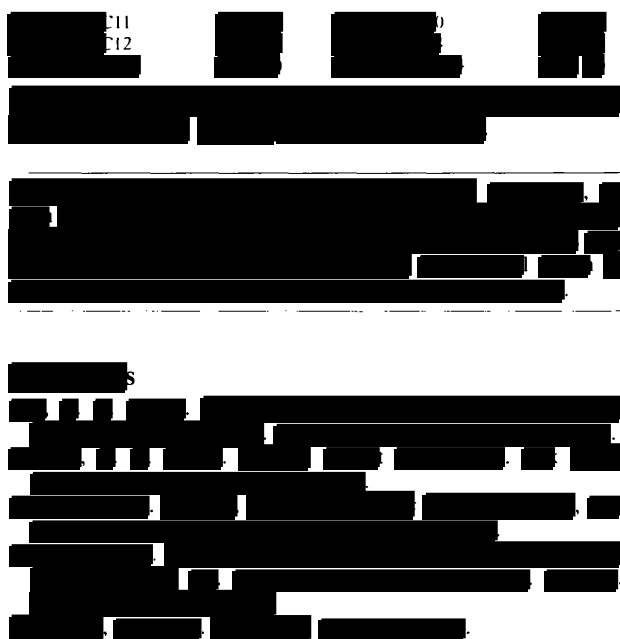
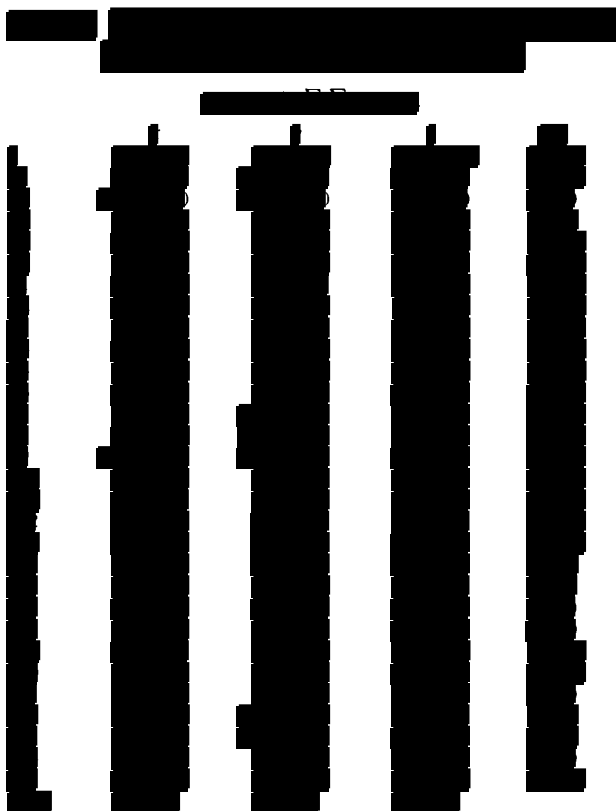
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***cis*-6-Methoxycarbonyl-2,10-dioxabicyclo[4.4.0]decane 1-Oxide**

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Abstract

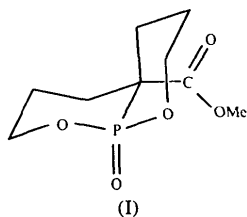
The crystal structure of the title compound, $C_9H_{15}O_5P$, is described. The molecule consists of two *cis*-fused six-membered rings, both in the chair conformation.

Comment

The crystal structure of the title compound, (I), was investigated in order to establish the stereochemistry of the methoxycarbonyl group relative to the phosphoryl group. Since the two analogous model compounds, decalin and 2,10-dioxabicyclo[4.4.0]decane (Descotes,



Lissac, Delmau & Duplan, 1968; Beaulieu, Dickinson & Deslongchamps, 1980) exist in both *cis* and *trans* isomeric forms, the goal was to synthesize both isomeric forms of this bicyclic phosphonate. For some as yet unknown reason only one isomer of the parent compound, 2,10-dioxa-1-phosphabicyclo[4.4.0]decane 1-oxide, (II), (Chérest & Whitham, 1976; Whitham, 1989; Bellard, Postle & Sheldrick, 1978) is produced regardless of the synthetic route employed (Rodriguez, Sommese & Cremer, 1993). It was hoped that the presence of the methoxycarbonyl substituent would lead to both the *cis* and *trans* isomers of (I). Surprisingly, as with (II), only the *cis* isomer of (I) has been observed so far (Rodriguez, Sommese & Cremer, 1993). The determination of the crystal structure was required in order to assign the *cis*-fused configuration unambiguously and therefore gain additional information about the apparent stability of the *cis* configuration (or instability of the *trans* configuration).



The two rings in (I), like the two rings in (II), are intrinsically non-equivalent in the solid state. Although the non-equivalence of the rings in (I) is not discernible from the P—O bond lengths [1.567 (2) and 1.573 (2) Å],

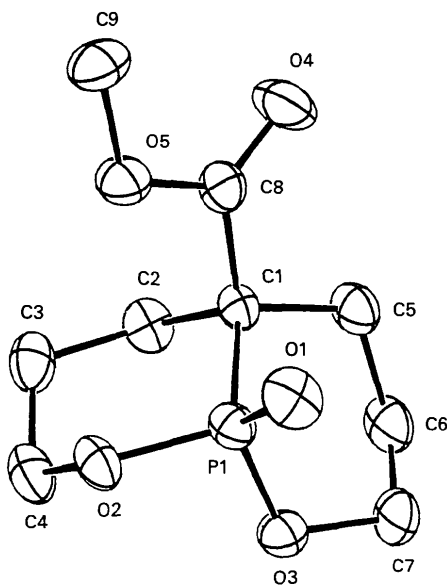


Fig. 1. Molecular structure of the title compound with displacement ellipsoids at the 35% probability level.

which differ by only 0.006 (3) Å, *i.e.* 2σ , the bond angle at O2 [119.1 (2)°] is significantly wider than the angle at O3 [116.8 (2)°].

The P1—C1 bond [1.814 (3) Å] is, as expected, the longest bond in (I), and is even longer than the corresponding bond in (II) [1.783 (4) Å]. The P—C torsion angle in (I) [O2—P1—C1—C8 86.8 (2)°] is also larger than that in (II) [O1—P1—C4—H7 46.4°]. These differences may be the result of a greater steric and electronic interaction between the methoxycarbonyl group and the phosphoryl group in (I) than between the α -H atom and the phosphoryl group in (II).

Further studies aimed at determining whether the preferential formation of *cis*-(I) and *cis*-(II) during the synthesis of these compounds is directed by thermodynamic or kinetic control are underway.

Experimental

The title compound was synthesized by the procedure described by Rodriguez, Sommese & Cremer (1993). Crystals (m.p. 397–398 K) were grown from a methylene chloride solution layered with diethyl ether.

Crystal data

C₉H₁₅O₅P
 $M_r = 234.12$
 Orthorhombic
Pbca
 $a = 26.377 (4) \text{ \AA}$
 $b = 8.297 (2) \text{ \AA}$
 $c = 9.994 (2) \text{ \AA}$
 $V = 2187.2 (8) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.422 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71069 \text{ \AA}$
 Cell parameters from 21 reflections
 $\theta = 3.09\text{--}7.91^\circ$
 $\mu = 0.24 \text{ mm}^{-1}$
 $T = 298 \text{ K}$
 Plate
 $0.40 \times 0.30 \times 0.30 \text{ mm}$
 Colorless

Data collection

Picker diffractometer
 θ – 2θ scans
 Absorption correction: none
 1690 measured reflections
 1426 independent reflections
 1021 observed reflections
 $[I > 2.0\sigma(I)]$

$\theta_{\max} = 23.5^\circ$
 $h = 0 \rightarrow 28$
 $k = 0 \rightarrow 8$
 $l = 0 \rightarrow 10$
 3 standard reflections
 frequency: 120 min
 intensity decay: none

Refinement

Refinement on F^2
 $R(F) = 0.034$
 $wR(F^2) = 0.055$
 $S = 2.55$
 1021 reflections
 138 parameters
 H-atom parameters not refined
 Weighting scheme based on measured e.s.d.'s
 $(\Delta/\sigma)_{\max} = 0.304$

$\Delta\rho_{\max} = 0.220 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.260 \text{ e \AA}^{-3}$
 Extinction correction:
 $F_c^* = kF_c [1 + (0.001x \times F_c^2 \lambda^3 / \sin 2\theta)]^{-1/4}$
 Extinction coefficient:
 $x = 0.0042 (3)$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
P1	0.16207 (3)	0.43031 (10)	0.16173 (9)	0.041 (1)
O1	0.17235 (9)	0.5013 (3)	0.2921 (2)	0.057 (1)
O2	0.13699 (7)	0.2596 (2)	0.1722 (2)	0.048 (1)
O3	0.20979 (7)	0.3968 (3)	0.0715 (2)	0.054 (1)
O4	0.07147 (10)	0.7729 (3)	0.1417 (3)	0.082 (2)
O5	0.05538 (9)	0.52581 (9)	0.2121 (2)	0.058 (2)
C1	0.12217 (12)	0.5540 (4)	0.0553 (3)	0.038 (2)
C2	0.0979 (1)	0.4501 (4)	-0.0567 (3)	0.054 (2)
C3	0.0781 (1)	0.2851 (4)	-0.0141 (3)	0.060 (2)
C4	0.1181 (1)	0.1829 (4)	0.0515 (4)	0.060 (2)
C5	0.1552 (1)	0.6890 (4)	-0.0064 (3)	0.055 (2)
C6	0.2037 (1)	0.6279 (4)	-0.0740 (3)	0.065 (2)
C7	0.2371 (1)	0.5378 (4)	0.0206 (3)	0.066 (2)
C8	0.0809 (1)	0.6332 (4)	0.1394 (3)	0.045 (2)
C9	0.0180 (1)	0.5882 (4)	0.3036 (3)	0.062 (2)

Table 2. Selected geometric parameters (\AA , $^\circ$)

P1—O2	1.567 (2)	O2—C4	1.454 (4)
C8—C1	1.523 (5)	C2—C3	1.527 (5)
P1—O1	1.455 (2)	O5—C8	1.334 (4)
C8—O4	1.186 (5)	C3—C4	1.504 (5)
P1—O3	1.573 (2)	O5—C9	1.441 (4)
C1—C2	1.551 (5)	C5—C6	1.535 (5)
P1—C1	1.814 (3)	O3—C7	1.465 (4)
C1—C5	1.548 (5)	C7—C6	1.492 (5)
O2—P1—O1	112.65 (14)	P1—O2—C4	119.1 (2)
P1—C1—C8	109.6 (2)	C1—C2—C3	116.0 (3)
O2—P1—O3	102.50 (13)	C8—O5—C9	116.9 (3)
P1—C1—C2	110.4 (2)	C2—C3—C4	112.7 (3)
O2—P1—C1	107.79 (14)	P1—O3—C7	116.8 (2)
P1—C1—C5	108.4 (2)	C1—C5—C6	114.0 (3)
O1—P1—O3	115.81 (14)	O5—C8—C1	111.9 (3)
C8—C1—C2	110.2 (3)	O2—C4—C3	110.9 (3)
O1—P1—C1	113.81 (15)	O5—C8—O4	122.4 (3)
C8—C1—C5	108.0 (3)	O3—C7—C6	109.3 (3)
O3—P1—C1	103.19 (14)	C1—C8—O4	125.7 (3)
C2—C1—C5	110.2 (3)	C5—C6—C7	112.2 (3)
O1—P1—O2—C4	171.6 (3)	O3—P1—O2—C4	-63.2 (2)
C1—P1—O2—C4	45.2 (2)	O1—P1—C1—C8	-38.9 (2)
O1—P1—O3—C7	-68.0 (2)	O1—P1—C1—C5	78.8 (3)
O2—P1—C1—C8	86.8 (2)	O1—P1—C1—C2	-160.4 (3)
O3—P1—C1—C5	-47.5 (2)		

All H-atoms were allowed to ride on the heavy atom with isotropic displacement factors 1.5 times the equivalent isotropic displacement factor of the heavy atom. The methyl group was refined as a rigid rotor. The data were globally sorted and collected using *PCXTL* data collection software (Weinrach & Bennett, 1991). Cell refinement and data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976) and *PLUTO84* (Motherwell, 1984).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms and torsion angles have been deposited with the IUCr (Reference: BK1069). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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