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4-[(2-Chloro-5-methylphenoxy)acetoxymethyl]-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane 1-oxide

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In the structure of the title compound, $C_{14}H_{16}ClO_7P$, the P atom is in a distorted tetrahedral configuration. The data reveal that some strain is probably present in the bicyclic structure. The terminal O═P bond distance is 1.4426 (16) Å, and the bridging P—O distances average 1.5728 (14) Å. The average value of the O═P—O angles is 114.36 (2)°, while the average value of the O—P—O angles is 104.18 (4)°.

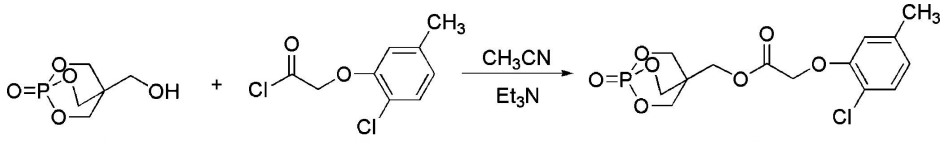
Key indicators

Single-crystal X-ray study
T = 292 K
Mean σ(C–C) = 0.003 Å
R factor = 0.047
wR factor = 0.119
Data-to-parameter ratio = 16.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Heterocyclic compounds containing a symmetric caged bicyclic phosphate have received much attention since they were first synthesized (Verkade & Reynolds, 1960). Some of these molecules exhibit good biological activity, being particularly useful as herbicides (Ratz, 1966) and as flame retardants (Li *et al.*, 2002). The title compound, (I) (Fig. 1), has been prepared as part of our work on the synthesis of 2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-methanol 1-oxide and its alkoxylated derivatives and chloroacetate esters.



(II) (III) (I)

Selected bond lengths and angles are listed in Table 1. The O═P bond length is shorter than the P—O bond lengths within the bicyclic cage, as observed previously in a similar compound (Nimrod *et al.*, 1968). The external O═P—O angles are larger than the internal O—P—O angles, indicating a distorted tetrahedral configuration for the P atom. Atom C4, at the opposite end of the cage, exhibits a fairly normal tetrahedral geometry with the C—C—C angles ranging from 107.48 (16) to 111.51 (15)°. The bicyclic cage consists of three four-atom planes separated by dihedral angles of approximately 120°, as was noted earlier for a similar compound (Miu *et al.*, 1991).

Experimental

2,6,7-Trioxa-1-phosphabicyclo[2.2.2]octane-4-methanol 1-oxide, (II), was prepared as described in the literature (Vyverberg & Chapman, 2002) in 95% yield. (2-Chloro-5-methylphenoxy)acetyl chloride, (III), was synthesized according to a literature method (Coutrot, 1986) in about theoretical yield. To a stirred solution of (II) (0.005 mol) and triethylamine (0.006 mol) in acetonitrile (25 ml), a solution of (III) (0.005 mol) in acetonitrile (5 ml) was added dropwise at 273–283 K. The mixture was then stirred at room temperature for

about 3 h. The solvent was then removed under reduced pressure and the residue was washed with water (20 ml). The raw product was recrystallized from acetonitrile, giving colorless block-shaped crystals of the title compound after 3 d.

Crystal data

$C_{14}H_{16}ClO_7P$
M_r = 362.69
Monoclinic, $P2_1/n$
a = 12.4504 (12) Å
b = 6.3281 (6) Å
c = 20.201 (2) Å
β = 101.926 (2)°
V = 1557.2 (3) Å^3
Z = 4
D_x = 1.547 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.38 mm^{-1}
T = 292 (2) K
Block, colorless
0.20 × 0.20 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
9387 measured reflections
3530 independent reflections
2528 reflections with $I > 2\sigma(I)$
R_{int} = 0.071
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.119
S = 0.96
3530 reflections
209 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0648P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P1—O1	1.4426 (16)	P1—O4	1.5724 (14)
P1—O3	1.5696 (14)	P1—O2	1.5766 (15)
O1—P1—O3	114.01 (9)	C5—C4—C3	110.94 (15)
O1—P1—O4	114.03 (9)	C5—C4—C2	111.51 (15)
O3—P1—O4	104.15 (7)	C3—C4—C2	109.37 (16)
O1—P1—O2	115.02 (9)	C5—C4—C1	108.72 (15)
O3—P1—O2	103.99 (8)	C3—C4—C1	107.48 (16)
O4—P1—O2	104.39 (8)	C2—C4—C1	108.70 (16)
C4—C1—O2—P1	1.4 (2)		

H atoms were refined using a riding model, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic, C—H = 0.98 Å and U_{iso}(H) = 1.2U_{eq}(C) for CH and C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

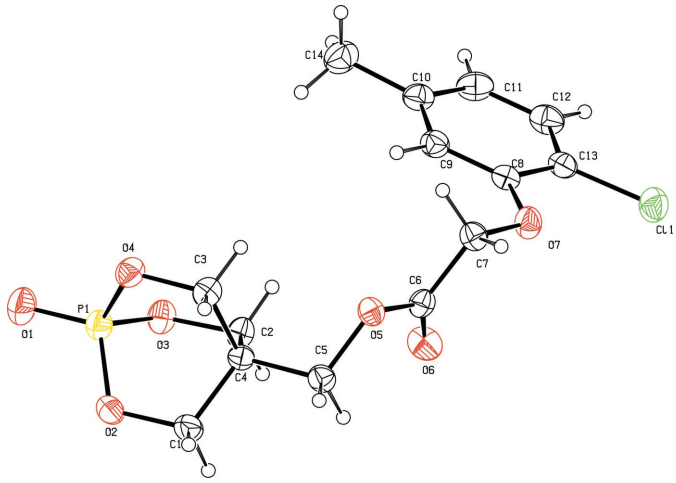


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsolids and the atom-labeling scheme.

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