

1-Benzoyl-3-(4-methylpyridin-2-yl)thiourea

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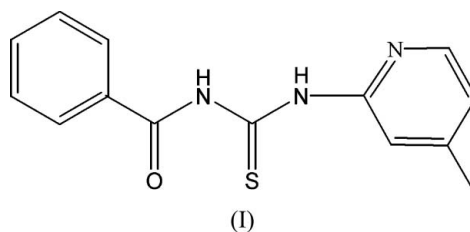
Key indicators

Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.050
 wR factor = 0.112
Data-to-parameter ratio = 18.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $\text{C}_{14}\text{H}_{13}\text{N}_3\text{OS}$, the dihedral angle between the two aromatic ring planes is 34.00 (8)°. The crystal packing shows centrosymmetric dimers formed by intermolecular $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds which are stacked along $[010]$.

Comment

Thiourea and its derivatives are a well known class of excellent ligands for transition metals, which also exhibit redox activity with reducible metal ions making the reaction systems complicated (Griffith *et al.*, 1978; Ainscough & Brodie, 1978; Doona & Stanbury, 1996, and references therein). Study of the *N*-benzoyl-*N'*-alkylthioureaides and the *N*-benzoyl-*N',N'*-dialkylthioureaides has recently received attention because of their potential use as highly selective reagents for the enrichment and separation of metal cations (Bourne & Koch, 1993; Beyer *et al.*, 1996; del Campo *et al.*, 2002). In this context, we have synthesized several new compounds, including the title compound, (I). The molecular structure is closely related to that of *N*-(2-pyridyl)-*N'*-benzoylthiourea (Kaminsky *et al.*, 2002) with similar bond lengths and angles. The conformation of the molecule with respect to the carbonyl and thiocarbonyl part is nearly planar, as is reflected by the torsion angles $\text{C}7-\text{N}3-\text{C}8-\text{O}1$ and $\text{C}8-\text{N}3-\text{C}7-\text{N}2$ of 2.9 (3) and -5.2 (3)°, respectively. This is associated with the typical thiourea intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond (Table 2). The largest deviation of the atoms defining the plane $\text{C}5/\text{N}2/\text{C}7/\text{N}3/\text{C}8/\text{O}1/\text{C}9$ is 0.024 (2) Å for C7, whereas S1 is 0.133 (1) Å out of this plane. The dihedral angles between this plane and ring planes $\text{C}9-\text{C}14$ and $\text{N}1/\text{C}1-\text{C}5$ are 24.16 (8) and 10.50 (9)°, respectively. Both aromatic ring planes make a dihedral angle of 34.00 (8)°, similar to that of 31.7 (2)° for the 2-pyridyl compound.



The crystal packing (Fig. 2) is determined by intermolecular $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds (Table 2), forming centrosymmetric dimers which are stacked along $[010]$ (Fig. 2); this is also a common structural feature for this type of compound (Arslan *et al.*, 2003; Saeed & Flörke, 2006).

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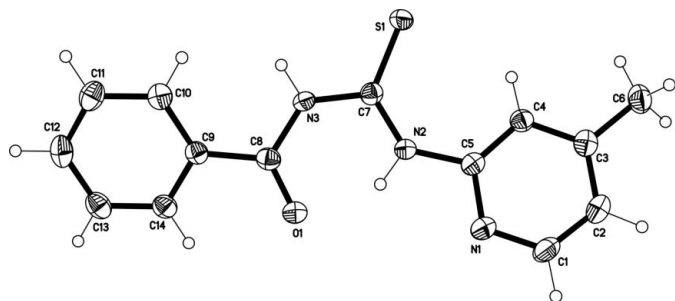


Figure 1

Molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

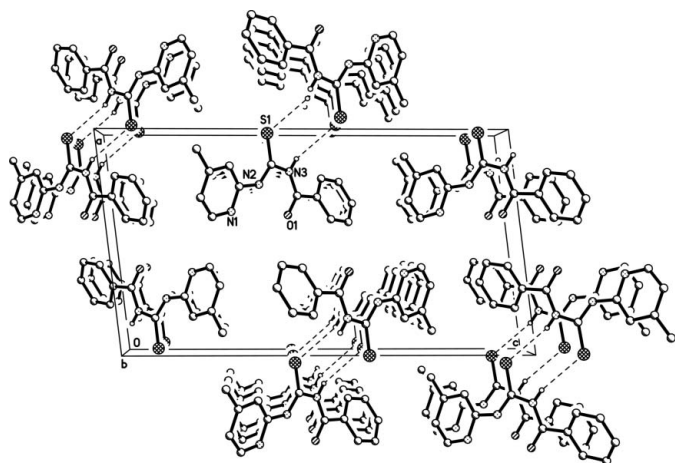


Figure 2

Crystal packing viewed along [010], with the intermolecular hydrogen-bonding pattern indicated as dashed lines. H atoms not involved in the hydrogen bonding have been omitted.

Experimental

A solution of benzoyl chloride (2 mmol) in 50 ml of acetone was added to KSCN (5 mmol) in 25 ml of acetone. The mixture was stirred for 30 min at 313 K and cooled to room temperature. A solution of 2-amino-4-methylpyridine (5 mmol) in 25 ml of acetone was added dropwise over a period of 15 min and the mixture was stirred for 2 h. The yellow precipitate was recrystallized from dichloromethane.

Crystal data

$C_{14}H_{13}N_3OS$
 $M_r = 271.33$
 Monoclinic, $P2_1/c$
 $a = 11.9247$ (15) Å
 $b = 5.1952$ (7) Å
 $c = 21.615$ (3) Å
 $\beta = 96.962$ (3)°
 $V = 1329.2$ (3) Å³

$Z = 4$
 $D_x = 1.356$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.24$ mm⁻¹
 $T = 120$ (2) K
 Needle, pale yellow
 $0.48 \times 0.18 \times 0.12$ mm

Data collection

Bruker SMART APEX
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2002)
 $T_{\min} = 0.912$, $T_{\max} = 0.971$

11451 measured reflections
 3254 independent reflections
 2026 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.062$
 $\theta_{\text{max}} = 28.2^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.112$
 $S = 0.88$
 3254 reflections
 173 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.044P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.38$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.31$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

S1—C7	1.6616 (19)	N3—C8	1.386 (2)
N2—C7	1.335 (2)	N3—C7	1.387 (2)
N2—C5	1.406 (2)	C8—C9	1.480 (3)
C7—N2—C5	133.23 (17)	N2—C7—N3	114.41 (16)
C8—N3—C7	128.30 (16)	N3—C8—C9	116.87 (16)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2B \cdots O1	0.88	1.83	2.594 (2)	143
N3—H3A \cdots S1 ⁱ	0.88	2.77	3.567 (2)	150

Symmetry code: (i) $-x, -y + 1, -z$.

H atoms were located in difference Fourier maps and refined at idealized positions riding on the C and N atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ and $1.5U_{\text{eq}}(\text{methyl C})$, $N-H = 0.88$ Å, and $C-H = 0.95$ and 0.98 Å. Methyl H atoms were clearly identified in difference syntheses, then idealized and refined as rigid groups allowed to rotate but not tip.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2002); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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