Ethyl {4-[5-(3-methylphenyl)-3-methylsulfanyl-4-oxo-1-phenylpyrazolo[3,4-*d*]pyrimidin-6-yloxy]-phenoxy}acetate

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The title compound, $C_{29}H_{26}N_4O_5S$, is based on an almost planar pyrazolo[3,4-*d*]pyrimidin-4-one core. Molecules are packed through weak intermolecular C—H···O and C—H···N interactions.

Comment

Pyrazolo[3,4-*d*]pyrimidin-4-one derivatives exhibit a wide spectrum of biological activity, including antibacterial, antiphlogistic and antitumour properties (Ali *et al.*, 2001; Armstrong *et al.*, 2000; EI-Bendary & Badria, 2000; Tetsuya *et al.*, 1996). The title compound, (I), may then be used as a precursor for obtaining new bioactive molecules. In this paper we present the X-ray crystallographic analysis of this compound.
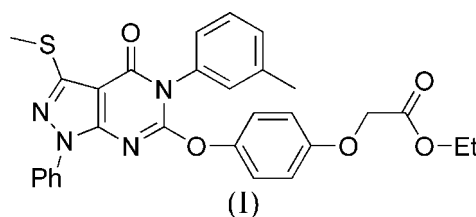
As shown in Fig. 1, ring atoms in the pyrazolo[3,4-*d*]-pyrimidin-4-one group form an essentially planar system. The C7=N2, C8=C9 and C12=N4 bond lengths of 1.313 (5), 1.374 (5) and 1.284 (5) Å, respectively, are longer than those of typical C=N (1.28 Å; Sasada, 1984; Chen & Jin, 2002) and C=C bonds (1.34 Å). In contrast, the single bond lengths C9—N1, C7—C8, C8—C11, C12—N3, and C9—N4, in the range 1.345 (5)–1.433 (5) Å, are significantly shorter than typical Csp^2—N (1.426 Å) and C—C (1.53 Å) bond lengths, reflecting a degree of delocalization in the pyrazolo[3,4-*d*]pyrimidin-4-one system.

Weak intermolecular C—H···O and C—H···N hydrogen bonds are present in the crystal packing (Table 1 and Fig. 2), as well as π–π and C—H···π interactions. Thus, the dihedral angle between five-membered rings defined by atoms N1/N2/C7/C8/C9 and the neighbouring symmetry-related pyrazole ring (symmetry code: $1 - y$, x, $\frac{1}{4} + z$) is 4.77 (1)°, and the distance between the corresponding ring centroids is 3.775 (2) Å.

Experimental

To a solution of 4-(ethoxycarbonyl)-3-(methylsulfanyl)-1-phenyl-1*H*-pyrazolo-5-yl iminophosphorane (2 mmol), prepared according to the reported procedure (Molina *et al.*, 1998), in dry dichloromethane
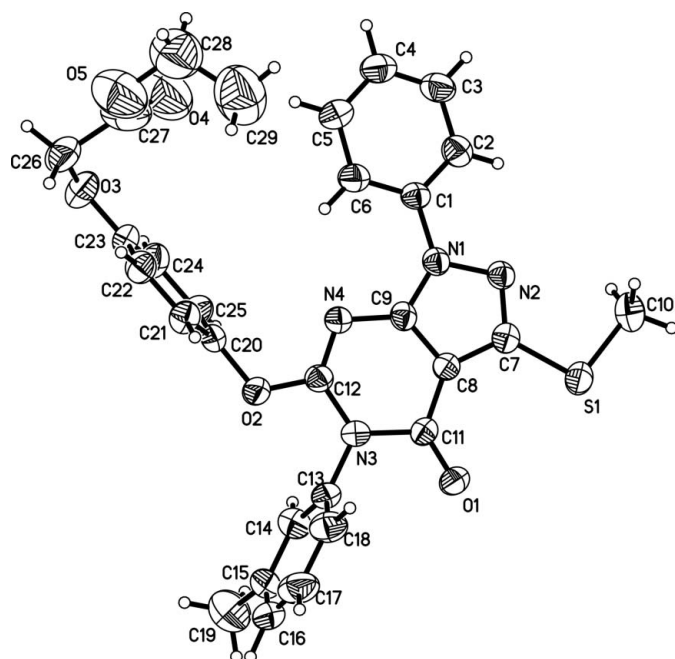
Figure 1
The molecular structure of (I), showing the atom-labelling scheme, and with displacement ellipsoids at the 30% probability level.
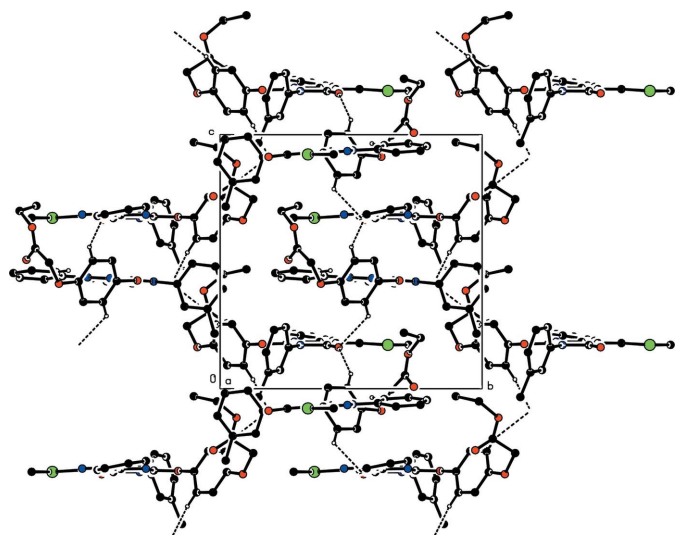

Figure 2
The packing of (I), viewed along [100]. Weak hydrogen bonds are indicated by dashed lines.

(25 ml) was added 3-methylphenyl isocyanate (2 mmol) under N_2 at room temperature. After the reaction mixture had been stirred for 2–5 h, the solvent was removed under reduced pressure, and then anhydrous acetonitrile (25 ml), 2-(4-hydroxyphenoxy)carboxylate (2.0 mmol) (Liu *et al.*, 2005) and anhydrous potassium carbonate (0.05 g) were added to the mixture. After refluxing for 5 h, the mixture was filtered and concentrated under reduced pressure. The resulting residue was recrystallized from ethanol to give (I) in 82% yield. Crystals suitable for X-ray diffraction were grown from $CHCl_3$ at 293 K.

Crystal data

$C_{29}H_{26}N_4O_5S$	$D_x = 1.301$ Mg m^{-3}
$M_r = 542.60$	Mo $K\alpha$ radiation
Tetragonal, $P4_1$	$\mu = 0.16$ mm^{-1}
$a = 14.1908$ (16) Å	$T = 292$ (2) K
$c = 13.760$ (3) Å	Plate, colourless
$V = 2771.0$ (8) Å^3	$0.30 \times 0.20 \times 0.04$ mm
$Z = 4$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	27946 measured reflections
φ and ω scans	5408 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)	3258 reflections with $I > 2\sigma(I)$
$T_{min} = 0.953$, $T_{max} = 0.987$	$R_{int} = 0.131$
	$\theta_{max} = 26.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.12P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.063$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.185$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.95$	$\Delta\rho_{max} = 0.58$ e Å^{-3}
5408 reflections	$\Delta\rho_{min} = -0.31$ e Å^{-3}
356 parameters	Absolute structure: Flack (1983), 2572 Friedel pairs
H-atom parameters constrained	Flack parameter: -0.11 (13)

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C22—H22$\cdots$O1^i	0.93	2.45	3.275 (6)	148
C25—H25$\cdots$O1^{ii}	0.93	2.49	3.141 (5)	127
C6—H6$\cdots$N4	0.93	2.32	2.969 (6)	126

Symmetry codes: (i) $-y + 1, x - 1, z + \frac{1}{4}$; (ii) $y, -x + 1, z - \frac{1}{4}$.

H atoms were included in calculated positions, with C—H distances constrained to 0.93 (aromatic CH), 0.96 (methyl CH_3) and 0.97 Å (methylene CH_2). Methyl groups were considered as rigid groups but were allowed to rotate freely about their C—C bonds. Isotropic displacement parameters for H atoms were fixed at $1.5U_{eq}$(carrier atom) for methyl H atoms and $1.2U_{eq}$(carrier atom) for other H atoms. Owing to unresolved disorder in the ethyl ester region, atoms C27, C28, C29, O4 and O5 were restrained so that their U^{ij} components approximated to isotropic behaviour.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); 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, 2001); software used to prepare material for publication: *SHELXTL*.

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