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# Ethyl 5-amino-1-(4-chlorophenyl-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphinan-2-yl)-3-(6-chloro-3-pyridylmethylamino)-1H-pyrazole-4-carboxylate

In the title compound, $C_{23}H_{26}Cl_2N_5O_5P$, the P atom adopts a distorted tetrahedral coordination. The terminal ethyl carboxylate group is almost coplanar with the plane of the pyrazole ring. Intramolecular N—H···O hydrogen bonds influence the overall conformation of the molecule. C—H···$\pi$ Interactions contribute to the crystal packing.

## Comment

Neonicotinoide insecticides as nicotinic acetylcholine receptor inhibitors have attracted increasing attention because of their safety, low toxicity, wide range of activities and high potency (Shiokawa *et al.*, 1986). It has been found that most biologically active nicotinic compounds contain the 3-aminomethyl-pyridine group (Yamamoto *et al.*, 1994). Pyrazole and phosphorus heterocyclic compounds appear to be very important due to their wide range of biological activities (Tomcufcik *et al.*, 1985; Hirashima *et al.*, 1986).



(I)
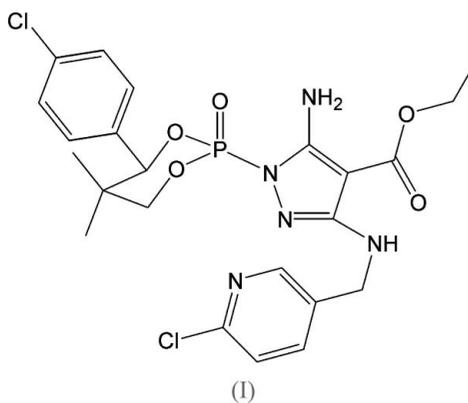
We report here the crystal structure of the title compound, (I) (Fig. 1), which was synthesized by attachement of a 1,3,2-dioxaphosphinane and a 3-aminomethylpyridine group to pyrazole. The distorted tetrahedral configuration of the P atom can be attributed to the presence of the dioxaphosphinane ring whose sterical and electronic properties influence the coordination. The values of the double P1=O3 and single P1—N1 bonds and the angles O—P—O′ and O—P—N illustrate the irregularities (Table 1). The dioxaphosphinane ring adopts a distorted chair conformation, with the parameters $Q = 0.5186$ (28) Å, $\theta = 151.45$ (26)° and $\varphi = 11.2$ (6)° (Cremer & Pople, 1975). Atoms C11, O1, C7 and O2 of the dioxaphosphinane ring are not coplanar; the average deviation is 0.0245 (3) Å. The P—O single and double bonds are shorter (Table 1) than the analogous chemical bonds observed previously [1.586 (2), 1.572 (2) and 1.468 (2) Å; Liu *et al.*,
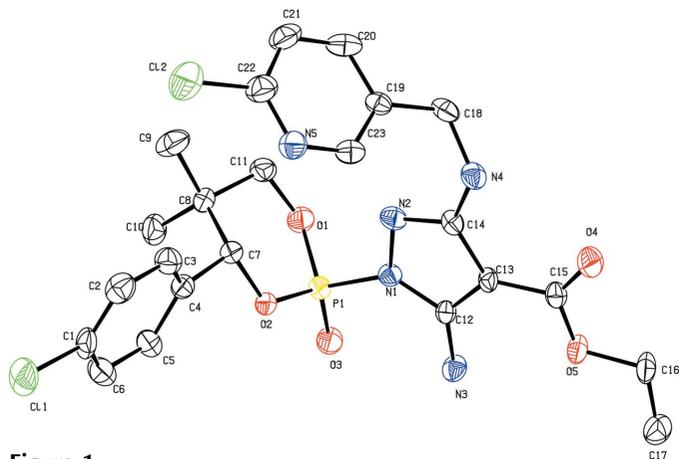
**Figure 1**
A view of the molecule of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity.
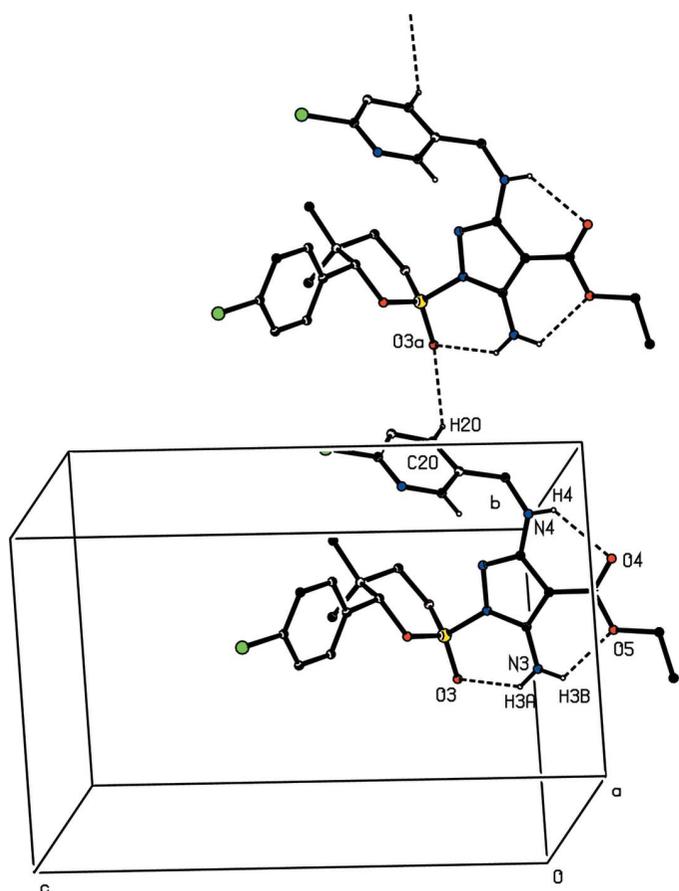


**Figure 2**
Part of the crystal packing of (I), showing a chain running along $b$ formed by C—H···O interactions (dashed lines). The suffix a indicates the symmetry position $x$, $y + 1$, $z$.

2005]; on the other hand, the P1—N1 bond [1.677 (2) Å] is longer than the literature value [1.605 (3) Å; Liu *et al.*, 2005]. The terminal ethyl carboxylate group is almost coplanar with the plane of the pyrazole ring (Table 1). The C16—C17 bond distance [1.481 (4) Å] can be attributed to a disorder of the terminal ethyl group.

Intramolecular N—H···O hydrogen bonds form six-membered rings (Table 2) and contribute to the stability of the overall conformation. The intermolecular C20—H···O3 interaction joins molecules into a chain along the $b$ axis (Table 2 and Fig. 2). Methyl atom C17 and methylene atom C18 are involved in C—H···$\pi$ interactions: C17···$Cg1$ = 3.669 (3) Å, H17$A$···$Cg1$ = 2.81 Å and C17—H17$A$···$Cg1$ = 148.97°; C18···$Cg2$ = 3.521 (3) Å, H18$A$···$Cg2$ = 2.63 Å and C18—H18$A$···$Cg2$ = 153.61° [$Cg1$ is the centroid of the pyrazole ring of the molecule at $(1 - x, 1 - y, -z)$ and $Cg2$ is the centroid of the pyrazole ring of the symmetry-related molecule at $(-x, 2 - y, -z)$]. The interaction of methyl and methylene groups with the aromatic $\pi$ systems, described by Desiraju (2002), contributes to the crystal packing of (I).

## Experimental

A solution of 5-amino-3-(6-chloro-3-pyridylmethylamino)-4-(ethoxycarbonyl)pyrazole (4 mmol) in anhydrous CH$_3$CN (20 ml) and NaOH powder (5 mmol) was added to a three-necked flask. After vigorously stirring for 5 min, a solution of 2-chloro-4-chloro-phenyl-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (4.5 mmol) was added dropwise while cooling in an ice-bath. After the addition was complete, the mixture was stirred at room temperature until the reaction was complete (monitored by thin-layer chromatography). The work-up involved stripping of the solvent followed by addition of water and extraction of the product mixture into chloroform; after phase separation, drying over Na$_2$SO$_4$, filtration and evaporation, the crude product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (2:1 $v/v$) as eluent, giving a white solid (yield: 35%, m.p. 453 K). A colourless crystal grown from absolute ethanol was selected for X-ray structure analysis.

*Crystal data*

| | |
|---|---|
| C$_{23}$H$_{26}$Cl$_2$N$_5$O$_5$P | $Z = 2$ |
| $M_r = 554.36$ | $D_x = 1.415$ Mg m$^{-3}$ |
| Triclinic, $P\bar{1}$ | Mo $K\alpha$ radiation |
| $a = 8.1968$ (11) Å | Cell parameters from 2290 |
| $b = 10.2180$ (14) Å | reflections |
| $c = 16.581$ (2) Å | $\theta = 2.7$–27.3° |
| $\alpha = 86.447$ (2)° | $\mu = 0.36$ mm$^{-1}$ |
| $\beta = 85.668$ (3)° | $T = 292$ (2) K |
| $\gamma = 70.083$ (2)° | Prism, colourless |
| $V = 1301.0$ (3) Å$^3$ | $0.40 \times 0.30 \times 0.20$ mm |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 4540 independent reflections |
| | 3469 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans | $R_{int} = 0.058$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2000) | $\theta_{max} = 25.0°$ |
| | $h = -9 \rightarrow 9$ |
| $T_{min} = 0.871$, $T_{max} = 0.932$ | $k = -12 \rightarrow 11$ |
| 6926 measured reflections | $l = -18 \rightarrow 19$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0711P)^2]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.050$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.140$ | $(\Delta/\sigma)_{max} = 0.001$ |
| $S = 1.05$ | $\Delta\rho_{max} = 0.44$ e Å$^{-3}$ |
| 4540 reflections | $\Delta\rho_{min} = -0.45$ e Å$^{-3}$ |
| 333 parameters | Extinction correction: *SHELXL97* |
| H-atom parameters constrained | Extinction coefficient: 0.044 (3) |

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

| | | | |
|---|---|---|---|
| C16—C17 | 1.481 (4) | O2—P1 | 1.5584 (17) |
| N1—P1 | 1.677 (2) | O3—P1 | 1.4529 (18) |
| O1—P1 | 1.5516 (19) | | |
| O3—P1—O1 | 114.92 (10) | O3—P1—N1 | 108.80 (10) |
| O3—P1—O2 | 113.32 (10) | O1—P1—N1 | 105.96 (10) |
| O1—P1—O2 | 106.83 (9) | O2—P1—N1 | 106.44 (10) |
| C12—C13—C15—O4 | 176.3 (3) | C17—C16—O5—C15 | 179.0 (2) |
| C14—C13—C15—O5 | −174.9 (2) | | |

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

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| C23—H23$\cdots$N4 | 0.93 | 2.55 | 2.904 (4) | 103 |
| C20—H20$\cdots$O3[i] | 0.93 | 2.58 | 3.253 (3) | 129 |
| N3—H3$A\cdots$O3 | 0.86 | 2.17 | 2.839 (3) | 134 |
| N3—H3$B\cdots$O5 | 0.86 | 2.29 | 2.832 (3) | 121 |
| N3—H3$B\cdots$O3[ii] | 0.86 | 2.63 | 3.108 (3) | 116 |
| N4—H4$\cdots$O4 | 0.80 (1) | 2.34 (3) | 2.938 (3) | 132 (3) |

Symmetry codes: (i) $x, y + 1, z$; (ii) $-x, -y + 1, -z$.

H atoms were treated as riding, with C—H distances in the range 0.93–0.98 Å and N—H distances of 0.86 Å, and $U_{\mathrm{iso}}$ (H) = 1.2 or 1.5$U_{\mathrm{eq}}$(parent atom).

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*.

## References

Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2000). *SMART, SAINT* and *SADABS* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Desiraju, G. R. (2002). *Acc. Chem. Res.* **35**, 565–573.

Hirashima, A., Ishaaya, I., Ueno, R., Ichiyama, Y., Wu, S. Y. & Eto, M. (1986). *Agric. Biol. Chem.* **50**, 1831–1835.

Liu, Y., Wei, J., Shi, D. Q. & Wang, C. G. (2005). *Chin. J. Struct. Chem.* **24**, 196–200.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Shiokawa, K., Tsubo, S. & Moriya, K. (1986). EP Patent 192,060.

Tomcufcik, A. S., Meyer, M. E. & Tseng, S. S. (1985). US Patent 4 562 189.

Yamamoto, I., Yabita, G.,Tomizawa, M. & Hissasomi, A. (1994). *J. Pesticide Sci.* **19**, 335–339.