Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

O,*O*-Diethyl ({1-[(6-chloropyridin-3-yl)methyl]-5-methyl-1*H*-1,2,3-triazol-4-ylcarbonyloxy}-phenylmethyl)phosphonate

Xiao-Bao Chen 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

Received 22 November 2006
Accepted 4 December 2006

Key indicators

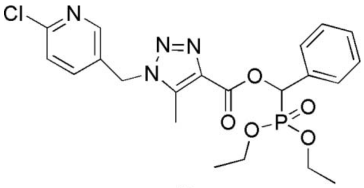
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.066
wR factor = 0.180
Data-to-parameter ratio = 15.4

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

In the title compound, $C_{21}H_{24}ClN_4O_5P$, the P atom adopts a distorted tetrahedral configuration. In the crystal structure, inter- and intramolecular C—H···O hydrogen bonds contribute to the stability of the structure, and π–π stacking interactions are also observed.

Comment

Imidacloprid insecticide acts as a nicotinic acetylcholine receptor inhibitor and is widely used in plant protection. 1,2,3-Triazole compounds have been proposed as insecticides, nematocides and acaricides (Rogers & Gerwick, 1984; Knox & Calif, 1988). 1-Hydroxyphosphonate and its derivatives play an important role in the development of new drugs and agrochemicals (Kolodiazhnyi, 2006).



(I)

We report here the crystal structure of the title compound, (I) (Fig. 1, Table 1), which was synthesized by introducing both triazole and pyridine rings into a 1-hydroxyphosphonate molecular framework. In (I), the C9—N4 and C8—N2 bonds are significantly shorter than a normal single C—N bond (1.47 Å; Sasada, 1984) and close to the value for a C═N bond (1.28 Å; Wang *et al.*, 1998). This indicates significant electron delocalization in the triazolyl system. The O5—P1—O4, O5—P1—O3 and O5—P1—C11 bond angles are larger than the O4—P1—O3, O4—P1—C11 and O3—P1—C11 bond angles (Table 1), indicating a distorted tetrahedral configuration for the P atom. Intra- and intermolecular C—H···O hydrogen bonds contribute strongly to the stability of the molecular conformation (Fig. 2 and Table 2). In addition, short intermolecular distances between the centroids of the N1–C1/C2/C3–C4–C5 rings (centroid *Cg*1) and the parallel pyridine rings of adjacent molecules indicate the presence of π–π stacking interactions in the crystal structure (Janiak, 2000) [$Cg1\cdots Cg1^{i}$ = 3.841 (2) Å, dihedral angle of 0.00 (1)°, and a shortest interplanar distance of 3.478 (1) Å; symmetry code: (i) $-1 - x$, $2 - y$, $-z$].

Experimental

A solution of 1-[(6-chloropyridin-3-yl)methyl]-5-methyl-1*H*-1,2,3-triazole- 4-carboxyl chloride (0.022 mol) in chloroform (10 ml) was added dropwise to a stirred mixture of *O*,*O*-diethyl 1-hydroxyphenylmethylphosphonate (0.020 mol) and triethylamine (0.022 mol) in chloroform (25 ml) at 275–278 K. The resulting mixture was stirred at room temperature for 5–6 h until the reaction was complete (monitored by thin layer chromatography); the solution was washed with dilute hydrochloric acid, followed by saturated sodium bicarbonate and brine, dried and evaporated. The product was purified by flash column chromatography on silica gel using acetone and petroleum ether (1:1 *v*/*v*) as eluant, to give a white solid (yield 85%). Colourless crystals of (I) suitable for X-ray structure analysis were grown from acetone and petroleum ether (1:2 *v*/*v*).

Crystal data

$C_{21}H_{24}ClN_4O_5P$
M_r = 478.86
Triclinic, $P\overline{1}$
a = 8.5297 (8) Å
b = 9.6214 (9) Å
c = 14.6389 (14) Å
α = 95.865 (2)°
β = 92.955 (2)°
γ = 90.536 (2)°

V = 1193.37 (19) Å^3
Z = 2
D_x = 1.333 Mg m^{-3}
Mo *Kα* radiation
μ = 0.27 mm^{-1}
T = 298 (2) K
Block, colourless
0.16 × 0.10 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{\min}$ = 0.959, $T_{\max}$ = 0.974

10004 measured reflections
5121 independent reflections
4282 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.021
$\theta_{\max}$ = 27.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.180
S = 1.07
5121 reflections
332 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0829P)^2 + 0.4732P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.35 e Å^{-3}
$\Delta\rho_{\min}$ = −0.26 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C8—N2	1.342 (3)	C9—N4	1.364 (3)
O5—P1—O4	116.88 (15)	O5—P1—C11	113.10 (13)
O5—P1—O3	117.06 (16)	O4—P1—C11	105.50 (13)
O4—P1—O3	102.06 (17)	O3—P1—C11	100.20 (13)

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

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7*B*···O1	0.96	2.59	3.158 (3)	118
C2—H2···O1$^{\rm i}$	0.93	2.44	3.333 (3)	162

Symmetry code: (i) $x, y+1, z$.

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

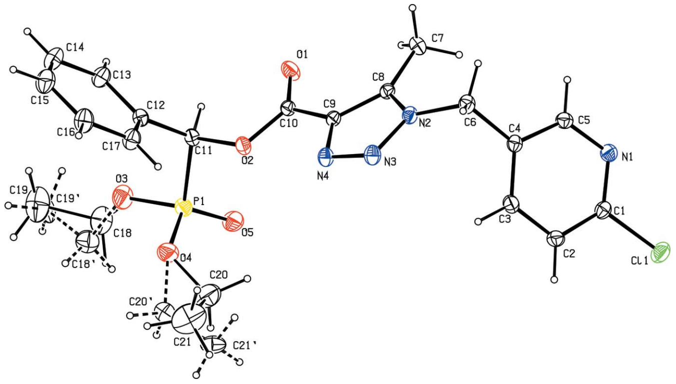


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. The minor components of disordered atoms are shown with dashed bonds.

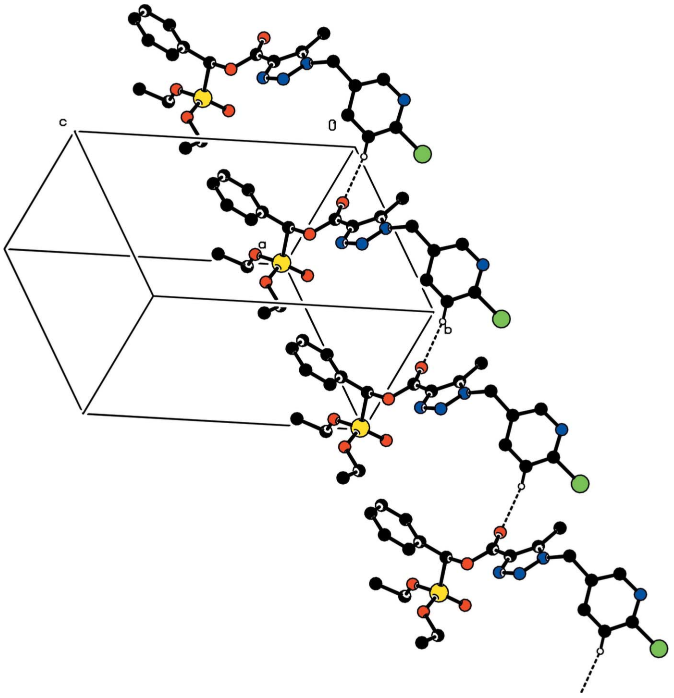


Figure 2
Part of the crystal packing of (I). Hydrogen bonds are shown as dashed lines. H atoms not involved in these interactions have been omitted. Only one disorder component is shown.

It was apparent at an early stage that the structure contained a small proportion of molecules adopting an alternative orientation. Refinement of the site-occupancy factors for the two components, constrained to sum to unity, give the most satisfactory outcome of 0.61/0.39 and 0.83/0.17 for the major and minor components of C18/C19 and C20/C21 groups, respectively, and accordingly the occupancies were thereafter fixed at these values.

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*.

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

References

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

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

Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.

Knox, I. L. & Calif, A. (1988). US Patent 4 775 762.

Kolodiazhnyi, O. I. (2006). *Russ. Chem. Rev.* **75**, 227–253.

Rogers, R. B. & Gerwick, B. C. (1984). US Patent No. 4 775 762.

Sasada, Y. (1984). *Molecular and Crystal Structures in Chemistry Handbook*, 3rd ed. Tokyo: The Chemical Society of Japan, Maruzen.

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

Sheldrick, G. M. (2001). *SADABS*. University of Göttingen, Germany.

Wang, Z., Jian, F., Duan, C., Bai, Z. & You, X. (1998). *Acta Cryst.* C**54**, 1927–1929.