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1-(1,3-Benzothiazol-2-yl)-3-benzoylthiourea

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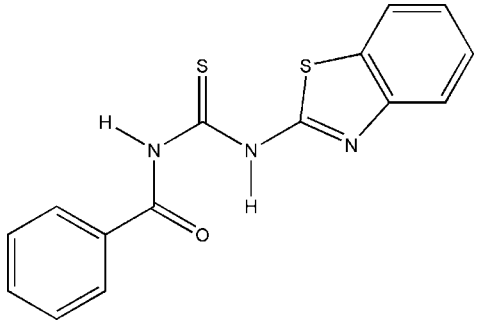
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.035; wR factor = 0.102; data-to-parameter ratio = 18.5.

The title compound, $C_{15}H_{11}N_3OS_2$, was synthesized from benzoyl thiocyanate and 2-aminobenzothiazole in dry acetone. The thiourea group is in the thioamide form. The molecules are stabilized by two intermolecular C—H···S and C—H···O hydrogen bonds. Intramolecular N—H···O hydrogen bonding results in a pseudo-S(6) planar ring with dihedral angles of 11.23 and 11.91° with the benzothiazole ring system and the phenyl ring, respectively.

Related literature

For related literature see: Büyükgüngör *et al.* (2004); del Campo *et al.* (2002); Chen *et al.* (2003); D'hooghe *et al.* (2005); Koketsu & Ishihara (2006); Morales *et al.* (2000); Rodríguez-Fernández *et al.* (2005); Yamin & Hassan (2004); Yunus *et al.* (2007); Zeng *et al.* (2003).



Experimental

Crystal data

$C_{15}H_{11}N_3OS_2$
M_r = 313.39
Monoclinic, $P2/c$
a = 12.4402 (8) Å
b = 5.8608 (4) Å
c = 19.7240 (13) Å
β = 90.223 (1)°
V = 1438.06 (16) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.37 mm^{-1}
T = 293 (2) K
0.32 × 0.26 × 0.20 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.933, T_{max} = 1.000
(expected range = 0.866–0.928)
8487 measured reflections
3508 independent reflections
2724 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.102
S = 1.04
3508 reflections
190 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2B···O1	0.86	1.86	2.5878 (17)	142
C1—H1A···S2^{i}	0.93	2.84	3.4017 (17)	120
C5—H5A···O1^{ii}	0.93	2.57	3.470 (2)	162

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+1$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2150).

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1-(1,3-Benzothiazol-2-yl)-3-benzoylthiourea

Uzma Yunus, Muhammad Kalim Tahir, Moazzam Hussain Bhatti, Saqib Ali and Wai-Yeung Wong

S1. Comment

Thiourea and its derivatives have found extensive applications in the fields of medicine, agriculture and analytical chemistry. They are known to exhibit a wide variety of biological activities such as antiviral, antibacterial, antifungal, antitubercular, herbicidal and insecticidal (Koketsu & Ishihara, 2006). Thioureas are also widely used as precursors or intermediates towards the syntheisis of a variety of heterocyclic compounds (Zeng *et al.*2003; D'hooghe, *et al.* 2005). Among thiourea derivatives acylthiourea with potential donor atoms (O and S) have been found to display remarkably rich coordination chemistry. Such coordination compounds of thiourea have been studied for different biological systems (Rodríguez-Fernández *et al.* 2005). In recent years some attention has also been paid for potential use of acylthioureas as highly selective reagents for the enrichment and separation of metal cations (del Campo *et al.* 2002). The condensation of acyl / aroyl thiocyanates with primary amine affords 1,3-disubstituted thioureas in excellent yield in a single step. However, our attempt to synthesize thiourea derivative by treating benzoyl thiocyanate with 2-aminothiazole resulted in a fused 1,3,5-triazine instead of the expected thiourea product (Yunus *et al.* 2007). This observation prompted us to explore the outcome of the reaction with 2-aminothiazole derivatives such as 2-aminobenzothiazole. The reaction of the benzoyl thiocyanate with 2-aminobenzothiazole yielded the title compound (I) which is reported here.

The title compound crystallizes in the thioamide form. The conformation of the molecule with respect to the carbonyl and thiocarbonyl part is nearly planar as reflected by the torsion angles O1—C7—N1—C8, C7—N1—C8—S2 and C7—N1—C8—N2 of -0.42(°), -179.58(°) and -0.06(°) respectively. The benzoyl and benzothiazole groups are *trans* and *cis*, respectively, to the S atom across the thiourea C—N bonds (Figure 1 and Table 1). The C8—S2 and C7—O1 bonds show a typical double bond character with bond lengths of 1.6578 (15) and 1.2179 (19) Å respectively, closely related to other thiourea derivatives (Yamin & Hassan, 2004). All of the C—N bonds of thiourea fragment C7—N1, C8—N1, C8—N2 and C9—N2 are in the range 1.3933 (19) - 1.338 (2) Å, intermediate between those expected for single and double C—N bonds (1.47 and 1.27 Å respectively). Among these C—N bonds the C7—N1 is the longest indicating Csp^2-Nsp^2 single bond while C8—N2 is the shortest bond with more double bond character. This further demonstrate that there is π conjugation only along S2—C8—N2 system but not along O1—C7—N1 and C7—N1—C8 as found in 1-(3-methoxy-benzoyl)-3,3-diethylthiourea (Morales *et al.*, 2000). The bond lengths in the benzothizole ring system are normal and agree with the corresponding values found in 2-(benzothiazole-2-yliminomethyl)-6-methoxyphenol and *N,N*-(2-benzo-thia-zole)(2-pyridylmethyl)amine (Büyükgüngör *et al.* 2004; Chen *et al.* 2003). The bond length C9—N2 is very close to the value determined for the 2-(benzothiazole-2-yliminomethyl)-6-methoxyphenol suggesting the existence of a delocalized double bond in the benzothiazole moiety (Büyükgüngör *et al.* 2004). All bond lengths and angles confirm the sp^2 hybridization for all C and N atoms of the benzothiazole ring with all C—C and C—N bond lengths intermediate between single and double bonds. The benzothiazole ring bonded to N2 is essentially planar and inclined at an angle -11.23(°) with respect to the plane of thiourea moiety. Similarly the phenyl ring bonded to C7 is at an angle of 11.91(°) with respect to the plane formed by the thiourea moiety.

The molecule is further stabilized by intermolecular and intramolecular hydrogen bonding. There are two types of intermolecular C1—H1A···S2i and C5—H5A···O1ii [Symmetry codes: (i) -*x*, -*y* + 1, -*z* + 1; (ii) -*x* + 1, -*y* + 1, -*z* + 1] hydrogen bonds. The intramolecular N2—H2B···O1 hydrogen bond is also observed. As a result, a pseudo six membered (O1—C7—N1—C8—N2···H2B) ring is formed.

S2. Experimental

A mixture of ammonium thiocyanate (26 mmol) and benzoyl chloride (26 mmol) in dry acetone (60 ml) was stirred for 30 min. Then 2-aminobenzothiazole (26 mmol) was added and the reaction mixture was refluxed for 2 h. After cooling, the reaction mixture was poured in an acidified cold water. The resulting yellow solid was filtered and washed with cold acetone. The title compound (I) was obtained as suitable single crystals for X-Ray analysis after recrystallization of the solid from an 1:1 ethanol-dichloromethane mixture.

S3. Refinement

H atoms were placed in idealized positions and refined using a riding model approximation. Bond lengths were fixed to 0.86 (amine NH) or 0.93 Å (aromatic CH). Isotropic displacement parameters were fixed to U_{iso}(H) = 1.2U_{eq}(carrier atom).

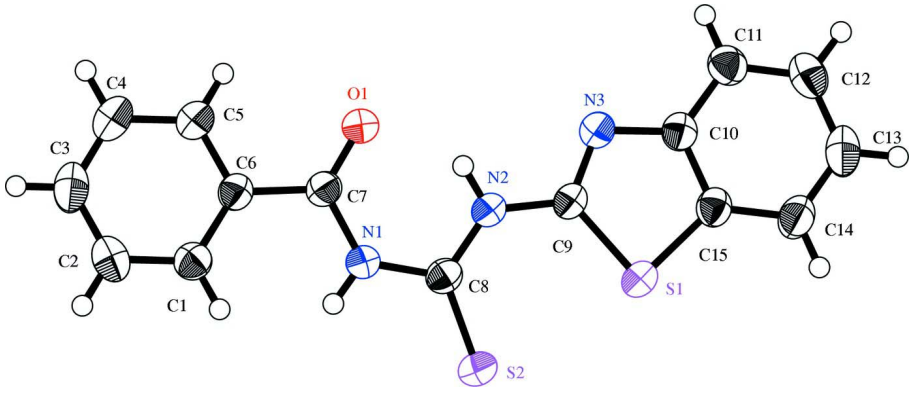

Figure 1

The molecular structure of (I) with atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

1-(1,3-Benzothiazol-2-yl)-3-benzoylthiourea

Crystal data

$C_{15}H_{11}N_3OS_2$
M_r = 313.39
Monoclinic, *P*2/*c*
Hall symbol: -P 2yc
a = 12.4402 (8) Å
b = 5.8608 (4) Å
c = 19.7240 (13) Å
β = 90.223 (1)°
V = 1438.06 (16) Å^3
Z = 4
F(000) = 648
D_x = 1.447 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 8487 reflections
θ = 2.6–28.3°
μ = 0.37 mm^{-1}
T = 293 K
Block, pale-yellow
0.32 × 0.26 × 0.20 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.933, T_{max} = 1.000
8487 measured reflections
3508 independent reflections
2724 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 28.3°, θ_{min} = 2.6°
$h = -16 \rightarrow 16$
$k = -7 \rightarrow 7$
$l = -19 \rightarrow 26$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.102
S = 1.04
3508 reflections
190 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 0.2538P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.21573 (13)	0.0594 (3)	0.53895 (8)	0.0416 (4)
H1A	0.1480	0.0792	0.5197	0.050*
C2	0.23408 (16)	−0.1206 (3)	0.58247 (9)	0.0515 (4)
H2A	0.1785	−0.2203	0.5932	0.062*
C3	0.33485 (18)	−0.1525 (4)	0.61000 (10)	0.0602 (5)
H3A	0.3473	−0.2749	0.6390	0.072*
C4	0.41698 (17)	−0.0051 (4)	0.59497 (11)	0.0646 (5)
H4A	0.4848	−0.0280	0.6137	0.078*
C5	0.39901 (14)	0.1779 (3)	0.55189 (9)	0.0529 (5)
H5A	0.4547	0.2781	0.5419	0.063*
C6	0.29787 (12)	0.2116 (3)	0.52370 (8)	0.0378 (3)
C7	0.28504 (12)	0.4117 (3)	0.47818 (8)	0.0380 (3)
C8	0.14589 (12)	0.6519 (3)	0.42051 (8)	0.0372 (3)
C9	0.22056 (12)	0.9776 (3)	0.35659 (7)	0.0354 (3)
C10	0.29090 (13)	1.2734 (3)	0.30503 (8)	0.0388 (3)
C11	0.36820 (14)	1.4337 (3)	0.28664 (9)	0.0472 (4)
H11A	0.4382	1.4225	0.3030	0.057*
C12	0.33920 (16)	1.6082 (3)	0.24397 (9)	0.0517 (4)
H12A	0.3902	1.7159	0.2313	0.062*
C13	0.23408 (17)	1.6266 (3)	0.21919 (9)	0.0551 (5)
H13A	0.2164	1.7450	0.1898	0.066*
C14	0.15669 (15)	1.4723 (3)	0.23769 (9)	0.0514 (4)
H14A	0.0867	1.4855	0.2214	0.062*
C15	0.18525 (13)	1.2952 (3)	0.28139 (8)	0.0412 (4)
N1	0.18011 (10)	0.4716 (2)	0.46078 (7)	0.0395 (3)

H1B	0.1303	0.3861	0.4770	0.047*
N2	0.22510 (10)	0.7819 (2)	0.39602 (7)	0.0385 (3)
H2B	0.2889	0.7372	0.4064	0.046*
N3	0.30872 (10)	1.0881 (2)	0.34739 (7)	0.0397 (3)
O1	0.36174 (9)	0.5195 (2)	0.45724 (6)	0.0482 (3)
S1	0.10503 (3)	1.08096 (8)	0.31634 (2)	0.04440 (13)
S2	0.01565 (3)	0.69188 (9)	0.40697 (2)	0.05128 (15)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0415 (8)	0.0417 (9)	0.0415 (8)	0.0026 (7)	0.0017 (7)	−0.0018 (7)
C2	0.0636 (11)	0.0424 (10)	0.0486 (10)	−0.0033 (8)	0.0075 (8)	0.0042 (8)
C3	0.0734 (13)	0.0535 (11)	0.0536 (11)	0.0096 (10)	−0.0028 (10)	0.0161 (9)
C4	0.0549 (11)	0.0708 (13)	0.0680 (13)	0.0098 (10)	−0.0134 (9)	0.0184 (11)
C5	0.0423 (9)	0.0610 (12)	0.0553 (11)	0.0008 (8)	−0.0066 (8)	0.0146 (9)
C6	0.0389 (8)	0.0385 (8)	0.0362 (8)	0.0038 (6)	0.0000 (6)	0.0004 (6)
C7	0.0358 (7)	0.0394 (8)	0.0388 (8)	0.0009 (6)	−0.0025 (6)	0.0003 (7)
C8	0.0360 (8)	0.0391 (8)	0.0366 (8)	0.0027 (6)	−0.0012 (6)	−0.0027 (6)
C9	0.0359 (7)	0.0363 (8)	0.0339 (7)	0.0054 (6)	−0.0023 (6)	−0.0005 (6)
C10	0.0422 (8)	0.0398 (8)	0.0343 (8)	0.0048 (7)	0.0034 (6)	0.0000 (6)
C11	0.0471 (9)	0.0494 (10)	0.0451 (9)	−0.0003 (8)	0.0056 (7)	0.0020 (8)
C12	0.0631 (11)	0.0460 (10)	0.0460 (10)	−0.0016 (8)	0.0126 (8)	0.0040 (8)
C13	0.0740 (13)	0.0474 (10)	0.0441 (10)	0.0154 (9)	0.0092 (9)	0.0106 (8)
C14	0.0511 (10)	0.0554 (11)	0.0476 (10)	0.0141 (8)	0.0005 (8)	0.0088 (8)
C15	0.0442 (9)	0.0414 (9)	0.0381 (8)	0.0061 (7)	0.0022 (7)	0.0018 (7)
N1	0.0324 (6)	0.0398 (7)	0.0461 (7)	−0.0007 (5)	−0.0018 (5)	0.0073 (6)
N2	0.0323 (6)	0.0392 (7)	0.0441 (7)	0.0031 (5)	−0.0024 (5)	0.0046 (6)
N3	0.0380 (7)	0.0413 (7)	0.0399 (7)	0.0021 (6)	−0.0018 (5)	0.0030 (6)
O1	0.0351 (6)	0.0515 (7)	0.0581 (7)	−0.0035 (5)	−0.0043 (5)	0.0143 (6)
S1	0.0367 (2)	0.0473 (3)	0.0491 (2)	0.00442 (17)	−0.00595 (17)	0.00779 (18)
S2	0.0328 (2)	0.0624 (3)	0.0586 (3)	0.00376 (19)	−0.00173 (18)	0.0142 (2)

Geometric parameters (Å, º)

C1—C2	1.379 (2)	C9—N3	1.287 (2)
C1—C6	1.390 (2)	C9—N2	1.387 (2)
C1—H1A	0.9300	C9—S1	1.7476 (15)
C2—C3	1.377 (3)	C10—N3	1.387 (2)
C2—H2A	0.9300	C10—C11	1.393 (2)
C3—C4	1.371 (3)	C10—C15	1.399 (2)
C3—H3A	0.9300	C11—C12	1.372 (2)
C4—C5	1.386 (3)	C11—H11A	0.9300
C4—H4A	0.9300	C12—C13	1.398 (3)
C5—C6	1.388 (2)	C12—H12A	0.9300
C5—H5A	0.9300	C13—C14	1.371 (3)
C6—C7	1.486 (2)	C13—H13A	0.9300
C7—O1	1.2179 (19)	C14—C15	1.395 (2)

C7—N1	1.3933 (19)	C14—H14A	0.9300
C8—N2	1.338 (2)	C15—S1	1.7471 (17)
C8—N1	1.388 (2)	N1—H1B	0.8600
C8—S2	1.6578 (15)	N2—H2B	0.8600
C2—C1—C6	120.37 (16)	N3—C10—C11	125.14 (15)
C2—C1—H1A	119.8	N3—C10—C15	114.84 (14)
C6—C1—H1A	119.8	C11—C10—C15	120.01 (15)
C3—C2—C1	119.85 (18)	C12—C11—C10	118.83 (17)
C3—C2—H2A	120.1	C12—C11—H11A	120.6
C1—C2—H2A	120.1	C10—C11—H11A	120.6
C4—C3—C2	120.47 (18)	C11—C12—C13	121.01 (18)
C4—C3—H3A	119.8	C11—C12—H12A	119.5
C2—C3—H3A	119.8	C13—C12—H12A	119.5
C3—C4—C5	120.11 (18)	C14—C13—C12	120.85 (17)
C3—C4—H4A	119.9	C14—C13—H13A	119.6
C5—C4—H4A	119.9	C12—C13—H13A	119.6
C4—C5—C6	119.95 (18)	C13—C14—C15	118.55 (17)
C4—C5—H5A	120.0	C13—C14—H14A	120.7
C6—C5—H5A	120.0	C15—C14—H14A	120.7
C5—C6—C1	119.24 (15)	C14—C15—C10	120.72 (16)
C5—C6—C7	116.71 (15)	C14—C15—S1	129.37 (14)
C1—C6—C7	124.06 (14)	C10—C15—S1	109.89 (12)
O1—C7—N1	121.35 (14)	C8—N1—C7	128.15 (13)
O1—C7—C6	122.16 (14)	C8—N1—H1B	115.9
N1—C7—C6	116.49 (14)	C7—N1—H1B	115.9
N2—C8—N1	114.57 (13)	C8—N2—C9	130.20 (13)
N2—C8—S2	125.60 (12)	C8—N2—H2B	114.9
N1—C8—S2	119.83 (12)	C9—N2—H2B	114.9
N3—C9—N2	117.53 (13)	C9—N3—C10	110.14 (13)
N3—C9—S1	117.47 (12)	C15—S1—C9	87.62 (7)
N2—C9—S1	124.97 (12)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*B*···O1	0.86	1.86	2.5878 (17)	142
C1—H1*A*···S2^{i}	0.93	2.84	3.4017 (17)	120
C5—H5*A*···O1^{ii}	0.93	2.57	3.470 (2)	162

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*+1, −*z*+1.