5-Methyl-2-(2-nitrophenyloxy)-3-*p*-tolyl-8,9,10,11-tetrahydrobenzo[4′,5′]thieno-[3′,4′:5,6]pyrido[4,3-*d*]pyrimidin-4(3*H*)-one

He-Lian Chen and Hong-Wu He*

Key Laboratory of Pesticide and Chemical Biology, College of Chemistry, Central China Normal University, Wuhan 430079, People's Republic of China

Correspondence e-mail:
he1208@mail.ccnu.edu.cn

Key indicators

Single-crystal X-ray study
T = 292 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.052
wR factor = 0.172
Data-to-parameter ratio = 12.4

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

In the title compound, $C_{27}H_{23}N_4O_4S$, the three fused heterocyclic rings are essentially coplanar. The crystal stacking is mainly due to π–π interactions and intermolecular C—H$\cdots$O hydrogen-bonding interactions.

Comment

Among many known heterocyclic compounds, derivatives containing pyridine groups have received much attention since they possess significant biological activity (Augusto *et al.*, 1995). The title compound, (I), belongs to this family of heterocyclic compounds and we present its crystal structure here.

(I)
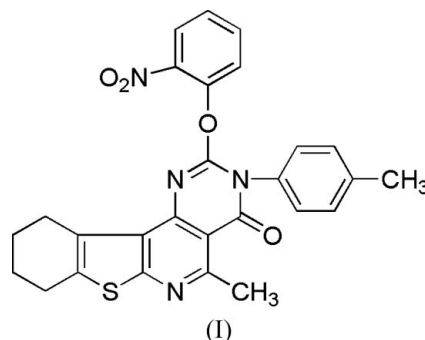
In (I) (Fig. 1), the C—S bond lengths are longer than those observed in free thiophene [1.714 (3) Å; Bonham & Momany, 1963] and thieno-[2,3-*c*]-pyridine [1.728 (1) and 1.731 (1) Å; Nerenz *et al.*, 1997]. Selected bond lengths and angles are listed in Table 1. The C8—S1—C1 angle in (I) is slightly less than that observed in free thiophene [92.2 (2)°]. The C6—C7—C8—N1 and C14—C11—C12—C7 torsion angles (Table 1) indicate the coplanarity of the three fused heterocyclic rings.

The short intermolecular distances between the centroids of the thiophene (*Cg*1) and pyrimidine (*Cg*3) rings [*Cg*1$\cdots$*Cg*3^{i} = 3.7496 (16) Å; symmetry code: (i) $\frac{1}{2} - x$, $\frac{3}{2} - y$, $-z$] indicate the existence of π–π stacking interactions (Janiak, 2000), which, together with hydrogen-bonding interactions (Table 2), stabilize the crystal packing (Fig. 2)

Experimental

2-Methyl-4-amino-3-ethoxycarbonyl-5,6,7,8-(4*H*)-tetrahydrobenzo-[4′,5′]thieno-[2,3-*b*]-pyridine, (II), was prepared according to literature procedures in 90% yield (Augusto *et al.*, 1995). The iminophosphorane of (II) was synthesized according to the literature procedure of Wamhoff *et al.* (1993) in 82% yield.

To a solution of the iminophosphorane of (II) (1 mmol) in dry CH_2Cl_2 (20 ml) and a catalytic amount of K_2CO_3 (0.05 mmol) was
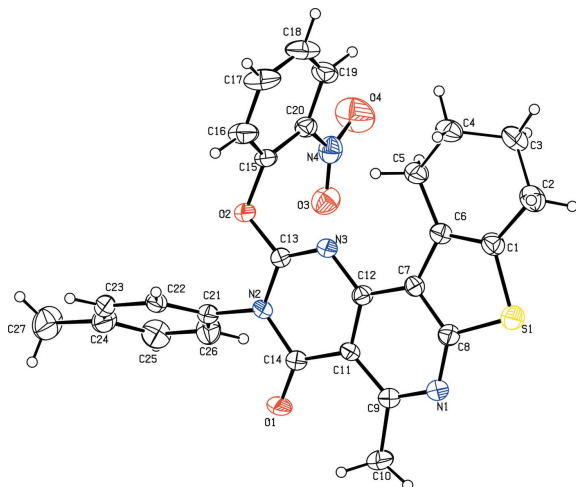
doi:10.1107/S1600536805040870

Figure 1
View of (I), showing the atom-labelling scheme for the non-H atoms and 50% probability displacement ellipsoids.
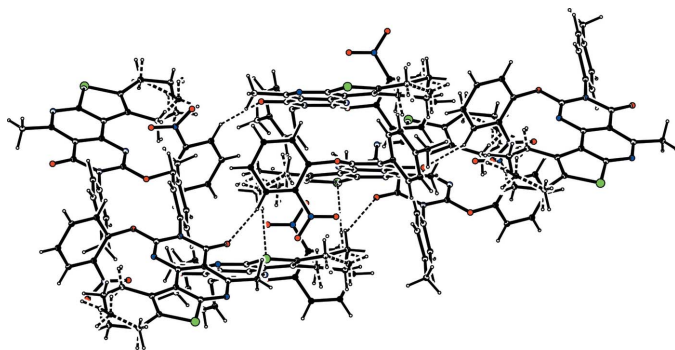

Figure 2
The crystal structure of (I), showing the formation of N—H···O hydrogen bonds (dashed lines).

added 4-methylphenyl isocyanate (1.1 mmol) (Ding *et al.*, 1999). After the reaction mixture had been left to stand for 6 h, the solvent was removed under reduced pressure and Et₂O/petroleum ether was added to precipitate the side-product triphenylphosphine oxide which was then removed by filtration. Subsequent removal of the solvent gave the corresponding carbodiimide, which was used directly without further purification.

To a solution of the carbodiimide in ethanol (15 ml) was added 2-nitrophenol (1.1 mmol) and a catalytic amount of sodium ethoxide in ethanol (Wang *et al.*, 2004). After the mixture had been stirred for 12 h at 300 K, the solution was concentrated and the residue was recrystallized from CH_3CN to give colourless blocks of the title compound (I) in one week.

Crystal data

$C_{27}H_{22}N_4O_4S$	$D_x = 1.378$ Mg m^{-3}
$M_r = 498.55$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 4220
$a = 9.1381$ (8) Å	reflections
$b = 17.0819$ (14) Å	$\theta = 1.8$–25.0°
$c = 16.0332$ (14) Å	$\mu = 0.18$ mm^{-1}
$\beta = 106.203$ (2)°	$T = 292$ (2) K
$V = 2403.3$ (4) Å^3	Block, colourless
$Z = 4$	$0.30 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	4220 independent reflections
	2922 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.040$
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	$\theta_{\text{max}} = 25.0°$
	$h = -10 \rightarrow 10$
$T_{\min} = 0.949$, $T_{\max} = 0.983$	$k = -20 \rightarrow 19$
12011 measured reflections	$l = -19 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0911P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.052$	$+ 0.0243P]$
$wR(F^2) = 0.172$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{\max} = 0.042$
4220 reflections	$\Delta\rho_{\max} = 0.28$ e Å^{-3}
340 parameters	$\Delta\rho_{\min} = -0.26$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C1—S1	1.747 (3)	C8—S1	1.734 (3)
C8—S1—C1	90.68 (13)		
C1—C2—C3—C4	45.2 (9)	C6—C7—C8—N1	−177.3 (3)
C1—C2—C3′—C4′	−45.2 (12)	C14—C11—C12—C7	−178.7 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
C19—H19···O1^i	0.93	2.43	3.256 (4)	148

Symmetry code: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$.

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.93–0.97 Å, with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ or $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(C)$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXL97*.

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