Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

3-(2-Chlorophenoxy)-1,5-dihydroxy-2,4,3-benzodioxaphosphepine 3-oxide

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Received 21 November 2005
Accepted 9 December 2005
Online 14 December 2005

In the title compound, $C_{14}H_{12}ClO_4P$, the seven-membered phosphepine ring exhibits a twist-chair conformation, with the phosphoryl O atom occupying an axial and the chlorophenoxy group an equatorial position. The P=O distance is 1.449 (2) Å and the average length of the three P—O bonds is 1.574 (2) Å.

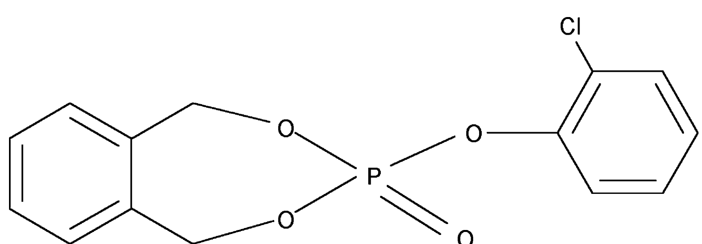
Key indicators

Single-crystal X-ray study
T = 293 K
Mean *σ*(C–C) = 0.005 Å
R factor = 0.051
wR factor = 0.115
Data-to-parameter ratio = 10.5

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

Comment

Organophosphorus compounds are widespread in nature and they have unique multifaceted applications as insecticides (Fest & Schmidt, 1982), anticancer agents (Papanastassiou & Bardos, 1962) and lubricating oil additives and polymer stabilizers (Spivack, 1982). Benzoannulated and related analogs (Ludeman & Zon, 1975) of cyclophosphamide possess antitumor activity against lymphoid leukemia in mice. The title compound, (I), has both antifungal and antibacterial activity; this prompted us to undertake the present crystal structure determination to examine the influence of the substituents on the conformation of the heterocyclic ring.



(I)

In the dioxaphosphepine ring system of (I), the corresponding bond lengths and angles (Table 1) of the two P—O—CH_2—C fragments are equal within experimental error. The endocyclic O—P—O and P—O—C bond angles [108.4 (4) and 123.2 (2)°] are in good agreement with the values of the corresponding seven-membered-ring structures [Selladurai & Subramanian, 1991; Sivakumar *et al.*, 1989; Grand & Robert, 1978]. As a result of the presence of the C10=C11 double bond, considerable differences in the C—O and P—O distances are observed in the dioxaphosphepine ring. The average values for the C—O [1.461 (4) Å] and P—O [1.555 (2) Å] bond distances are similar to the values observed in the structures reported by Grand & Robert (1978).

The C14—Cl bond length of 1.732 (2) Å and its associated endocyclic C13—C14—C15 angle of 120.3 (3)° agree well with values in P-sustituted chlorobenzene (Domenicano *et al.*, 1975: Sivakumar *et al.*, 1989), but are slightly different from the corresponding values of 1.68 (3) Å and 118.2 (3)° in dithiaphosphepine (Reddy *et al.*, 1985). The torsion angles (Table 1)

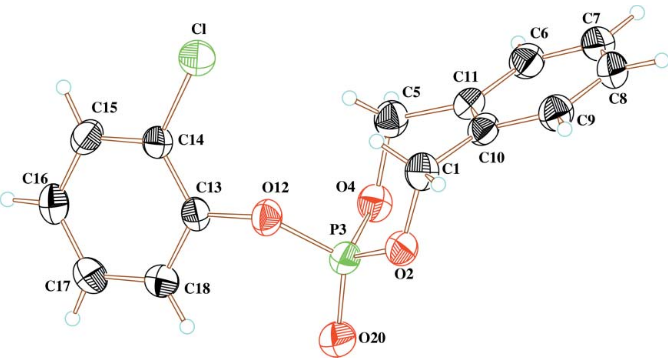


Figure 1
View of the molecule, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary radius.

indicate that the heterocyclic ring exhibits a twist-chair conformation with the C1/O2/O4/C5 atoms nearly coplanar, and the C10/C11 and P3 atoms puckered in opposite directions in a conformation similar to that observed in tetramethylene phosphoric acid (Coulter, 1975). However, this conformation is different from those generally found, *viz.* distorted-boat, twist-boat, and boat forms of the dioxaphosphepine ring (Krishnaiah *et al.*, 2005; Selladurai & Subramanian, 1991; Sivakumar *et al.*, 1989), which have bulky substituents on the heterocyclic ring.

Experimental

A solution of 2-chlorophenylphosphorodichloridate (0.48 g, 2 mmol) in dry tetrahydrofuran (20 ml) was added dropwise over a period of 20 minutes at 273 K to a stirred solution of 1,2-benzenedimethanol (0.27 g, 2 mmol) and triethylamine (0.404 g, 4 mmol) in dry tetrahydrofuran (30 ml). After completion of the addition, the temperature was slowly raised to room temperature and the reaction mixture stirred for 4 h. The progress of the reaction was monitored by TLC analysis (ethyl acetate-hexane 1:2). The precipitated triethylamine hydrochloride was filtered and the filtrate evaporated under vacuum. The residue obtained was washed with water and recrystallized from ethanol to afford 0.38 g (62%) of pure title compound.

Crystal data

$C_{14}H_{12}ClO_4P$
M_r = 310.66
Monoclinic, $P2_1/c$
a = 13.585 (2) Å
b = 8.719 (1) Å
c = 13.106 (2) Å
β = 118.15 (2)°
V = 1368.8 (4) Å^3
Z = 4
D_x = 1.508 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 989 reflections
θ = 2.9–25.0°
μ = 0.41 mm^{-1}
T = 293 (2) K
Prism, yellow
0.25 × 0.25 × 0.13 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.906, T_{max} = 0.949
6682 measured reflections
2410 independent reflections
2236 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 25.0°
h = −16 → 15
k = −7 → 10
l = −15 → 15

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.115
S = 1.31
2410 reflections
229 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 0.766P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.046 (3)

Table 1
Selected geometric parameters (Å, °).

P3—O20	1.449 (2)	O2—C1	1.461 (4)
P3—O2	1.553 (2)	O4—C5	1.461 (4)
P3—O4	1.562 (2)	C5—C11	1.499 (4)
P3—O12	1.594 (2)	C1—C10	1.492 (4)
Cl—C14	1.732 (3)	C11—C10	1.397 (4)
O12—C13	1.398 (3)		
O20—P3—O2	113.2 (1)	C13—O12—P3	123.3 (2)
O2—P3—O4	108.4 (1)	C1—O2—P3	123.2 (2)
O20—P3—O12	116.3 (1)	C5—O4—P3	123.0 (2)
O4—P3—O12	106.1 (1)	C15—C14—C13	120.3 (3)
O4—P3—O2—C1	52.6 (2)	O4—C5—C11—C10	−63.7 (4)
O2—P3—O4—C5	−52.1 (2)	C5—C11—C10—C1	−0.7 (4)
P3—O4—C5—C11	78.6 (3)	O2—C1—C10—C11	64.6 (4)
P3—O2—C1—C10	−79.3 (3)		

All the H atoms were clearly identified in difference Fourier syntheses and refined isotropically.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEPII* (Zsolnai, 1997); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004) and *PARST* (Nardelli, 1995).

One of the authors, Professor M. Krishnaiah, thanks the University Grants Commission, New Delhi for financial support.

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