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# *trans*-4-(4-Chlorophenyl)-2-[(2-chlorophenyl)-(3-pyridylmethylamino)methyl]-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide

**Feng-Mei Sun, Man-Man Tian, Zai-Gang Luo and De-Qing Shi***

Key Laboratory of Pesticide and Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, Hubei, People's Republic of China

Correspondence e-mail: chshidq@yahoo.com.cn

**Key indicators**

Single-crystal X-ray study
$T$ = 292 K
Mean $\sigma$(C–C) = 0.005 Å
$R$ factor = 0.057
$wR$ factor = 0.138
Data-to-parameter ratio = 16.3

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



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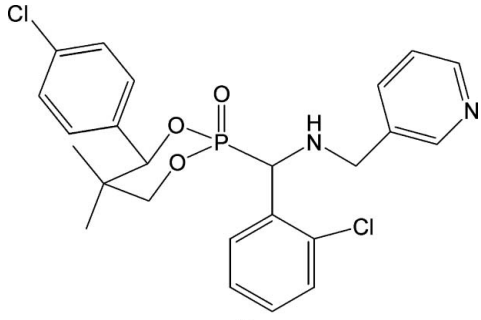
In the title compound, $C_{24}H_{25}Cl_2N_2O_3P$, the P atom adopts a distorted tetrahedral configuration. Weak intermolecular N—H···N and C—H···O hydrogen bonds are observed, and C—H···$\pi$ interactions also contribute to the crystal packing.

## Comment

As phosphorus analogues of natural aminocarboxylic acids, 1-aminophosphonates have attracted attention for decades (Palacios *et al.*, 2005). Recently, 1,3,2-dioxaphosphinane compounds have appeared to be very important in pesticide and medicinal science, owing to their wide biological activities and stereochemistry (Hirashima *et al.*, 1986; Matsumoto *et al.*,1992; Meier, 1996). 3-Aminomethylpyridine is also a very important group in neonicotinoid compounds (Yamamoto *et al.*,1994). We synthesized a series of new cyclic phosphonates containing 3-aminomethylpyridine, in order to find compounds presenting both low toxicity and high activity.




(I)

We report here the crystal structure of the title compound, (I) (Fig. 1), which was synthesized by the addition reaction of an imine with a cyclic phosphite (see *Experimental*). The distorted tetrahedral configuration of the P atom can be attributed to the presence of the dioxaphosphinane ring, which has a steric demand influencing the coordination. The bond length for the P1═O1 double bond and the angles around the P atom (Table 1) illustrate this distortion. The dioxaphosphinane ring adopts a distorted chair conformation, with the parameters $Q$ = 0.499 (3) Å, $\theta$ = 148.2 (3)° and $\varphi$ = 341.70 (2)° (Cremer & Pople, 1975). The P1═O1 double bond is slightly shorter (Table 1) than the analogous bond observed in previously characterized compounds [*e.g.* 1.468 (2) Å; Liu *et al.*, 2005].

Intermolecular N2—H2*A*···N1 and C3—H3···O1 hydrogen bonds (Table 2) contribute to the stability of the overall conformation and influence the crystal packing. Atoms C14 and C16 are involved in C—H···$\pi$ interactions:

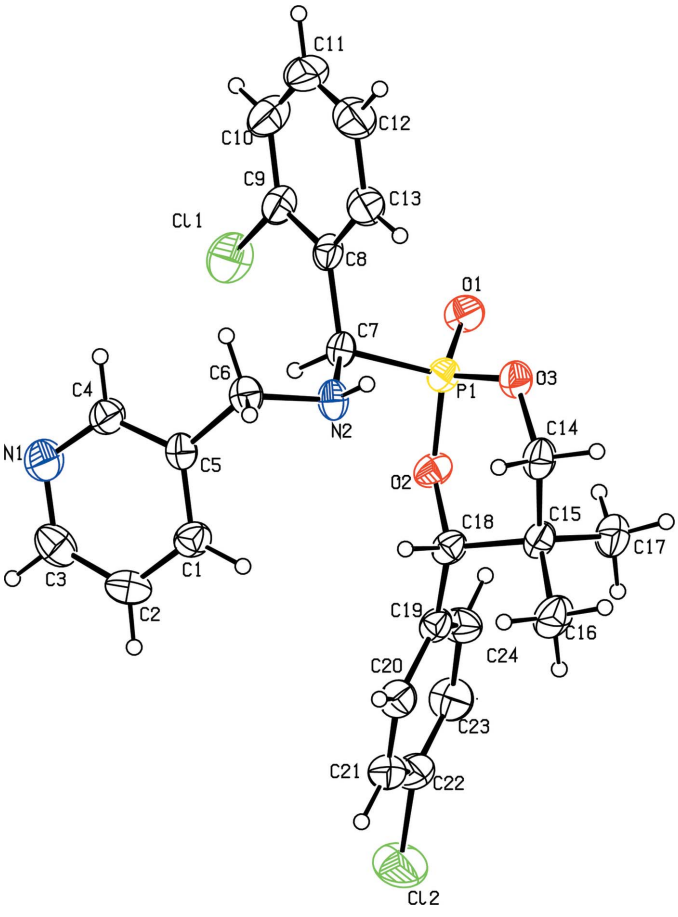



**Figure 1**
A view of the molecule of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids for non-H atoms.

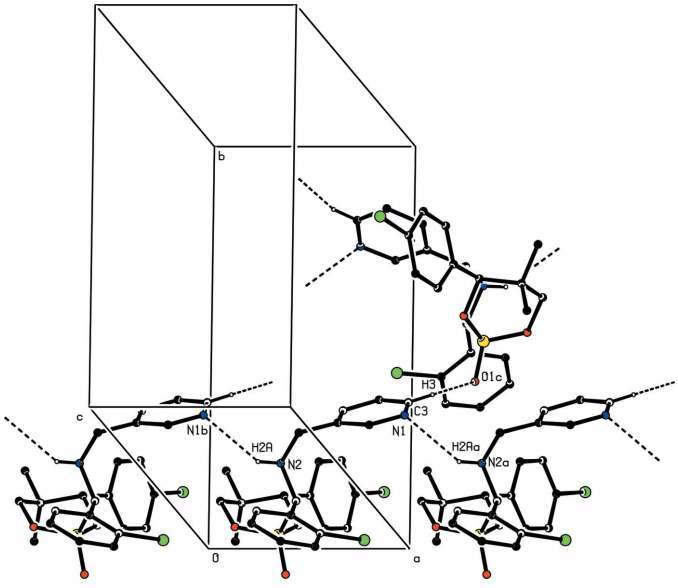



**Figure 2**
Part of the crystal structure of (I), showing chains running along [100], formed by C—H···O and N—H···N interactions (dashed lines). H atoms not involved in the interactions shown have been omitted. [Symmetry codes: (*a*) $1 + x, y, z$; (*b*) $-1 + x, y, z$; (*c*) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$.]

C14···*Cg*2 = 3.83 (3) Å, H14*A*···*Cg*2 = 3.02 Å, C14—H14···*Cg*2 = 141.84°; C16···*Cg*4 = 3.81 (5) Å, H16*B*···*Cg*4 = 2.95 Å, C16—H16*B*···*Cg*4 = 148° [*Cg*2 is the centroid of the pyridine ring and *Cg*4 is the centroid of the 4-chlorophenyl ring, both with symmetry code $(x - 1, y, z)$]. These interactions of methyl and methylene groups with aromatic $\pi$ systems contribute to the crystal packing of the title compound (Desiraju, 2002).

## Experimental

A solution of *N*-(2-chlorobenzylidene) pyridin-3-ylmethylamine (5 mmol) and 4-chlorophenyl-5,5-dimethyl-1,3,2-dioxaphosphine 2-oxide (5 mmol) in anhydrous toluene (20 ml) was stirred under reflux until the reaction was completed (monitored by thin-layer chromatography). After removal of toluene under reduced pressure, the residue was recrystallized from ethanol, to give the target compound as a colourless solid (yield 58%, m.p. 457–458 K). A crystal grown from a dichloromethane–ethanol solution (1:3) was selected for X-ray structure analysis.

### *Crystal data*

$C_{24}H_{25}Cl_2N_2O_3P$
$M_r$ = 491.33
Monoclinic, $P2_1/c$
$a$ = 7.0888 (6) Å
$b$ = 14.4398 (13) Å
$c$ = 24.085 (2) Å
$\beta$ = 96.112 (2)°
$V$ = 2451.4 (4) Å$^3$
$Z$ = 4
$D_x$ = 1.331 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 2345 reflections
$\theta$ = 2.8–19.1°
$\mu$ = 0.36 mm$^{-1}$
$T$ = 292 (2) K
Block, colourless
0.30 × 0.20 × 0.08 mm

### *Data collection*

Bruker SMART APEX CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min}$ = 0.900, $T_{max}$ = 0.972
13139 measured reflections
4804 independent reflections
3147 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.045
$\theta_{max}$ = 26.0°
$h = -8 \rightarrow 8$
$k = -17 \rightarrow 14$
$l = -28 \rightarrow 29$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.138
$S$ = 1.03
4804 reflections
295 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 0.4363P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.37 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.31 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| O1—P1 | 1.456 (2) | | |
| O1—P1—O2 | 111.96 (11) | O1—P1—C7 | 112.65 (12) |
| O1—P1—O3 | 112.56 (12) | O2—P1—C7 | 105.70 (12) |
| O2—P1—O3 | 105.97 (10) | O3—P1—C7 | 107.52 (11) |

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C3—H3···O1$^{i}$ | 0.93 | 2.59 | 3.394 (4) | 145 |
| N2—H2$A$···N1$^{ii}$ | 0.81 (2) | 2.52 (3) | 3.206 (4) | 143 (2) |

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

Atom H2*A* bonded to N2 was found in a difference map and refined with the N—H distance restrained to 0.81 (2) Å and a free $U_{iso}$ parameter. Other H atoms were included in calculated positions and refined using a riding-model approximation. [Constrained C—H bond lengths and isotropic $U_{iso}$(H) parameters: 0.93 Å and $U_{iso}$(H) = $1.2U_{eq}$(C) for aromatic CH; 0.96 Å and $U_{iso}$(H) = $1.5U_{eq}$(C) for methyl $CH_3$; 0.97 Å and $U_{iso}$(H) = $1.2U_{eq}$(C) for methylene $CH_2$; 0.98 Å and $U_{iso}$(H) = $1.2U_{eq}$(C) for methine CH.]

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, 2000); software used to prepare material for publication: *SHELXTL*.

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