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

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Key indicators

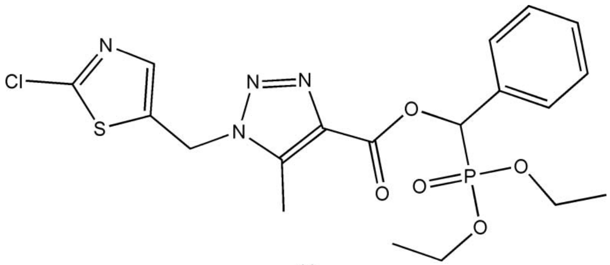
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.067
wR factor = 0.189
Data-to-parameter ratio = 14.6

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

In the title compound, $C_{19}H_{22}ClN_4O_5PS$, the P atom adopts a distorted tetrahedral configuration. Intra- and intermolecular C—H···O hydrogen bonds, together with weak C—H···π hydrogen bonding and strong π–π stacking interactions, stabilize the crystal structure.

Comment

Neonicotinoid insecticides act as nicotinic acetylcholine receptor inhibitors and 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 or aminomethylthiazole system (Yamamoto *et al.*, 1994). 1,2,3-Triazoles have also been widely used in pharmaceuticals, agrochemicals, dyes and photographic materials, and in corrosion inhibition (Fan & Katritsky, 1996; Dehne, 1994; Abu-Orabi *et al.*, 1989). As structure–activity relationships are very useful in the rational design of pharmaceuticals and agrochemicals, we report here the crystal structure of the title triazole derviative, (I) (Fig. 1), which was synthesized by introducing a 1-hydroxyalkylphosphonate into a 1,2,3-triazole molecular framework.



(I)

In compound (I), the C5—N2 and C6—N4 bonds (Table 1) are significantly shorter than a normal single C—N bond [1.47 Å; Sasada, 1984] and are 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—C9 bond angles are larger than the O4—P1—O3, O4—P1—C9 and O3—P1—C9 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 configuration (Fig. 2 and Table 2). Two C—H···π hydrogen bonds are also observed in the crystal structure of (I). It is known that methyl groups can function as hydrogen-bond donors to aromatic π systems (Desiraju, 2002). The C17′ and C18′

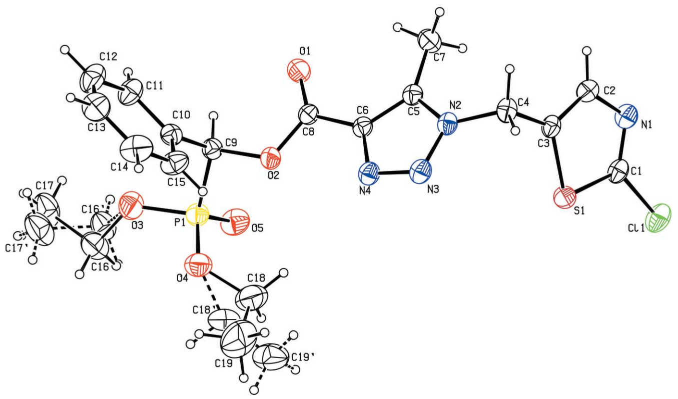


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. Both disorder components are shown.

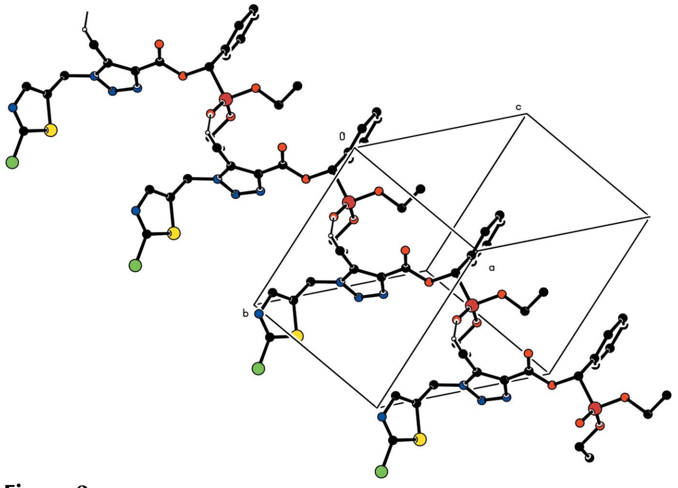


Figure 2
Part of the crystal packing of (I). Hydrogen bonds are shown as dashed lines.

methylene groups are involved in C—H$\cdots\pi$ interactions with the C10–C15 phenyl ring (centroid *Cg*1) [C17′$\cdots$*Cg*1 = 3.65 Å, H17*E*$\cdots$*Cg*1 =2.98 Å, C17′—H17*E*$\cdots$*Cg*1 = 128°; C18′$\cdots$*Cg*1 = 3.66 Å, H18*D*$\cdots$*Cg*1 =2.89 Å, C18′—H18*D*$\cdots$*Cg*1 = 166°]. Strong π–π stacking interactions are also found between adjacent S1/C1/N1/C2–C3 rings, parallel by symmetry, with a centroid-to-centroid distance of 3.641 (1) Å and a shortest interplanar distance of 3.393 (1) Å.

Experimental

A solution of 1-((2-chlorothiazol-5-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 resultant mixture was stirred at room temperature for 6 h until the reaction was complete (monitored by thin-layer chromatography). The solution was then 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 eluent, to give a white solid (yield 78%). Colourless crystals of (I) suitable for X-ray structure analysis were grown from a solution in a mixture of acetone and petroleum ether (1:2 *v*/*v*).

Crystal data

$C_{19}H_{22}ClN_4O_5PS$
$M_r = 484.89$
Triclinic, $P\overline{1}$
$a = 8.7691\ (12)$ Å
$b = 9.3196\ (13)$ Å
$c = 14.389\ (2)$ Å
$\alpha = 97.715\ (2)^\circ$
$\beta = 94.826\ (2)^\circ$
$\gamma = 92.492\ (2)^\circ$
$V = 1159.4\ (3)$ Å^3
$Z = 2$
$D_x = 1.389$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.36$ mm^{-1}
$T = 298\ (2)$ K
Block, colourless
0.36 × 0.30 × 0.30 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.881$, $T_{max} = 0.899$
8265 measured reflections
4709 independent reflections
3943 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 26.5^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.189$
$S = 1.09$
4709 reflections
323 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1034P)^2 + 0.3921P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C5—N2	1.343 (4)	C6—N4	1.367 (4)
O5—P1—O4	115.69 (16)	O5—P1—C9	113.34 (16)
O5—P1—O3	116.12 (17)	O4—P1—C9	105.89 (14)
O4—P1—O3	104.09 (17)	O3—P1—C9	99.98 (14)

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

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
C7—H7*B*$\cdots$O1	0.96	2.48	3.145 (4)	126
C7—H7*A*$\cdots$O5^{i}	0.96	2.58	3.311 (5)	133

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

H atoms were placed in calculated positions, with C—H = 0.93–0.97 Å, and included in the final cycles of refinement using a riding-model approximation, with U_{iso}(H) = 1.2–1.5U_{eq}(carrier atom). A rotating-group model was used for the methyl groups. 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 0.64/0.36 and 0.70/0.30 for the major and minor components of C16/C17 and C18/C19 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*.

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