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Crystal structure of 4-methyl-*N*-[(4-methylpyridin-2-yl)carbamothioyl]benzamide

Farook Adam,[a]* Nadiah Ameram[a] and Naser Eltaher Eltayeb[b]‡

[a]School of Chemical Sciences, 11800, USM Pulau Pinang, Malaysia, and [b]College of Sciences and Arts, Rabigh, King Abdulaziz University, Saudi Arabia, and International University of Africa, Khartoum, Sudan. *Correspondence e-mail: farook@usm.my

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‡ Additional correspondence author, e-mail: nasertaha90@hotmail.com.

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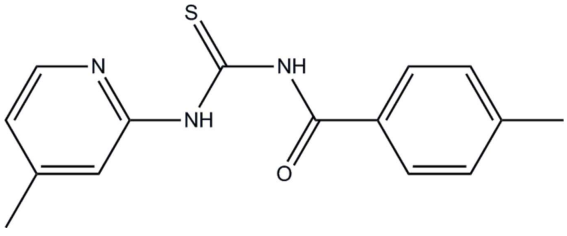
In the title compound, $C_{15}H_{15}N_3OS$, the dihedral angle between the planes of the benzene and pyridine rings is 26.86 (9)°. Intramolecular N—H···O and C—H···S hydrogen bonds both generate $S(6)$ rings. The C=O and C=S bonds lie to opposite sides of the molecule. In the crystal, inversion dimers linked by pairs of N—H···S hydrogen bonds generate $R_2^2(8)$ loops.

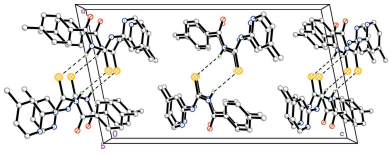
1. Chemical context

The role of benzoyl thiourea derivatives in coordination chemistry has been extensively studied and quite satisfactorily elucidated. As benzoyl thioureas have suitable C=O and C=S functional groups, they can be considered as useful chelating agents due to their ability to encapsulate metal ions into their coordinating moiety. Thiourea and its derivatives have found extensive applications in the fields of medicine, agriculture and analytical chemistry. Thioureas are also known to exhibit a wide range of biological activities including anti-cancer (Saeed *et al.*, 2010*a*), antifungal (Saeed *et al.*, 2010*b*) and as agrochemicals (Xu *et al.*, 2003). As part of our studies in this area, we now describe the synthesis and structure of the title compound, (I).



2. Structural commentary

The title compound (Fig. 1) is a benzoyl thiourea derivative and analogous to a compound recently reported by us (Adam *et al.*, 2014), except that the other substituent is changed to methylpyridine and the thiourea moiety is still in a *para* position. The dihedral angle between the planes of the benzene and pyridine rings is 26.86 (9)°. The C=O bond length of 1.225 (2) Å is comparable to that observed in *N*-benzoyl-*N*′-phenylthiourea (Hassan *et al.*, 2008*a*). The C—N bond lengths are in the range 1.328 (2)–1.417 (2) Å, shorter than the normal single C—N bond length (1.469 Å), indicating partial double-bond character owing to the resonance effect at the carbonylthiourea moiety.



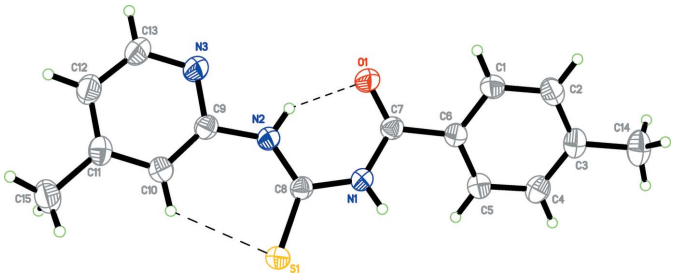


Figure 1
The molecular structure of the title compound, with 50% probability displacement ellipsoids. Hydrogen bonds are shown as dashed lines.

As in most benzoyl thiourea derivatives, an intramolecular N—H···O hydrogen bond leads to the formation of an *S*(6) ring, namely, C7/N1/C8/N2/H2/O1. An intramolecular C—H···S interaction (C9/N2/C8/S1/H10/C10) also generates an *S*(6) ring (Fig. 1, Table 1).

3. Supramolecular features

In the crystal of (I), inversion dimers linked by pairs of N—H···S hydrogen bonds (Table 1, Fig. 2) generate $R_2^2(8)$ loops. As free rotation about the N1—C7 and N2—C8 single bonds is hindered, the C=O and C=S bonds are unlikely to align at the same side of the molecule in order to form a chelate with a metal ion.

4. Synthesis and crystallization

The title compound was prepared according to a slight modification of the method described by Hassan *et al.* (2008*b*). *p*-Benzoyl chloride (13 mmol) was added dropwise to a stirred acetone solution (30 ml) of ammonium thiocyanate (13 mmol). The mixture was stirred for 10 min. A solution of 2-amino-4-picoline in acetone was added and the reaction mixture was refluxed for 3 h, after which the solution was poured into a beaker containing some ice cubes. The resulting precipitate was collected by filtration, washed several times with a cold ethanol/water mixture and purified by recrystallization from an ethanol solution.

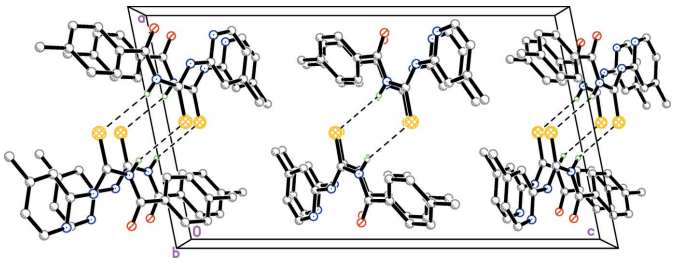


Figure 2
The crystal packing of the title compound viewed down the *c* axis. Hydrogen bonds are shown as dashed lines.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1*N*2···O1	0.82 (2)	1.94 (2)	2.644 (2)	144 (2)
N1—H1*N*1···S1^{i}	0.81 (2)	2.74 (2)	3.511 (2)	158 (2)
C10—H10*A*···S1	0.93	2.57	3.221 (2)	127

Symmetry code: (i) $-x+1, -y+2, -z+1$.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H-atoms on the N atoms were located in a difference-Fourier map and were freely refined. All other H atoms were positioned geometrically and refined using a riding model with C—H = 0.93–0.96 Å and U_{iso}(H) = 1.2U_{eq}(aromatic C) or 1.5U_{eq}(methyl C).

Acknowledgements

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Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_{15}N_3OS$
M_r	285.36
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	294
a, *b*, *c* (Å)	11.5297 (12), 6.1860 (6), 20.657 (2)
β (°)	101.431 (2)
V (Å^3)	1444.1 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.22
Crystal size (mm)	0.38 × 0.34 × 0.09
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2005)
T_{min}, T_{max}	0.920, 0.981
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15813, 4233, 2790
R_{int}	0.028
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.706
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.164, 1.05
No. of reflections	4233
No. of parameters	191
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.27, −0.19

Computer programs: *APEX2* and *SAINT* (Bruker, 2005), *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

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supporting information

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Crystal structure of 4-methyl-*N*-[(4-methylpyridin-2-yl)carbamothioyl]benzamide

Farook Adam, Nadiah Ameram and Naser Eltaher Eltayeb

Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

4-Methyl-*N*-[(4-methylpyridin-2-yl)carbamothioyl]benzamide

Crystal data

$C_{15}H_{15}N_3OS$
$M_r = 285.36$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 11.5297$ (12) Å
$b = 6.1860$ (6) Å
$c = 20.657$ (2) Å
$\beta = 101.431$ (2)°
$V = 1444.1$ (3) Å^3
$Z = 4$
$F(000) = 600$
$D_x = 1.313$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3960 reflections
$\theta = 2.4$–25.9°
$\mu = 0.22$ mm^{-1}
$T = 294$ K
Plate, colourless
0.38 × 0.34 × 0.09 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.920$, $T_{max} = 0.981$
15813 measured reflections
4233 independent reflections
2790 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 30.1°$, $\theta_{min} = 1.8°$
$h = -16 \rightarrow 16$
$k = -8 \rightarrow 8$
$l = -29 \rightarrow 29$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.164$
$S = 1.05$
4233 reflections
191 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0866P)^2 + 0.1249P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.47752 (4)	0.82687 (9)	0.41107 (2)	0.0655 (2)
O1	0.10758 (10)	1.0358 (2)	0.43058 (7)	0.0664 (4)
N1	0.30931 (13)	1.0520 (2)	0.44717 (7)	0.0489 (3)
N2	0.24183 (13)	0.7757 (3)	0.37524 (7)	0.0499 (3)
N3	0.11827 (13)	0.5315 (3)	0.31789 (8)	0.0656 (4)
C1	0.11290 (16)	1.3270 (3)	0.53813 (9)	0.0549 (4)
H1A	0.0514	1.2271	0.5317	0.066*
C2	0.11387 (17)	1.4947 (3)	0.58230 (9)	0.0618 (5)
H2A	0.0534	1.5049	0.6060	0.074*
C3	0.20271 (18)	1.6472 (3)	0.59200 (9)	0.0585 (5)
C4	0.29222 (18)	1.6283 (3)	0.55643 (9)	0.0595 (5)
H4A	0.3525	1.7306	0.5622	0.071*
C5	0.29362 (16)	1.4598 (3)	0.51247 (8)	0.0525 (4)
H5A	0.3547	1.4492	0.4892	0.063*
C6	0.20408 (14)	1.3073 (3)	0.50317 (8)	0.0463 (4)
C7	0.20039 (14)	1.1224 (3)	0.45721 (8)	0.0481 (4)
C8	0.33584 (14)	0.8813 (3)	0.40921 (7)	0.0456 (4)
C9	0.23136 (14)	0.5873 (3)	0.33544 (7)	0.0485 (4)
C10	0.32251 (15)	0.4763 (3)	0.31581 (8)	0.0546 (4)
H10A	0.4004	0.5224	0.3292	0.065*
C11	0.29672 (18)	0.2966 (3)	0.27621 (8)	0.0549 (4)
C12	0.18012 (19)	0.2358 (4)	0.25798 (10)	0.0673 (5)
H12A	0.1591	0.1146	0.2316	0.081*
C13	0.0953 (2)	0.3570 (4)	0.27931 (12)	0.0766 (6)
H13A	0.0167	0.3150	0.2661	0.092*
C14	0.2033 (3)	1.8322 (4)	0.64013 (11)	0.0836 (7)
H14A	0.2708	1.9228	0.6397	0.125*
H14B	0.2073	1.7754	0.6838	0.125*
H14C	0.1322	1.9156	0.6274	0.125*
C15	0.3924 (2)	0.1738 (4)	0.25264 (13)	0.0834 (7)
H15A	0.4636	0.1785	0.2858	0.125*
H15B	0.4068	0.2380	0.2126	0.125*

H15C	0.3682	0.0262	0.2443	0.125*
H1N2	0.181 (2)	0.810 (4)	0.3871 (12)	0.083 (7)*
H1N1	0.3673 (18)	1.100 (3)	0.4720 (10)	0.055 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0427 (3)	0.0886 (4)	0.0651 (3)	−0.0032 (2)	0.0107 (2)	−0.0266 (2)
O1	0.0437 (7)	0.0727 (10)	0.0793 (9)	0.0008 (6)	0.0035 (6)	−0.0220 (7)
N1	0.0440 (7)	0.0525 (9)	0.0488 (7)	−0.0028 (6)	0.0057 (6)	−0.0086 (6)
N2	0.0429 (7)	0.0548 (9)	0.0498 (7)	0.0016 (6)	0.0040 (6)	−0.0088 (6)
N3	0.0508 (8)	0.0691 (11)	0.0723 (10)	−0.0025 (8)	0.0012 (7)	−0.0189 (8)
C1	0.0478 (9)	0.0604 (11)	0.0555 (9)	0.0019 (8)	0.0083 (7)	−0.0018 (8)
C2	0.0624 (11)	0.0725 (13)	0.0510 (9)	0.0149 (10)	0.0124 (8)	−0.0027 (8)
C3	0.0731 (12)	0.0516 (11)	0.0464 (9)	0.0149 (9)	0.0011 (8)	0.0002 (7)
C4	0.0701 (12)	0.0457 (10)	0.0602 (10)	−0.0014 (9)	0.0066 (9)	0.0008 (8)
C5	0.0597 (10)	0.0466 (10)	0.0520 (9)	0.0011 (8)	0.0127 (7)	0.0038 (7)
C6	0.0475 (8)	0.0447 (9)	0.0452 (8)	0.0044 (7)	0.0053 (6)	0.0016 (6)
C7	0.0454 (8)	0.0494 (10)	0.0480 (8)	0.0005 (7)	0.0054 (7)	−0.0004 (7)
C8	0.0457 (8)	0.0501 (9)	0.0401 (7)	−0.0016 (7)	0.0064 (6)	−0.0001 (6)
C9	0.0495 (9)	0.0526 (10)	0.0407 (7)	−0.0004 (7)	0.0029 (6)	−0.0006 (7)
C10	0.0548 (10)	0.0566 (11)	0.0534 (9)	−0.0008 (8)	0.0131 (7)	−0.0033 (8)
C11	0.0730 (12)	0.0469 (10)	0.0460 (8)	0.0014 (8)	0.0148 (8)	0.0007 (7)
C12	0.0770 (13)	0.0601 (12)	0.0648 (11)	−0.0072 (10)	0.0138 (10)	−0.0136 (9)
C13	0.0624 (12)	0.0760 (15)	0.0862 (14)	−0.0093 (10)	0.0022 (10)	−0.0282 (12)
C14	0.114 (2)	0.0673 (15)	0.0669 (13)	0.0168 (12)	0.0112 (13)	−0.0144 (10)
C15	0.0940 (17)	0.0733 (16)	0.0907 (16)	0.0025 (12)	0.0374 (14)	−0.0172 (12)

Geometric parameters (Å, º)

S1—C8	1.6609 (16)	C4—H4A	0.9300
O1—C7	1.225 (2)	C5—C6	1.384 (2)
N1—C7	1.383 (2)	C5—H5A	0.9300
N1—C8	1.385 (2)	C6—C7	1.482 (2)
N1—H1N1	0.81 (2)	C9—C10	1.382 (2)
N2—C8	1.339 (2)	C10—C11	1.377 (3)
N2—C9	1.417 (2)	C10—H10A	0.9300
N2—H1N2	0.82 (2)	C11—C12	1.375 (3)
N3—C9	1.328 (2)	C11—C15	1.498 (3)
N3—C13	1.337 (3)	C12—C13	1.373 (3)
C1—C2	1.380 (3)	C12—H12A	0.9300
C1—C6	1.394 (2)	C13—H13A	0.9300
C1—H1A	0.9300	C14—H14A	0.9600
C2—C3	1.378 (3)	C14—H14B	0.9600
C2—H2A	0.9300	C14—H14C	0.9600
C3—C4	1.385 (3)	C15—H15A	0.9600
C3—C14	1.515 (3)	C15—H15B	0.9600
C4—C5	1.385 (3)	C15—H15C	0.9600

C7—N1—C8	129.34 (15)	N2—C8—S1	127.11 (13)
C7—N1—H1N1	116.6 (14)	N1—C8—S1	117.91 (12)
C8—N1—H1N1	112.9 (14)	N3—C9—C10	123.61 (16)
C8—N2—C9	132.25 (15)	N3—C9—N2	109.77 (15)
C8—N2—H1N2	111.7 (17)	C10—C9—N2	126.61 (15)
C9—N2—H1N2	114.2 (17)	C11—C10—C9	119.22 (17)
C9—N3—C13	116.14 (17)	C11—C10—H10A	120.4
C2—C1—C6	120.01 (18)	C9—C10—H10A	120.4
C2—C1—H1A	120.0	C12—C11—C10	117.90 (18)
C6—C1—H1A	120.0	C12—C11—C15	121.03 (18)
C3—C2—C1	121.29 (17)	C10—C11—C15	121.07 (19)
C3—C2—H2A	119.4	C13—C12—C11	118.87 (19)
C1—C2—H2A	119.4	C13—C12—H12A	120.6
C2—C3—C4	118.38 (17)	C11—C12—H12A	120.6
C2—C3—C14	121.3 (2)	N3—C13—C12	124.3 (2)
C4—C3—C14	120.3 (2)	N3—C13—H13A	117.9
C5—C4—C3	121.21 (18)	C12—C13—H13A	117.9
C5—C4—H4A	119.4	C3—C14—H14A	109.5
C3—C4—H4A	119.4	C3—C14—H14B	109.5
C6—C5—C4	119.94 (17)	H14A—C14—H14B	109.5
C6—C5—H5A	120.0	C3—C14—H14C	109.5
C4—C5—H5A	120.0	H14A—C14—H14C	109.5
C5—C6—C1	119.15 (16)	H14B—C14—H14C	109.5
C5—C6—C7	122.77 (15)	C11—C15—H15A	109.5
C1—C6—C7	118.08 (15)	C11—C15—H15B	109.5
O1—C7—N1	122.22 (16)	H15A—C15—H15B	109.5
O1—C7—C6	122.46 (15)	C11—C15—H15C	109.5
N1—C7—C6	115.31 (15)	H15A—C15—H15C	109.5
N2—C8—N1	114.97 (14)	H15B—C15—H15C	109.5

C6—C1—C2—C3	1.2 (3)	C9—N2—C8—N1	−174.80 (16)
C1—C2—C3—C4	−0.3 (3)	C9—N2—C8—S1	4.2 (3)
C1—C2—C3—C14	179.57 (18)	C7—N1—C8—N2	3.2 (3)
C2—C3—C4—C5	−0.5 (3)	C7—N1—C8—S1	−175.97 (14)
C14—C3—C4—C5	179.64 (17)	C13—N3—C9—C10	0.3 (3)
C3—C4—C5—C6	0.4 (3)	C13—N3—C9—N2	179.18 (18)
C4—C5—C6—C1	0.5 (3)	C8—N2—C9—N3	173.13 (18)
C4—C5—C6—C7	−179.68 (16)	C8—N2—C9—C10	−8.0 (3)
C2—C1—C6—C5	−1.2 (3)	N3—C9—C10—C11	−0.4 (3)
C2—C1—C6—C7	178.91 (16)	N2—C9—C10—C11	−179.18 (16)
C8—N1—C7—O1	−1.1 (3)	C9—C10—C11—C12	0.0 (3)
C8—N1—C7—C6	177.94 (15)	C9—C10—C11—C15	178.80 (19)
C5—C6—C7—O1	−152.85 (18)	C10—C11—C12—C13	0.7 (3)
C1—C6—C7—O1	27.0 (2)	C15—C11—C12—C13	−178.2 (2)
C5—C6—C7—N1	28.1 (2)	C9—N3—C13—C12	0.4 (4)
C1—C6—C7—N1	−152.03 (16)	C11—C12—C13—N3	−0.9 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1*N*2···O1	0.82 (2)	1.94 (2)	2.644 (2)	144 (2)
N1—H1*N*1···S1^{i}	0.81 (2)	2.74 (2)	3.5106 (15)	157.8 (18)
C10—H10*A*···S1	0.93	2.57	3.2211 (19)	127

Symmetry code: (i) −*x*+1, −*y*+2, −*z*+1.