

O-(E)-1-[1-[(6-Chloropyridin-3-yl)methyl]-5-methyl-1H-1,2,3-triazol-4-yl]ethyleneamino O-ethyl O-phenyl phosphorothioate

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Key indicators

Single-crystal X-ray study

$T = 292$ K

Mean $\sigma(C-C) = 0.005$ Å

R factor = 0.060

wR factor = 0.174

Data-to-parameter ratio = 15.4

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

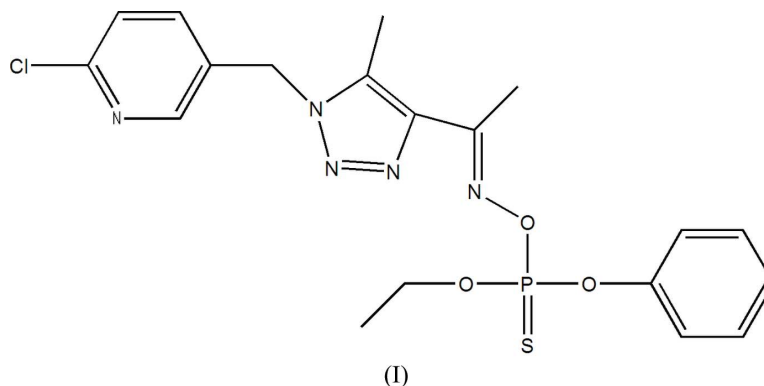
In the title compound, $C_{19}H_{21}ClN_5O_3PS$, the P atom adopts a distorted tetrahedral configuration. In the crystal structure, weak intermolecular $C-H \cdots N$ hydrogen bonds link molecules into chains along the c axis and inversion-related $C-H \cdots S$ hydrogen bonds join parallel chains, forming a network; weak $\pi-\pi$ stacking interactions also contribute to the stability of the structure.

Received 5 September 2006

Accepted 12 September 2006

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-aminomethylpyridine group (Yamamoto *et al.*, 1994). The 1,2,3-triazole (ν -triazole) heterocyclic system has been known for more than a hundred years. Triazoles have been proposed as insecticides, nematocides and acaricides (Rogers & Gerwick, 1984; Knox & Calif, 1988). Thiophosphorate oxime ethers and their derivatives have also been extensively used in pesticides (Yang *et al.*, 1991; Liu *et al.*, 2005).



We report here the crystal structure of the title compound, (I) (Fig. 1), which was synthesized by introducing both triazole and pyridine rings into a thiophosphorate molecular framework. Selected bond lengths and angles are listed in Table 1. The $S1-P1-O1$, $S1-P1-O2$ and $S1-P1-C3$ angles are larger than the $O1-P1-O2$, $O1-P1-C3$ and $O2-P1-C3$ angles, indicating a distorted tetrahedral configuration for the P atom.

In the crystal structure, weak intermolecular $C-H \cdots N$ hydrogen bonds link molecules into chains along the c axis, while weak inversion-related $C-H \cdots S$ hydrogen bonds join parallel chains, forming a network (Fig. 2 and Table 2). In addition, short intermolecular distances between the centroids of the $C8-C9/N2-N4$ ($Cg1$) and $C1-C5/N1$ ($Cg2$) rings of adjacent molecules indicate the presence of $\pi-\pi$ stacking

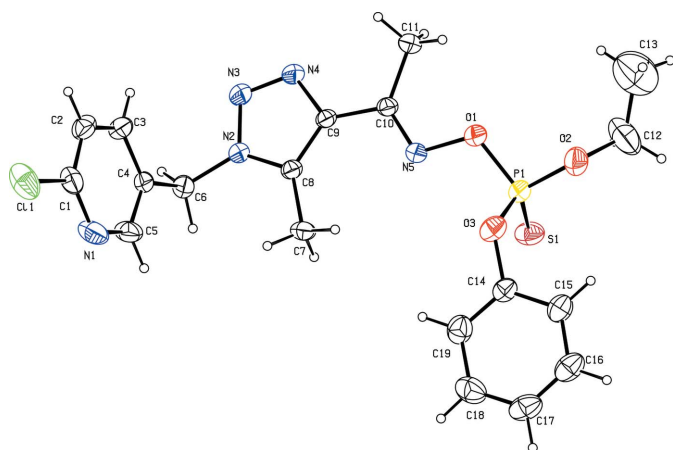


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

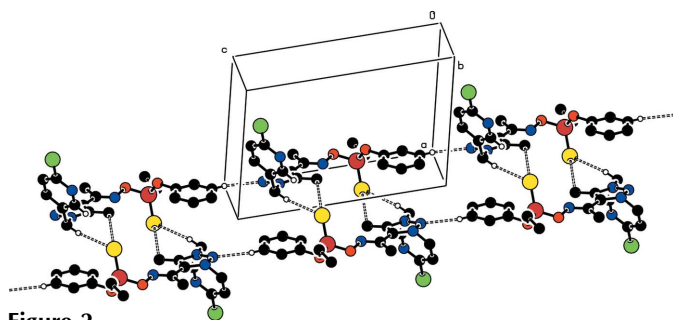


Figure 2
The crystal packing of (I), showing the formation of C—H...O and C—H...S hydrogen bonds (dashed lines).

interactions in the crystal structure (Janiak, 2000) [$Cg1 \cdots Cg2^i$ = 3.894 (2) Å; symmetry code: (i) $1 - x, 3 - y, 2 - z$] (Fig. 2).

Experimental

A solution of 1-[1-[(6-chloropyridin-3-yl)methyl]-5-methyl-1H-1,2,3-triazol-4-yl]ethanone oxime (2 mmol) in anhydrous CH_3CN (10 ml) and NaOH powder (2 mmol) was stirred vigorously for 5 min, then a solution of *O*-ethyl *O*-phenyl phosphorochloridothioate (2 mmol) in anhydrous CH_3CN (5 ml) was added dropwise. The mixture was stirred at room temperature until the reaction was complete (monitored by thin-layer chromatography); the solid was filtered off and the filtrate concentrated under vacuum. The residue was purified by column chromatography on silica gel using (1:1 *v/v*) petroleum ether/ethyl acetate as the eluent, giving a yellow solid (yield 81%, m.p. 364 K). A colourless crystal grown from ethyl acetate and petroleum ether (1:3 *v/v*) was selected for X-ray structure analysis.

Crystal data

$C_{19}H_{21}ClN_5O_3PS$	$V = 1144.7 (3) \text{ \AA}^3$
$M_r = 465.89$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.352 \text{ Mg m}^{-3}$
$a = 8.5491 (11) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.7464 (14) \text{ \AA}$	$\mu = 0.36 \text{ mm}^{-1}$
$c = 13.8045 (17) \text{ \AA}$	$T = 292 (2) \text{ K}$
$\alpha = 89.373 (2)^\circ$	Block, colourless
$\beta = 76.631 (2)^\circ$	$0.30 \times 0.20 \times 0.20 \text{ mm}$
$\gamma = 68.565 (2)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	4242 independent reflections
φ and ω scans	3111 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{int} = 0.045$
9681 measured reflections	$\theta_{max} = 25.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0966P)^2 + 0.1292P]$
$R[F^2 > 2\sigma(F^2)] = 0.060$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.174$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.45 \text{ e \AA}^{-3}$
4242 reflections	$\Delta\rho_{min} = -0.22 \text{ e \AA}^{-3}$
275 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

O1—P1	1.588 (2)	O3—P1	1.577 (2)
O2—P1	1.555 (3)	P1—S1	1.9031 (12)
O2—P1—O3	103.17 (14)	O2—P1—S1	117.60 (11)
O2—P1—O1	99.71 (12)	O3—P1—S1	115.93 (10)
O3—P1—O1	100.90 (12)	O1—P1—S1	116.82 (10)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C16-H16 \cdots N3^i$	0.93	2.65	3.413 (5)	140
$C5-H5 \cdots S1^{ii}$	0.93	2.98	3.877 (4)	162
$C6-H6A \cdots S1^{ii}$	0.97	2.97	3.914 (3)	166

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

H atoms were placed in calculated positions, with C—H = 0.93–0.97 Å, and refined using a riding-model approximation, with $U_{iso}(H) = 1.2$ or 1.5 times $U_{eq}(C)$. 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 and publication material: *SHELXTL* (Bruker, 1997).

The authors are grateful to the Natural Science Foundation of China (grant No. 20302002) for financial support.

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