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Key indicators

Single-crystal X-ray study
 $T = 292$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.046
 wR factor = 0.127
Data-to-parameter ratio = 17.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**cis-Ethyl 5-amino-1-[4-(4-chlorophenyl)-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphinan-1-yl]-3-(6-chloro-3-pyridylmethylamino)-1H-pyrazole-4-carboxylate**

In the title compound, $\text{C}_{23}\text{H}_{26}\text{Cl}_2\text{N}_5\text{O}_5\text{P}$, the P atom adopts a distorted tetrahedral configuration. The carboxyl fragment of the ethylcarboxylate group is almost coplanar with the pyrazole ring. The dihedral angle between the pyrazole and pyridine rings is $82.7(1)^\circ$. Intramolecular $\text{C}-\text{H}\cdots\text{O}$, $\text{C}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds contribute strongly to the stability of the molecular configuration. $\text{C}-\text{H}\cdots\text{O}$ intermolecular hydrogen bonds link inversion-related molecules into a centrosymmetric $R_2^2(10)$ dimer. In addition, $\text{C}-\text{H}\cdots\pi$ hydrogen bonds are observed in the crystal structure.

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Comment

Neonicotinioid insecticides as nicotinic acetylcholine receptor inhibitors have attracted increasing attention because of their safety, low toxicity and high activities (Shiokawa *et al.*, 1986). It is found that most biologically active nicotinic compounds contain the 3-aminomethylpyridine group (Yamamoto *et al.*, 1994). Pyrazole and phosphorus heterocyclic compounds appear to be very important owing to their biological activities (Tomcufcik *et al.*, 1985; Hirashima *et al.*, 1986). We report here the crystal structure of the title compound, (I), which was synthesized by introducing 1,3,2-dioxaphosphinane and 3-aminomethylpyridine molecules into pyrazole.

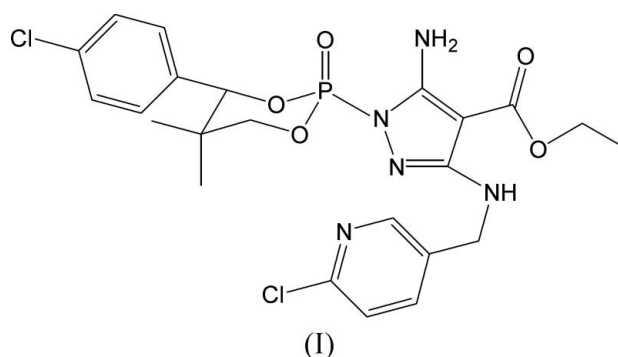


Fig. 1 shows the molecular structure of (I). The P atom is in a slightly distorted tetrahedral geometry. The deformation of the tetrahedron can be described by the different bond types, *viz.* the $\text{P}=\text{O}$ double bond, $\text{P}-\text{O}$ single bond and $\text{P}-\text{N}$ single bond, and associated angles (Table 1). The $\text{P1}-\text{O4}$ [1.5554 (15) Å], $\text{P1}-\text{O5}$ [1.5584 (13) Å] and $\text{P1}=\text{O3}$ [1.4581 (15) Å] distances are shorter than those observed in a related structure [1.586 (2), 1.572 (2) and 1.468 (2) Å; Liu *et al.*, 2005], but the $\text{P1}-\text{N4}$ distance of 1.6604 (17) Å is longer than that observed [1.605 (3) Å] in the above structure. The variation in the lengths may be a result of steric and electronic effects. The dioxaphosphinane ring adopts a chair conforma-

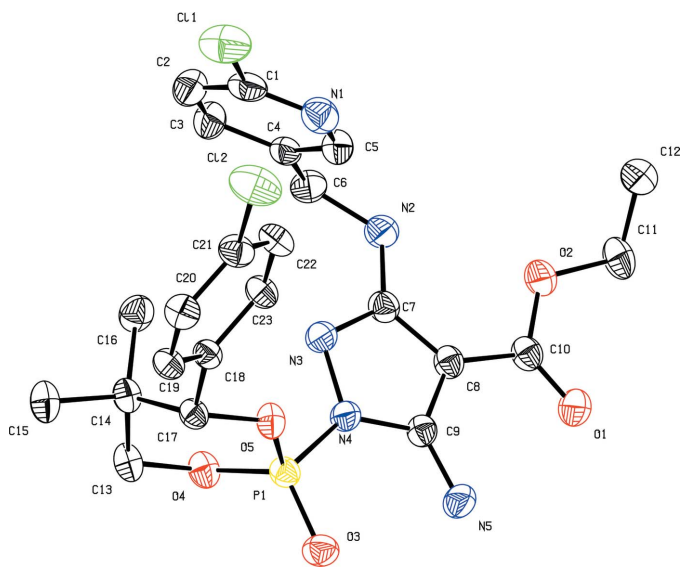


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. For clarity, H atoms have been omitted.

tion, with puckering parameters $Q = 0.495(2) \text{ \AA}$, $\theta = 25.6(2)^\circ$ and $\varphi = 180.8(5)^\circ$ (Cremer & Pople, 1975).

The $C9-C8-C10-O1$ [$6.1(3)^\circ$] and $C7-C8-C10-O2$ [$7.7(3)^\circ$] torsion angles indicate that the carboxyl fragment of the ethylcarboxylate group is almost coplanar with the pyrazole ring. This orientation results in an intramolecular $N5-H5B \cdots O1$ hydrogen bond (Table 2), which forms a pseudo-six-membered ring. The terminal carbon C12 is twisted substantially out of the plane of the pyrazole ring, the $C12-C11-O2-C10$ torsion angle being $-143.2(2)^\circ$. The short $C11-C12$ bond distance [$1.474(4) \text{ \AA}$] can probably be attributed to unresolved disorder of the terminal methyl group, as indicated by the unusual displacement parameters for atoms C11 and C12 (Patel *et al.*, 2003).

Intramolecular $C-H \cdots O$, $C-H \cdots N$ and $N-H \cdots O$ hydrogen bonds (Table 2) contribute strongly to the stability of the molecular configuration. As a result of the hydrogen-bonding interactions, the benzene and pyridine rings lie on the same side of the pyrazole ring; the dihedral angle between the pyrazole and pyridine rings is $82.7(1)^\circ$.

The crystal packing shows that the intermolecular $C11-H11B \cdots O1^i$ [symmetry code: (i) $1-x, 2-y, 1-z$] hydrogen bond between inversion-related molecules leads to the formation of a centrosymmetric $R_2^2(10)$ dimer (Bernstein *et al.*, 1995) (Fig. 2). In addition, two $C-H \cdots \pi$ hydrogen bonds are observed in the crystal structure of (I). It is known that methyl groups can function as hydrogen-bond donors towards aromatic π systems (Desiraju, 2002). The C6 and C11 methylene groups are involved in $C-H \cdots \pi$ interactions with the C18-C23 benzene ring, with its centroid at Cg1 (Table 2).

Experimental

A solution of 3-(6-chloro-3-pyridylmethylamino)-4-ethoxycarbonyl-5-aminopyrazole (4 mmol) in anhydrous CH_3CN (20 ml) and NaOH

powder (5 mmol) were placed in a three-necked flask; after vigorous stirring for 5 min, a solution of 2-chloro-4-chlorophenyl-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (4.5 mmol) in anhydrous acetonitrile (5 ml) was added dropwise while the mixture was cooled in an ice-bath. After the addition was finished, the mixture was stirred at room temperature until the reaction finished (monitored by thin layer chromatography). The workup involved removal of the solvent followed by addition of water and extraction of the product mixture into chloroform; after phase separation, drying over Na_2SO_4 , filtration and evaporation, the crude product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as eluant, giving a white solid (yield 45%, m.p. 433 K). Single crystals of (I) were obtained from an absolute ethanol solution.

Crystal data

$C_{23}H_{26}Cl_2N_5O_5P$
 $M_r = 554.36$
Monoclinic, $P2_1/n$
 $a = 12.4196(11) \text{ \AA}$
 $b = 12.1995(11) \text{ \AA}$
 $c = 17.5992(15) \text{ \AA}$
 $\beta = 107.198(2)^\circ$
 $V = 2547.3(4) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.446 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 5782 reflections
 $\theta = 2.4-22.9^\circ$
 $\mu = 0.36 \text{ mm}^{-1}$
 $T = 292(2) \text{ K}$
Block, colourless
 $0.30 \times 0.20 \times 0.18 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\min} = 0.899$, $T_{\max} = 0.938$
21527 measured reflections

5812 independent reflections
3999 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -16 \rightarrow 16$
 $k = -15 \rightarrow 14$
 $l = -22 \rightarrow 22$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.127$
 $S = 1.02$
5812 reflections
328 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0617P)^2 + 0.368P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$

Table 1

Selected bond angles ($^\circ$).

$O3-P1-O4$	116.88 (9)	$O3-P1-N4$	109.80 (9)
$O3-P1-O5$	115.40 (9)	$O4-P1-N4$	103.86 (8)
$O4-P1-O5$	105.50 (7)	$O5-P1-N4$	104.06 (8)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C11-H11B \cdots O1^i$	0.97	2.52	3.290 (3)	136
$C16-H16A \cdots N3$	0.96	2.54	3.486 (3)	167
$N2-H2A \cdots O2$	0.86	2.26	2.829 (2)	124
$N5-H5A \cdots O3$	0.86	2.17	2.834 (2)	134
$N5-H5B \cdots O1$	0.86	2.36	2.909 (2)	122
$C6-H6A \cdots Cg1^{ii}$	0.97	2.80	3.680 (3)	152
$C11-H11A \cdots Cg1^{iii}$	0.97	2.89	3.753 (3)	149

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x-\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$. Cg1 is the centroid of the C18-C23 ring.

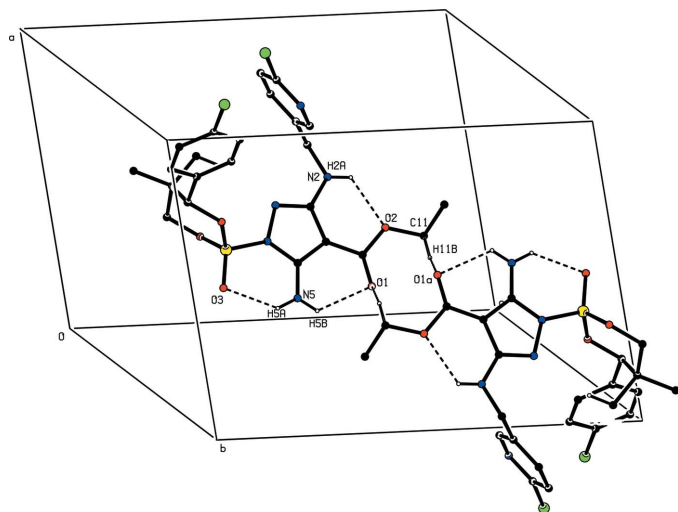


Figure 2

Part of the crystal structure of (I), showing the formation of an $R_2^2(10)$ ring [centred at $(\frac{1}{2}, 1, \frac{1}{2})$]. Hydrogen bonds are shown as dashed lines. Atoms labelled with the suffix 'a' are at the symmetry position $(1 - x, 2 - y, 1 - z)$. C—H... π interactions are shown as dotted lines.

The H atoms were placed in calculated positions, with N—H = 0.86 Å and C—H = 0.93–0.98 Å, and included in the final cycles of refinement using a riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{carrier atom})$. A rotating group model was used for the methyl groups.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; 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*.

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