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Key indicators

Single-crystal X-ray study
 T = 292 K
 Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
 R factor = 0.056
 wR factor = 0.159
 Data-to-parameter ratio = 16.7

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

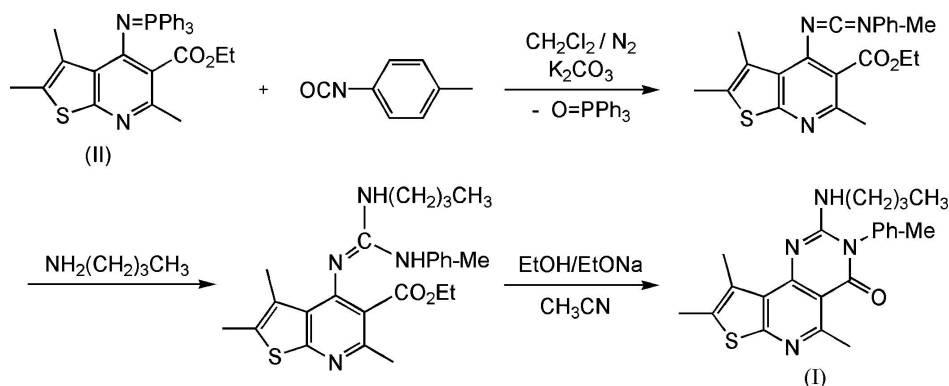
**8-Butylamino-1,2,5-trimethyl-7-p-tolyl-3-thia-
 4,7,9-triazacyclopenta[a]naphthalen-6(7H)-one**

In the title compound, $\text{C}_{23}\text{H}_{26}\text{N}_4\text{OS}$, the fused tricyclic system is essentially planar. The crystal stacking is mainly due to $\pi-\pi$ interactions and intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen-bond interactions.

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Comment

Among many known heterocyclic compounds, derivatives containing the pyridine system have received much attention since they have been demonstrated to 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.



In (I) (Fig. 1), the C–S bond lengths [1.733 (2) and 1.741 (2) Å] are greater 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 C3–S1–C6 angle of 91.43 (10)° in (I) is slightly less than that observed in free thiophene [92.2 (2)°]. As expected for a non-

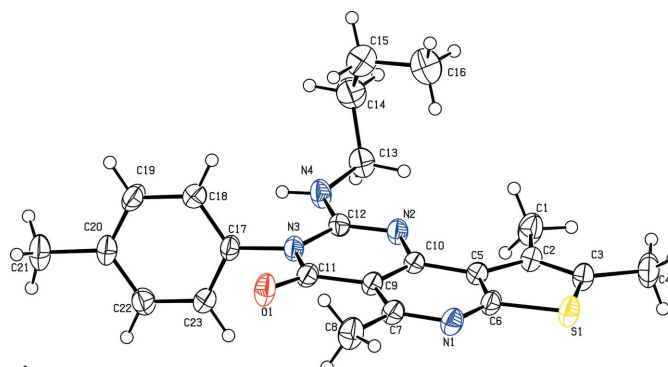


Figure 1
 View of (I), showing the labelling scheme for the non-H atoms and 50% probability displacement ellipsoids.

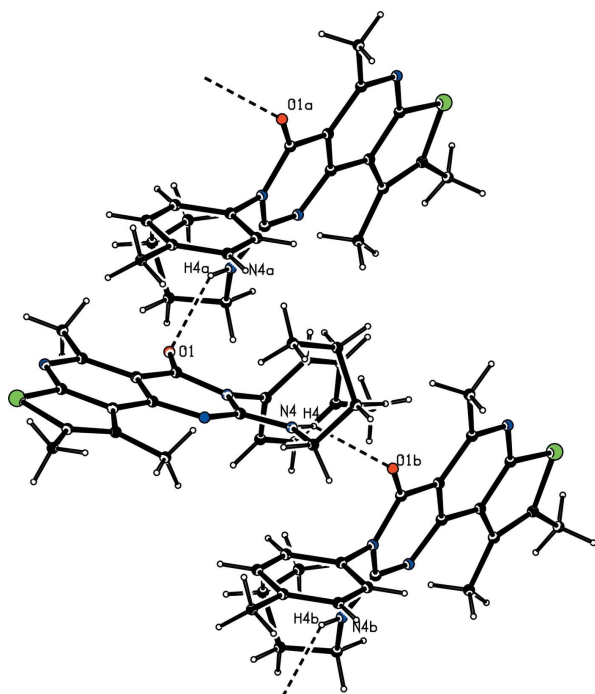


Figure 2
The crystal structure of (I), showing the formation of N–H···O hydrogen bonds (dashed lines).

protonated ring system, the C12–N2–C10 angle of 118.22 (18)° is smaller than 120° (Ghosh & Simonsen, 1993). The torsion angles S1–C6–C5–C10 and N2–C10–C9–C7 are –178.57 (15) and –176.09 (19)°, respectively, showing the essential planarity of the fused tricyclic system. There are some weak intermolecular N–H···O hydrogen-bonding interactions (Table 2).

The short intermolecular distances between the centroids of the thiophene (*Cg*1) and pyridine (*Cg*2) rings [*Cg*1···*Cg*2ⁱ = 3.691 (1) Å and *Cg*2···*Cg*2ⁱ = 3.843 (1) Å; symmetry code: (i) $\frac{1}{2} - x, \frac{3}{2} - y, -z$] indicate the existence of π – π stacking interactions (Janiak, 2000), which stabilize the crystal packing (Fig. 2) together with the hydrogen-bonding interactions.

Experimental

2,3,6-Trimethyl-4-amino-5-ethoxycarbonylthieno[2,3-*b*]pyridine, (II), was prepared according to a literature procedure in 63% yield (Augusto *et al.*, 1995). The iminophosphorane of (II) was synthesized according to a literature report in 93% yield (Wamhoff *et al.*, 1993). To a solution of the iminophosphorane of (II) (1 mmol) in dry CH₂Cl₂ (20 ml) containing a catalytic amount of K₂CO₃ (0.05 mmol) was added 4-methylphenyl isocyanate (1.1 mmol) under an N₂ atmosphere at room temperature (Ding *et al.*, 1999). After the reaction mixture was allowed to stand for 5–12 h, the solvent was removed under reduced pressure and Et₂O and petroleum ether were 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 prepared above in ethanol (15 ml) was added *n*-butylamine (1.1 mmol) and a catalytic amount of sodium ethoxide in ethanol (Wang *et al.*, 2004). After the mixture had been stirred for 14 h at

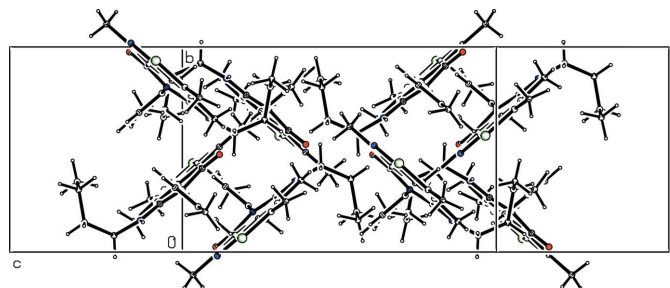


Figure 3
Part of the crystal structure of (I), showing the π – π stacking interactions.

303 K, the solution was concentrated and the residue was recrystallized from CH₃CN to give colorless prisms of the title compound, (I), after one week.

Crystal data

C₂₃H₂₆N₄OS
M_r = 406.54
 Monoclinic, *C*2/*c*
a = 21.5659 (19) Å
b = 9.0711 (8) Å
c = 22.646 (2) Å
 β = 109.746 (2)°
V = 4169.7 (6) Å³
Z = 8

D_x = 1.295 Mg m^{–3}
 Mo *K*α radiation
 Cell parameters from 2860 reflections
 θ = 2.3–25.9°
 μ = 0.18 mm^{–1}
T = 292 (2) K
 Prism, colorless
 0.30 × 0.20 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
T_{min} = 0.949, *T_{max}* = 0.965
 11954 measured reflections

4535 independent reflections
 3493 reflections with *I* > 2σ(*I*)
R_{int} = 0.031
 θ_{\max} = 27.0°
h = –27 → 25
k = –11 → 11
l = –28 → 26

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.056
wR(*F*²) = 0.159
S = 1.05
 4535 reflections
 271 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0773P)^2 + 3.0234P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.003$
 $\Delta\rho_{\max} = 0.55 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.29 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C3–S1	1.741 (2)	C6–S1	1.733 (2)
C12–N2–C10	118.22 (18)	C6–S1–C3	91.43 (10)
C10–C5–C6–S1	–178.57 (15)	C7–C9–C10–N2	–176.08 (19)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N4–H4···O1 ⁱ	0.89 (1)	2.22 (2)	2.948 (2)	139 (2)
C13–H13B···N2	0.97	2.40	2.814 (3)	106

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

All C-bound H atoms were positioned geometrically, with C–H distances of 0.96, 0.93 and 0.97 Å, respectively, for methyl, methylene

and aromatic H atoms. The H atoms were allowed to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$. The N-bound atom H4 was located in a difference Fourier map and refined with the N–H distance restrained to 0.89 (1) Å, with $U_{\text{iso}}(\text{H}) = 0.05 \text{ \AA}^2$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; 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: *SHELXTL*.

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