organic papers

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Key indicators

Single-crystal X-ray study

T = 273 K

Mean σ(C–C) = 0.003 Å

R factor = 0.053

wR factor = 0.126

Data-to-parameter ratio = 16.8

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

2-Morpholino-3-*p*-tolylbenzo[4,5]thieno-[3,2-*d*]pyrimidin-4(3*H*)-one

In the crystal structure of the title compound, $C_{21}H_{19}N_3O_2S$, there are two crystallographically independent molecules, which are linked by C—H···O hydrogen bonds and π–π interactions.

Comment

We have recently focused on the synthesis of fused heterocyclic systems containing a fused pyrimidinone unit using the aza-Wittig reaction (Ding *et al.*, 2004). Some X-ray crystal structures of benzo[4,5]thieno[3,2-*d*]pyrimidinone derivatives have been reported (Cao *et al.*, 2006; Xu *et al.*, 2005). We present here the structure of one such thienopyrimidine derivative, (I).

(I)
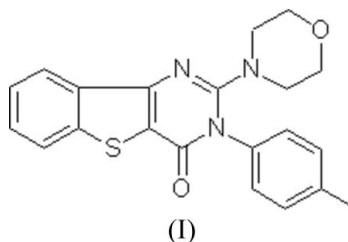
The title compound has two crystallographically independent molecules in the asymmetric unit (Fig. 1 and Table 1). The three fused rings of the benzo[4,5]thieno[3,2-*d*]-pyrimidinone system are essentially coplanar. The two morpholine rings show a distorted chair conformation [φ = 62.9 (2)°, θ = 177.2 (2)° and puckering amplitude = 0.574 (2) Å for O2/C19/C18/N3/C20/C21; φ = 168.8 (2)°, θ = 1.07 (2)° and puckering amplitude = 0.571 (2) Å for O4/C40/C39/N6/C41/C42]. Intermolecular C—H···O hydrogen bonds (Fig. 2 and Table 2) seem to be effective in stabilizing the crystal structure. There is also an intermolecular π–π interaction (Janiak, 2000); the interplanar and centroid–centroid distances between adjacent benzo[4,5]thieno[3,2-*d*]pyrimidinone systems related by an inversion center are 3.535 (1) and 3.891 (1) Å.

Experimental

To a solution of ethyl 3-triphenylphosphoranylideneamino-benzo[*b*]thiophene-2-carboxylate (3 mmol) in dry dichloromethane (5 ml) was added *p*-tolylisocyanate (3 mmol) under nitrogen at room temperature. After the reaction mixture was left to stand for 10 h at 273–278 K, the solvent was removed under reduced pressure and ether/petroleum ether (1:2 *v*/*v*, 12 ml) was added to precipitate triphenylphosphine oxide. After filtration, the solvent was removed to give the carbodiimide 3-*p*-tolyliminomethyleneaminobenzo[*b*]-

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thiophene-2-carboxylic acid ethyl ester, (II), which was used directly without further purification. To a solution of (II) (15 ml) in dichloromethane (15 ml) was added morpholine (3 mmol). After the reaction mixture had been allowed to stand for 0.5 h, the solvent was removed and anhydrous ethanol (10 ml) with several drops of EtONa in EtOH was added. The mixture was stirred for 2 h at room temperature. The solution was concentrated under reduced pressure and the residue was crystallized from ethanol to give the title compound, (I). The product was recrystallzied from ethanol/dichloromethane (1/2 v/v) at room temperature to give single crystals suitable for X-ray diffraction.

Crystal data

$C_{21}H_{19}N_3O_2S$	$Z = 8$
$M_r = 377.45$	$D_x = 1.335$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 16.693$ (3) Å	$\mu = 0.19$ mm^{-1}
$b = 12.970$ (2) Å	$T = 273$ (2) K
$c = 17.392$ (3) Å	Block, colorless
$\beta = 94.002$ (3)°	$0.30 \times 0.26 \times 0.12$ mm
$V = 3756.6$ (12) Å^3	

Data collection

Bruker SMART 4K CCD area-detector diffractometer	38099 measured reflections
φ and ω scans	8200 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	5715 reflections with $I > 2\sigma(I)$
$T_{min} = 0.944$, $T_{max} = 0.977$	$R_{int} = 0.105$
	$\theta_{max} = 27.0°$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.053$	$w = 1/[\sigma^2(F_o^2) + (0.0634P)^2]$
$wR(F^2) = 0.126$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.96$	$(\Delta/\sigma)_{max} < 0.001$
8200 reflections	$\Delta\rho_{max} = 0.31$ e Å^{-3}
489 parameters	$\Delta\rho_{min} = -0.37$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C7—S1	1.7355 (18)	C29—S2	1.7387 (18)
C27—S2	1.741 (2)		
C5—C6—S1	126.64 (16)	C22—C27—S2	112.83 (14)
C1—C6—S1	112.61 (13)	C28—C29—S2	113.65 (14)
C8—C7—S1	113.86 (14)	C30—C29—S2	124.19 (15)
C9—C7—S1	124.02 (14)	C7—S1—C6	90.10 (9)
C26—C27—S2	126.31 (17)	C29—S2—C27	90.08 (9)

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

| D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C17—H17C$\cdots$O1^i	0.96	2.58	3.304 (3)	133
C16—H16$\cdots$O3^{ii}	0.93	2.59	3.479 (3)	160
C4—H4$\cdots$O2^{iii}	0.93	2.57	3.395 (3)	148

Symmetry codes: (i) $-x+2, -y, -z+2$; (ii) $-x+1, -y+1, -z+2$; (iii) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.

All H atoms were located in a difference map and treated as riding atoms, with C—H = 0.93 (aromatic), 0.96 (CH$_3$) and 0.97 Å (CH$_2$), and U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C).
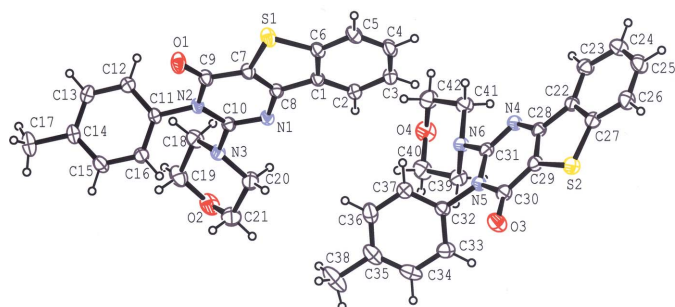
Figure 1
The asymmetric unit of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.
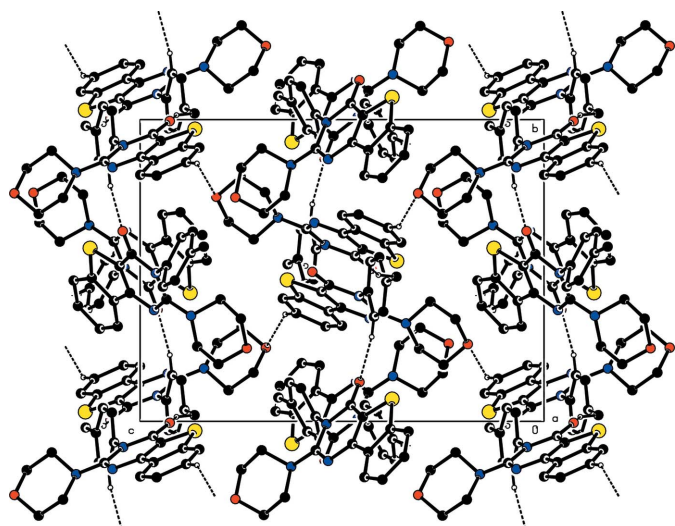
Figure 2
A packing view of (I) along the a axis, showing the C—H$\cdots$O hydrogen bonds (dashed lines). H atoms except those involved in hydrogen bonds have been omitted for clarity.

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: PLATON (Spek, 2003); software used to prepare material for publication: SHELXTL (Sheldrick, 2001).

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