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5,5-Dimethyl-2-[6-methyl-2-(methylsulfanyl)pyrimidin-4-yloxy]-1,3,2-dioxaphosphorinane-2-thione

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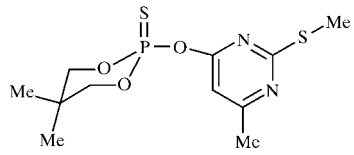
The title compound, $C_{11}H_{17}N_2O_3PS_2$, is a cyclic thiophosphoryl pyrimidine derivative exhibiting insecticidal properties. The crystal structure determination gives evidence for the presence of the thione isomer of the compound. The pyrimidine nucleus is planar and its substituents have small deviations from the least-squares plane. The dioxaphosphorinane ring adopts a chair conformation. The lack of classical hydrogen bonds and the weak intermolecular interactions lead to a 'loose' packing characterized by channels in the structure.

Comment

The biological activity of organophosphorus compounds enables their utilization both as pesticides and as sterilization agents in the food industry and medicine (Almasi, 1976; Safe & Hutzinger, 1976; Durand & Barcelo, 1991). Pyrimidine thiophosphoric esters are also known for their application as performance insecticides (Imperial Chemical Industries Ltd, 1966, 1970; Wegler, 1981). In order to extend the activity domain of these insecticides, cyclic thiophosphoryl compounds have been synthesized. From among the 2-(*O*-2-substituted-6-methylpyrimidine-4-yl)-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane derivatives obtained, the structure of the title compound, (I), was studied because of its insecticidal properties (Musat *et al.*, 1990). From the two possible isomers of (I), *i.e.* the thione P(S)—O– and thiol P(O)—S– forms, the present structure determination gives evidence for the formation of the thione isomer (Fig. 1).

The dioxaphosphorinane ring in (I) adopts an almost perfect $_{P1}C^{C2}$ chair conformation (Saenger, 1984; Haromy *et al.*, 1989), in which atoms P1 and C2 are displaced from the least-squares plane by 0.147 (1) and −0.276 (3) Å, respectively. The torsion angles of the dioxaphosphorinane ring are listed in Table 1. The O-pyrimidine substituent is axial and atom S1 is equatorial with respect to the dioxaphosphorinane ring.



(I)

The pyrimidine ring is planar, with a maximum deviation of 0.006 (3) Å for atom C5. Also, atom S2 is situated in the pyrimidyl plane, 0.004 (1) Å from the pyrimidyl least-squares plane, and the deviations of methyl atoms C10 and C11, and atom O3 from the pyrimidyl least-squares plane are less than 0.074 (2) Å. The torsion angle about the O3—C4 bond [P1—

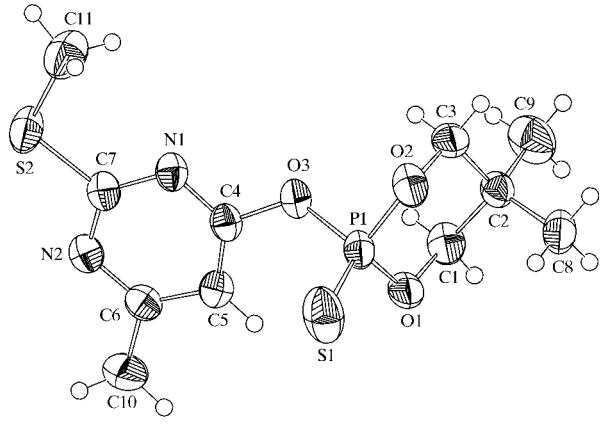


Figure 1
A view of the molecular structure of (I) showing the atom-labelling scheme and 50% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii.

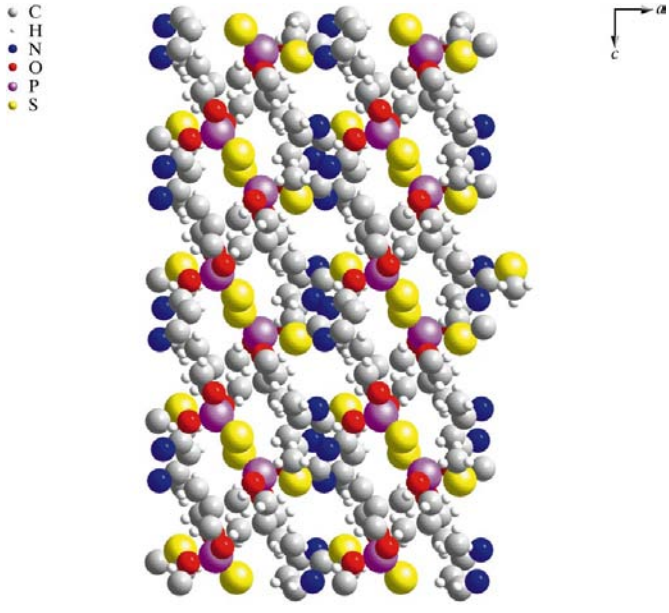


Figure 2
A packing diagram for (I) viewed down the *b* axis. Note the two channel types formed along *b*.

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O3—C4—N1 139.23 (18)°] corresponds to an *anti* conformation and the orientation about the exocyclic S2—C7 bond [C11—S2—C7—N1 −2.1 (2)°] is periplanar.

The dioxaphosphorinane units in (I) are bridged *via* a weak intermolecular C8—H82···O2 bond [C8—H82 0.96 Å, H82···O2 2.51 Å, C8···O2 3.429 (3) Å and C8—H82···O2 160°], forming zigzag chains running along the [101] direction. These chains are situated in layers approximately parallel to the crystallographic *bc* plane. The planar pyrimidine rings are packed in columns running along the *b* axis and form an angle of 36.20 (8)° with this axis. This packing (Fig. 2) leaves two types of channels in the structure along *b*, namely, empty channels and channels containing the phosphoryl S atoms. The two channel types alternate along the [101] and [10$\bar{1}$] directions, and are bordered *via* C—H···π intermolecular interactions between the dioxaphosphorinane C3 and C9 atoms and the pyrimidine nuclei (Table 2), and *via* short interactions between parallel pyrimidine rings [*Cg*···*Cg*(2 − *x*, −*y*, −*z*) 3.4659 (15) Å; *Cg* is the ring centroid]. The 'loose' packing of the molecules of (I) can be explained by the presence of exclusively weak intermolecular interactions.

Experimental

Compound (I) was synthesized by reacting 2-chloro-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane with 2-*S*-methyl-6-methyl-4-hydroxypyrimidine in the presence of K_2CO_3 and dimethylformamide as solvent at 323 K. Analytical and spectroscopic (IR, ^{1}H NMR, ^{31}P NMR, ^{13}C NMR and MS) data confirmed the formation of (I). Single crystals of (I) were obtained from a 1:1 mixture of ethanol and diethyl ether.

Crystal data

$C_{11}H_{17}N_2O_3PS_2$
M_r = 320.36
Monoclinic, $P2_1/c$
a = 9.900 (2) Å
b = 9.330 (2) Å
c = 17.010 (3) Å
β = 90.23 (2)°
V = 1571.2 (5) Å^3
Z = 4
D_x = 1.354 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 23 reflections
θ = 40.0–43.5°
μ = 4.09 mm^{-1}
T = 293 (2) K
Prism, colourless
0.30 × 0.30 × 0.25 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
3703 measured reflections
3185 independent reflections
2626 reflections with $I > 2\sigma(I)$
R_{int} = 0.089
θ_{max} = 74°
$h = -11 \rightarrow 11$
$k = -3 \rightarrow 12$
$l = -21 \rightarrow 10$
2 standard reflections
frequency: 60 min
intensity decay: 6%

Table 1
Selected torsion angles (°).

P1—O1—C1—C2	58.1 (3)	C2—C3—O2—P1	−57.6 (3)
O1—C1—C2—C3	−62.2 (3)	C3—O2—P1—O1	46.5 (2)
C1—C2—C3—O2	58.7 (3)	O2—P1—O1—C1	−43.60 (19)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.154
S = 1.07
3185 reflections
177 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0947P)^2 + 0.4685P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.005
$\Delta\rho_{max}$ = 0.97 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0099 (9)

Table 2
Geometry of X—H···*Cg* (π-ring) interactions (Å, °).

*Cg*2 is the centroid of the N1/C4–C6/N2/C7 ring.

X—H···*Cg*	H···*Cg*	X—H···*Cg*	H···*Cg*
C3—H32···*Cg*2^{i}	3.23	135	3.973 (3)
C9—H93···*Cg*2^{i}	3.12	138	3.888 (4)

Symmetry code: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

All H atoms were placed in geometric positions and refined as riding atoms, with C—H = 0.93–0.97 Å and U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992); cell refinement: local program; data reduction: *PLATON* (Spek, 1999); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ACD*/*ChemSketch* (Advanced Chemistry Developments Inc., 2001), *PLATON* and *DIAMOND* (Crystal Impact, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1105). Services for accessing these data are described at the back of the journal.

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