organic papers

Ethyl 2-(5,7-dimethyl-1,2,4-triazolo[1,5-*a*]-pyrimidin-2-yloxy)benzoate

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In the title compound, $C_{16}H_{16}N_4O_3$, which displays good herbicidal activity, the planar bicyclic triazolopyrimidine system is bound to an ethyl benzoate moiety *via* an oxo bridge, with a dihedral angle of 73.98 (2)° between the bicyclic triazolopyrimidine system and the benzene ring. In the crystal structure, molecules are linked by intermolecular C—H···O hydrogen bonds and π–π stacking interactions between the triazolopyrimidine rings.

Comment

Triazolopyrimidine compounds exhibit a wide spectrum of biological activity. Many triazolopyrimidines have been developed as effective herbicides, and others have been used as therapeutic agents (Kleschick *et al.*, 1985). The title compound, (I), may be used as a new precursor for obtaining bioactive molecules and its structure is reported here (Fig. 1 and Table 1).

(I)
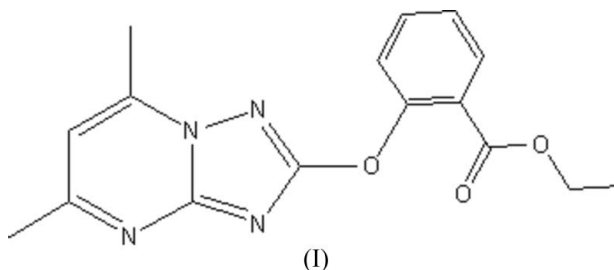
The triazolopyrimidine ring system is almost planar (r.m.s. deviation = 0.005 Å). It is bound to the ethyl benzoate moiety *via* an oxo bridge, with a dihedral angle of 73.98 (2)° between
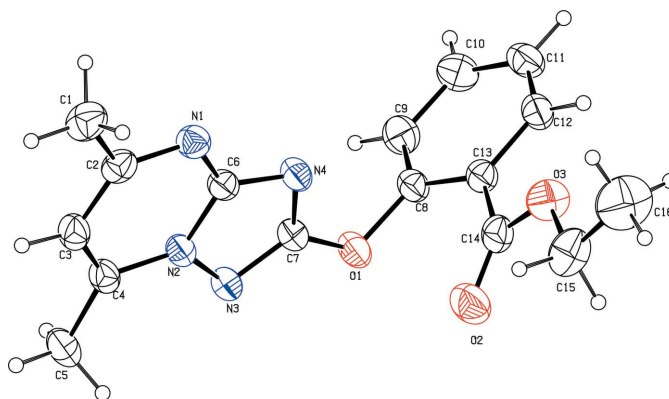

Figure 1
A view of the molecule of (I) showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.
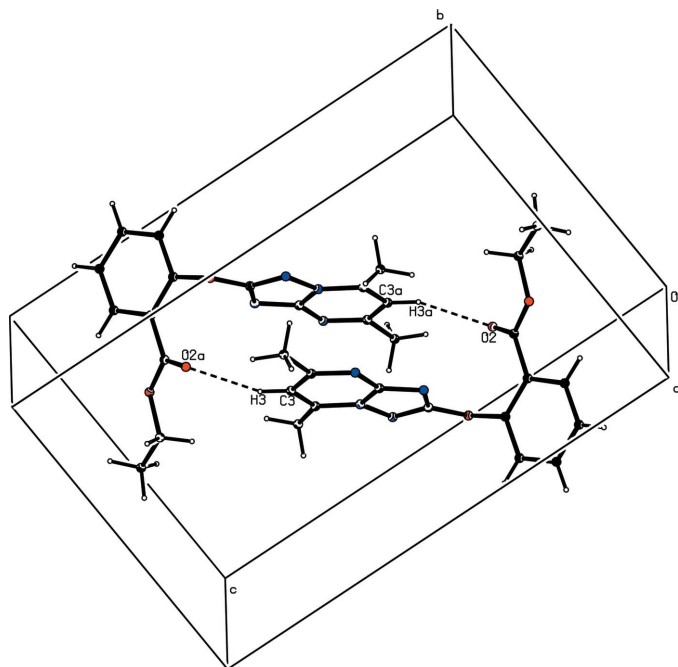
Figure 2
A view of the π–π stacking and intermolecular hydrogen bonding in the crystal structure of (I). Hydrogen bonds are shown as dashed lines. [Symmetry code: (a) −x, −y, −z + 2]

the bicylic triazolopyrimidine system (C7/N3/N2/C4/C3/C2/N1/C6/N4) and the benzene ring (C8–C13). In the crystal structure, adjacent pairs of molecules are linked by C—H⋯O hydrogen bonds (Table 2). Also, the two pyrimidine rings in these molecular pairs are exactly parallel by symmetry, with a distance between ring centroids of 3.488 (1) Å, suggesting further stabilization by way of offset π–π stacking interactions (Fig. 2).

Experimental

A mixture of ethyl 2-hydroxybenzoate (4 mmol) and sodium hydride (4 mmol) in anhydrous toluene (60 ml) was stirred at 373 K for 2 h. 2-Methylsulfonyl-1,2,4-triazolo[1,5-a]pyrimidine (1 mmol) was then added. The resulting reaction mixture was refluxed for about 20 h. After filtration, the solvent was removed under reduced pressure and the residue purified by column chromatography on silica gel (eluent: petroleum/acetone, 4:1 v/v) to afford compound (I) (yield 40%, m.p. 372 K). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.34–8.04 (m, 4H, Ar—H), 6.75 (s, 1H, 6-H), 4.21 (q, 2H, CH$_2$), 2.70 (s, 3H, 7-CH$_3$), 2.59 (s, 3H, 5-CH$_3$), 1.16 (t, 3H, CH$_3$). MS (EI 70 eV) m/z (%): 312 (2), 267 (26), 239 (100), 224 (3), 196 (10), 92 (5), 67 (6). Crystals suitable for X-ray analysis were grown from acetone at 277 K.

Crystal data

C$_{16}$H$_{16}$N$_4$O$_3$	D_x = 1.306 Mg m^{-3}
M_r = 312.33	Mo Kα radiation
Monoclinic, $P2_1/n$	Cell parameters from 2092
a = 9.0013 (13) Å	reflections
b = 10.5217 (15) Å	θ = 2.3–21.6°
c = 17.152 (3) Å	μ = 0.09 mm^{-1}
β = 102.038 (3)°	T = 292 (2) K
V = 1588.8 (4) Å^3	Block, colorless
Z = 4	0.30 × 0.20 × 0.20 mm

Data collection

Bruker SMART 4K CCD area-detector diffractometer	2093 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.065
Absorption correction: none	θ_{max} = 27.0°
9593 measured reflections	h = −11 → 10
3470 independent reflections	k = −6 → 13
	l = −21 → 21

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.051	$w = 1/[\sigma^2(F_o^2) + (0.0644P)^2]$
$wR(F^2)$ = 0.128	where $P = (F_o^2 + 2F_c^2)/3$
S = 0.91	$(\Delta/\sigma)_{max}$ = 0.003
3470 reflections	$\Delta\rho_{max}$ = 0.26 e Å^{-3}
211 parameters	$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected geometric parameters (°).

N4—C7—O1	123.75 (14)	O3—C15—C16	107.8 (2)
C9—C8—O1	116.19 (15)	C7—O1—C8	116.31 (12)
O3—C14—C13	111.83 (17)	C14—O3—C15	116.58 (17)
O1—C8—C13—C14	0.3 (2)	C9—C8—O1—C7	−98.75 (18)
C12—C13—C14—O3	22.5 (2)	C13—C14—O3—C15	−178.31 (14)
N4—C7—O1—C8	−16.9 (2)	C16—C15—O3—C14	−178.88 (19)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C3—H3⋯O2^i	0.93	2.36	3.248 (2)	160

Symmetry code: (i) −x, −y, −z + 2.

H atoms were placed in calculated positions and treated as riding (C—H = 0.93–0.97 Å), with displacement parameters U_{iso} set equal to 1.2 (CH and CH$_2$) or 1.5 (CH$_3$) times U_{eq} of the parent atom.

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1999); 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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