1-Ethyl-5-(4-methoxybenzoyl)-4-(4-methoxyphenyl)pyrimidine-2(1H)-thione

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The title compound, $C_{21}H_{20}N_2O_3S$, is a derivative of pyrimidine-2-thione and consists of planar fragments. The molecules are linked by C—H$\cdots$O/C—H$\cdots$S hydrogen bonds and by π–π and C—H$\cdots$$\pi$ interactions.

Comment

In general, pyrimidines have found much interest for their widespread potential biological activities (Kleemann & Engel, 1982) and medicinal applications, and so their chemistry has been investigated extensively (Brown, 1984, 1985). In particular, various analogues of pyrimidinethiones possess effective antibacterial, antifungal, antiviral, anti-AIDS, insecticidal and miticidal activities (Sankyo Co., 1984; De Clerq & Walker, 1985). Furthermore, many condensed heterocyclic systems, especially when linked to a pyrimidine ring, play an important role as analgesic, antipyretic and anti-inflammatory drugs (Vega et al., 1990), and also as herbicides (Chakaravorty et al., 1992) and plant growth regulators (Shishoo & Jain, 1992). In this paper, we report the crystal structure of the title compound, (I), a pyrimidine-2-thione derivative.

(I)
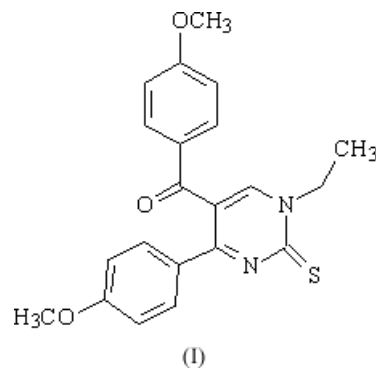
Compound (I) has a pyrimidine ring (N1/C19/N2/C18/C9/C10), a methoxybenzoyl group (C1/O1/C11–C16/O3/C17) and a methoxyphenyl group (C2–C7/O2/C8) (Fig. 1 and Table 1). In the pyrimidine ring, the S1═C19 bond distance of 1.666 (3) Å is longer than the 1.61 Å expected for an S═C double bond (Pauling, 1963). The C3—C2—C10—N1 torsion angle is 32.5 (4)° and the mean plane of the methoxyphenyl ring forms a dihedral angle of 72.39 (12)° with the mean plane of the methoxybenzoyl group. The pyrimidine ring forms a dihedral angle of 57.08 (13)° with the plane of the methoxybenzoyl group.

There is an intramolecular C—H$\cdots$S interaction (Fig. 1 and Table 2). There are also two types of intermolecular hydrogen bonds, C—H$\cdots$S and C—H$\cdots$O (Fig. 2). In the first of these intermolecular interactions, atom C18 acts as hydrogen-bond
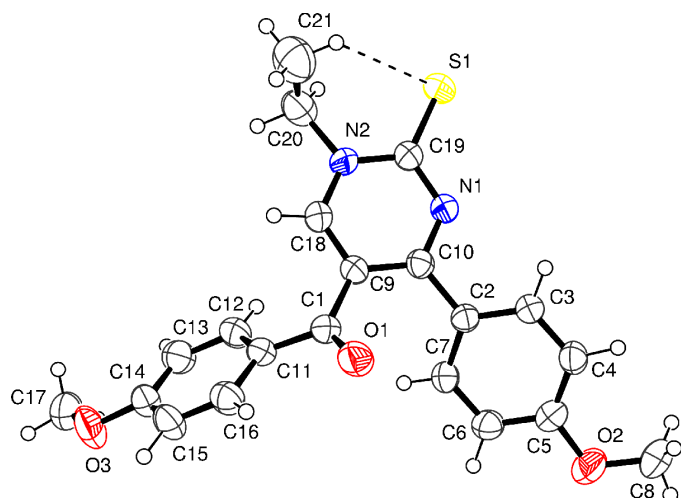
organic papers

Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of (I), showing the atomic numbering scheme and the intramolecular interaction. Displacement ellipsoids are drawn at the 50% probability level.
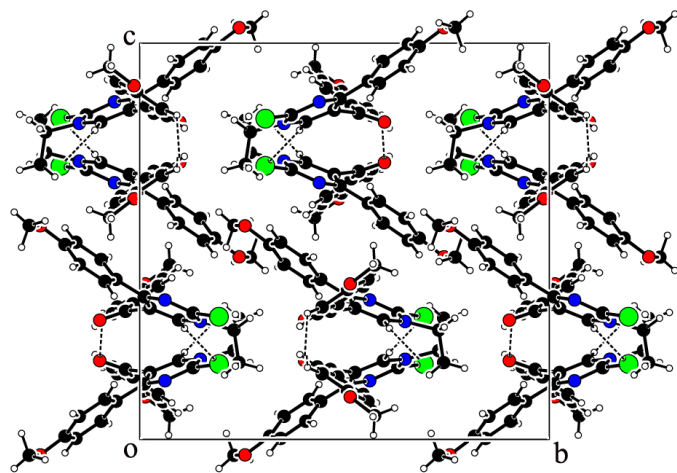

Figure 2
PLATON plot (Spek, 1997) of the crystal packing of (I), viewed down the *a* axis and showing the intermolecular hydrogen bonds as dashed lines.

donor to S1 at $(x - \frac{1}{2}, y, \frac{3}{2} - z)$. In the second type, atom C15 acts as donor to O1 at $(x - \frac{1}{2}, y, \frac{3}{2} - z)$. The crystal structure is also stabilized by π–π stacking interactions between the pyrimidine ring and benzene ring C11–C16 at $(\frac{1}{2} + x, y, \frac{1}{2} - z)$. The distance between the centroids of these rings is 3.784 (3) Å. The crystal structure also contains two C—H$\cdots\pi$ interactions (Table 2).

Experimental

An equimolar mixture of 4-(4-methoxybenzoyl)-5-(4-methoxy-phenyl)-2,3-dihydro-2,3-furandione (0.49 g, 1.48 mmol), easily obtained from oxalyl dichloride and 4,4′-dimethoxydibenzoyl-methane as described by Ziegler *et al.* (1967), and ethylthiourea was refluxed in 30 ml boiling benzene for 3.5 h. After evaporation of the solvent, the oily residue was treated with dry diethyl ether to give a yellow precipitate, which was filtered off and recrystallized from ethanol (yield 0.49 g, 88%; m.p. 466–467 K; Hökelek *et al.*, 2002; Yıldırım *et al.*, 2002). IR (KBr, cm^{-1}): ν 3060–2840 (*w*, aromatic and aliphatic C—H), 1650 (*s*, C=O), 1600 (*s*), 1570 (*m*), 1470 (*m*, C=C,

aromatic rings), 1110 (*m*, C=S); ^{1}H NMR (60 MHz, CDCl$_3$, p.p.m.): δ 8.08 (*s*, 1H at C-6), 7.83–7.50 (two *d*, 4H, Ph-H), 6.94–6·58 (two *d*, 4H, Ph-H), 4.82–4.36 (*q*, 2H, N-CH$_2$), 3.84 (*s*, 3H, OCH$_3$), 3.78 (*s*, 3H, OCH$_3$), 1.61 (*t*, 3H, CH$_3$). Elemental analysis calculated for C$_{21}$H$_{20}$N$_2$O$_3$S: C 66.29, H 5.30, N 7.36, S 8.42%; found: C 66.49, H 5.21, N 7.14, S 7.93%.

Crystal data

C$_{21}$H$_{20}$N$_2$O$_3$S	Mo $K\alpha$ radiation
$M_r = 380.45$	Cell parameters from 10 649
Orthorhombic, *Pbca*	reflections
$a = 12.472$ (7) Å	$\theta = 1.6$–$26.8°$
$b = 17.6737$ (13) Å	$\mu = 0.20$ mm^{-1}
$c = 17.0718$ (12) Å	$T = 293$ (2) K
$V = 3763$ (2) Å^3	Prism, yellow
$Z = 8$	$0.32 \times 0.27 \times 0.22$ mm
$D_x = 1.343$ Mg m^{-3}	

Data collection

Stoe IPDS-2 diffractometer	3313 independent reflections
ω rotation scans	1903 reflections with $I > 2\sigma(I)$
Absorption correction: by	$R_{int} = 0.124$
integration (*X-RED*32;	$\theta_{max} = 25.0°$
Stoe &Cie, 2002)	$h = -14 \rightarrow 14$
$T_{min} = 0.951$, $T_{max} = 0.975$	$k = -20 \rightarrow 20$
33 217 measured reflections	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	H atoms treated by a mixture of
$R[F^2 > 2\sigma(F^2)] = 0.048$	independent and constrained
$wR(F^2) = 0.097$	refinement
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2]$
3313 reflections	where $P = (F_o^2 + 2F_c^2)/3$
306 parameters	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.48$ e Å^{-3}
	$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C19	1.666 (3)	N2—C19	1.386 (3)
O1—C1	1.212 (3)	N2—C20	1.544 (4)
N1—C10	1.322 (3)	C9—C18	1.350 (4)
N1—C19	1.358 (3)	C9—C10	1.426 (3)
N2—C18	1.352 (3)		
C5—O2—C8	118.1 (3)	N1—C19—N2	117.7 (2)
O1—C1—C11	120.8 (2)	N1—C19—S1	121.18 (19)
O1—C1—C9	119.7 (2)	N2—C19—S1	121.0 (2)
C11—C1—C9	119.5 (2)	C21—C20—N2	108.6 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C18—H18$\cdots$S1^i	0.95 (3)	2.86 (3)	3.755 (3)	159 (2)
C15—H15$\cdots$O1^i	0.99 (3)	2.54 (3)	3.291 (4)	133 (2)
C21—H21$B\cdots$S1	0.96	2.80	3.383 (4)	120
C17—H17$B\cdots$Cg3^{ii}	0.94 (4)	2.86 (3)	3.618 (6)	139 (3)
C21—H21$A\cdots$Cg2^{iii}	0.96	2.76	3.567 (4)	142

Symmetry codes: (i) $x - \frac{1}{2}, y, \frac{3}{2} - z$; (ii) $-x, -y, -z$; (iii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$. Cg2 and Cg3 denote the centroids of benzene rings C2–C7 and C11–C16, respectively.

H atoms, except those belonging to atom C21, were located in difference Fourier maps and their positional and isotropic displacement parameters were refined. The C—H distances are in the range 0.84 (3)–1.05 (4) Å. H atoms bonded to C21 were positioned geometrically (C—H = 0.96 Å) and included in the subsequent refinement in the riding model approximation [U_{iso}(H) = 1.5U_{eq}(C)].

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32 (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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