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1-Benzoyl-4-thiobiuret

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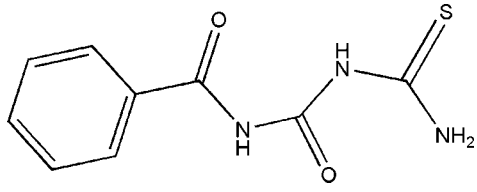
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.037; wR factor = 0.097; data-to-parameter ratio = 16.6.

In the title compound (systematic name: {[(phenylformamido)carbonyl]amino}methanethioamide), $C_9H_9N_3O_2S$, both benzoyl and terminal thiourea fragments adopt *transoid* conformations with respect to the central carbonyl O atom. The benzoyl and thiobiuret groups are almost coplanar, making a dihedral angle of 4.40 (8)°. The molecular structure is stabilized by two intramolecular N—H···O hydrogen bonds. In the crystal, N—H···O and N—H···S hydrogen bonds link the molecules into a tape running along [101].

Related literature

For the structure and reactivity of thiadiazole derivatives, see: Cho, Ra *et al.* (1996); Cho, Cho *et al.* (1996). For the structure of a thiobiuret isomer, see: Kang *et al.* (2012).



Experimental

Crystal data

$C_9H_9N_3O_2S$
M_r = 223.25
Triclinic, $P\overline{1}$
a = 5.6616 (1) Å
b = 7.8407 (2) Å
c = 11.7631 (3) Å
α = 97.169 (2)°
β = 94.992 (3)°
γ = 101.390 (2)°
V = 504.53 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.30 mm^{-1}
T = 296 K
0.2 × 0.15 × 0.07 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.94, T_{max} = 0.97
17356 measured reflections
2516 independent reflections
1485 reflections with $I > 2\sigma(I)$
R_{int} = 0.055

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.097
S = 0.87
2516 reflections
152 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N9—H9···O11^{i}	0.843 (18)	2.172 (18)	2.9891 (18)	163.3 (16)
N12—H12···O8	0.882 (19)	1.919 (19)	2.6171 (17)	135.0 (17)
N15—H15A···O11	0.91 (2)	1.99 (2)	2.684 (2)	132.0 (17)
N15—H15B···S14^{ii}	0.85 (2)	2.58 (2)	3.4295 (17)	171.3 (17)

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

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2013); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2013); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS5292).

References

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Cho, N. S., Cho, J. J., Ra, D. Y., Moon, J. H., Song, J. S. & Kang, S. K. (1996). *Bull. Korean Chem. Soc.* **17**, 1170–1174.
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Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Kang, S. K., Cho, N. S. & Jeon, M. K. (2012). *Acta Cryst.* E**68**, o395.
Sheldrick, G. M. (2013). University of Göttingen, Germany.

supporting information

Acta Cryst. (2013). E**69**, o1327 [doi:10.1107/S1600536813019983]

1-Benzoyl-4-thiobiuret

Sung Kwon Kang

S1. Comment

5-Amino-2*H*-1,2,4-thiadiazol-3-one is the analog of cytosine. As an analog of cytosine, the tautomeric structure and reactivity of this compound have been examined (Cho, Ra *et al.*, 1996). Within the framework of our interest in the synthesis of novel potential anti-metabolites of nucleic acid components which would possess cytostatic activity, we have synthesized derivatives of 5-amino-3*H*-1,3,4-thiadiazol-2-one (Cho, Cho *et al.*, 1996). The title compound, 1-benzoyl-4-thiobiuret, is an isomer of 1-benzoyl-2-thiobiuret (Kang *et al.*, 2012). This compound is an intermediate for the formation of the thiobiuret which is a good starting material to make 5-amino-2*H*-1,2,4-thiadizolin-3-one *via* oxidative ring-closure reaction.

The dihedral angle between the benzoyl unit (C1–C7/O8) and thiobiuret group (N9/C10/O11/N12/C13/S14/N15) is 4.40 (8)°. Both carbonyl O8 and S14 atoms are positioned *anti* conformations with respect to the O11 atom (Fig. 1). The intramolecular O8···H12—N12 and O11···H15—N15 hydrogen bonds stabilize the molecule (Fig. 1 and Table 1). The intermolecular N—H···O and N—H···S hydrogen bonds link the molecules into a tape along the [101] direction (Fig. 2 and Table 1).

S2. Experimental

Benzoyl chloride (48 ml, 58.1 g, 0.41 mol) was added to warm solution of potassium thiocyanate (48.0 g, 0.49 mol) in acetone (400 ml). The solution became milky white and yellow when the addition had been completed. The mixture was stirred for 3.5 h at 50°C and left to cool to room temperature. The filtrate was heated to 55°C for 5 h with urea (24.0 g, 0.40 mol). And the resulting solution was cooled to room temperature and then placed in an ice bath for several hours. The cold mixture was filtered to give 1-benzoyl-4-thiobiuret as a bright yellow solid. Recrystallization from methyl alcohol afforded the yellow crystals suitable for X-ray diffraction.

S3. Refinement

H atoms of the NH and NH_2 groups were located in a difference Fourier map and refined freely [refined N—H distances = 0.84 (2)–0.91 (2) Å]. Other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å, and with U_{iso}(H) = 1.2U_{eq}(C).

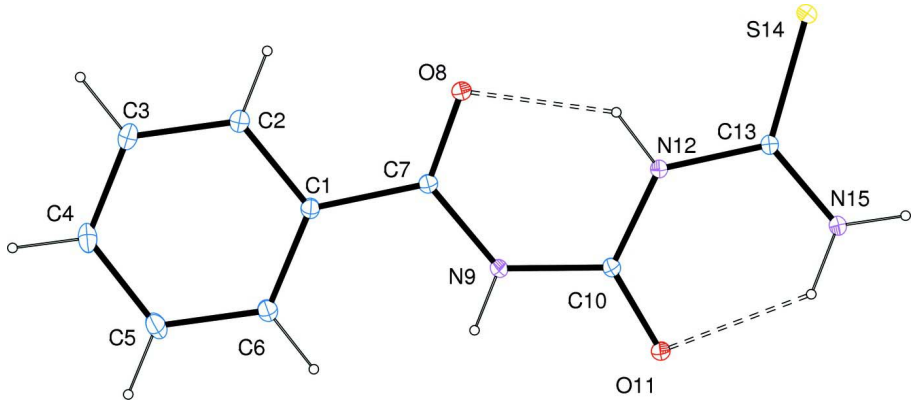

Figure 1

Molecular structure of the title compound, showing the atom-numbering scheme and 30% probability ellipsoids. Two intramolecular N—H···O hydrogen bonds are indicated by dashed lines.

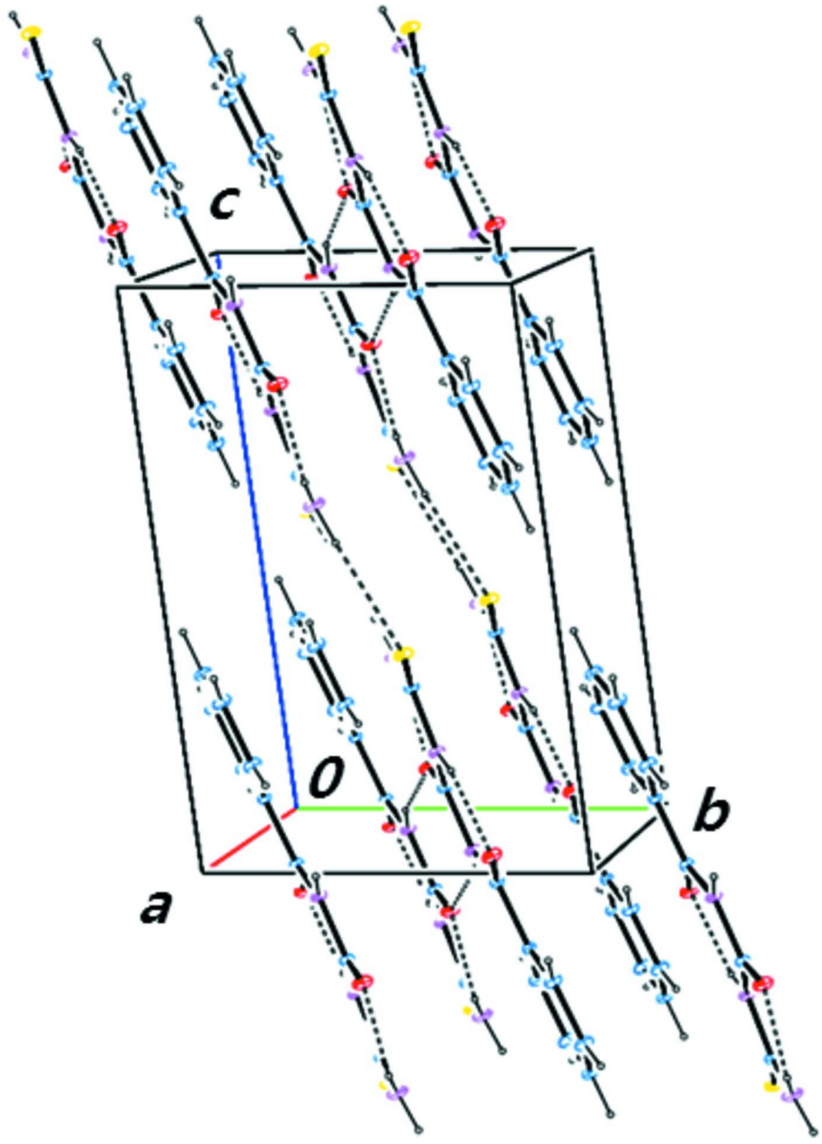

Figure 2

Part of the packing diagram of the title compound, showing a molecular tape formed by intermolecular N—H···O and N—H···S hydrogen bonds (dashed lines).

{[(Phenylformamido)carbonyl]amino}methanethioamide

Crystal data

$C_9H_9N_3O_2S$
$M_r = 223.25$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 5.6616$ (1) Å
$b = 7.8407$ (2) Å
$c = 11.7631$ (3) Å
$\alpha = 97.169$ (2)°
$\beta = 94.992$ (3)°
$\gamma = 101.390$ (2)°
$V = 504.53$ (2) Å^3
$Z = 2$
$F(000) = 232$
$D_x = 1.47$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3132 reflections
$\theta = 2.7$–22.3°
$\mu = 0.30$ mm^{-1}

T = 296 K
Block, yellow

0.2 × 0.15 × 0.07 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.94, T_{max} = 0.97
17356 measured reflections

2516 independent reflections
1485 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
θ_{max} = 28.3°, θ_{min} = 1.8°
h = −7→7
k = −10→10
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.097
S = 0.87
2516 reflections
152 parameters
0 restraints

Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.052P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 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.

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

	x	y	z	U_{iso}*/U_{eq}
C1	0.0374 (3)	0.8224 (2)	−0.12506 (14)	0.0447 (4)
C2	0.2488 (3)	0.9206 (2)	−0.15393 (16)	0.0597 (5)
H2	0.3881	0.9477	−0.1014	0.072*
C3	0.2552 (4)	0.9785 (3)	−0.25952 (19)	0.0729 (6)
H3	0.398	1.0453	−0.2778	0.087*
C4	0.0539 (4)	0.9383 (3)	−0.33677 (18)	0.0723 (6)
H4	0.06	0.9763	−0.4085	0.087*
C5	−0.1598 (4)	0.8419 (3)	−0.31035 (18)	0.0753 (6)
H5	−0.2979	0.8154	−0.3636	0.09*
C6	−0.1672 (3)	0.7846 (3)	−0.20373 (16)	0.0615 (5)
H6	−0.3114	0.7203	−0.1851	0.074*
C7	0.0480 (3)	0.7661 (2)	−0.00927 (14)	0.0442 (4)
O8	0.2338 (2)	0.80629 (17)	0.05733 (11)	0.0633 (4)
N9	−0.1594 (2)	0.66558 (19)	0.02071 (12)	0.0467 (4)
H9	−0.284 (3)	0.634 (2)	−0.0281 (16)	0.054 (5)*
C10	−0.1998 (3)	0.6059 (2)	0.12532 (14)	0.0446 (4)
O11	−0.3996 (2)	0.52249 (17)	0.13780 (10)	0.0603 (4)
N12	−0.0057 (2)	0.64570 (19)	0.20766 (11)	0.0467 (4)
H12	0.131 (4)	0.707 (2)	0.1906 (17)	0.067 (6)*

C13	0.0039 (3)	0.6057 (2)	0.31929 (13)	0.0447 (4)
S14	0.27039 (8)	0.66392 (7)	0.40142 (4)	0.05930 (19)
N15	−0.1971 (3)	0.5267 (3)	0.35341 (15)	0.0646 (5)
H15A	−0.336 (4)	0.507 (2)	0.3052 (18)	0.075 (6)*
H15B	−0.199 (3)	0.486 (2)	0.4173 (18)	0.066 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0468 (9)	0.0459 (10)	0.0402 (9)	0.0048 (8)	0.0046 (7)	0.0100 (8)
C2	0.0539 (10)	0.0726 (13)	0.0505 (11)	0.0013 (9)	0.0049 (8)	0.0214 (10)
C3	0.0714 (13)	0.0858 (16)	0.0630 (14)	0.0016 (12)	0.0175 (11)	0.0337 (12)
C4	0.0944 (16)	0.0782 (15)	0.0503 (12)	0.0174 (13)	0.0138 (12)	0.0294 (11)
C5	0.0810 (15)	0.0890 (16)	0.0523 (12)	0.0069 (13)	−0.0107 (11)	0.0263 (11)
C6	0.0564 (11)	0.0714 (13)	0.0518 (12)	−0.0029 (9)	−0.0038 (9)	0.0230 (10)
C7	0.0403 (9)	0.0483 (10)	0.0410 (9)	0.0009 (7)	0.0013 (7)	0.0102 (8)
O8	0.0426 (6)	0.0882 (10)	0.0501 (7)	−0.0140 (6)	−0.0047 (6)	0.0269 (7)
N9	0.0392 (7)	0.0609 (10)	0.0353 (8)	−0.0021 (7)	−0.0023 (6)	0.0141 (7)
C10	0.0411 (9)	0.0546 (11)	0.0349 (9)	0.0016 (8)	0.0012 (7)	0.0099 (8)
O11	0.0397 (6)	0.0898 (10)	0.0432 (7)	−0.0107 (6)	−0.0017 (5)	0.0213 (6)
N12	0.0370 (7)	0.0637 (10)	0.0359 (8)	−0.0022 (7)	0.0008 (6)	0.0165 (7)
C13	0.0401 (8)	0.0588 (11)	0.0355 (9)	0.0069 (8)	0.0047 (7)	0.0129 (8)
S14	0.0402 (2)	0.0911 (4)	0.0424 (3)	0.0002 (2)	−0.00342 (18)	0.0213 (2)
N15	0.0403 (8)	0.1120 (15)	0.0414 (9)	0.0026 (9)	0.0021 (7)	0.0336 (10)

Geometric parameters (Å, º)

C1—C6	1.377 (2)	C7—O8	1.2181 (18)
C1—C2	1.383 (2)	C7—N9	1.378 (2)
C1—C7	1.483 (2)	N9—C10	1.391 (2)
C2—C3	1.376 (3)	N9—H9	0.843 (18)
C2—H2	0.93	C10—O11	1.2205 (18)
C3—C4	1.353 (3)	C10—N12	1.3591 (19)
C3—H3	0.93	N12—C13	1.387 (2)
C4—C5	1.377 (3)	N12—H12	0.882 (19)
C4—H4	0.93	C13—N15	1.305 (2)
C5—C6	1.385 (3)	C13—S14	1.6679 (16)
C5—H5	0.93	N15—H15A	0.91 (2)
C6—H6	0.93	N15—H15B	0.85 (2)
C6—C1—C2	118.74 (16)	O8—C7—N9	120.79 (15)
C6—C1—C7	124.45 (15)	O8—C7—C1	121.33 (14)
C2—C1—C7	116.81 (15)	N9—C7—C1	117.87 (14)
C3—C2—C1	120.69 (18)	C7—N9—C10	128.80 (14)
C3—C2—H2	119.7	C7—N9—H9	119.4 (12)
C1—C2—H2	119.7	C10—N9—H9	111.8 (12)
C4—C3—C2	120.02 (18)	O11—C10—N12	124.46 (15)
C4—C3—H3	120	O11—C10—N9	119.83 (14)

C2—C3—H3	120	N12—C10—N9	115.71 (14)
C3—C4—C5	120.70 (19)	C10—N12—C13	127.81 (14)
C3—C4—H4	119.7	C10—N12—H12	117.8 (13)
C5—C4—H4	119.7	C13—N12—H12	114.4 (13)
C4—C5—C6	119.38 (19)	N15—C13—N12	117.68 (14)
C4—C5—H5	120.3	N15—C13—S14	124.41 (13)
C6—C5—H5	120.3	N12—C13—S14	117.91 (12)
C1—C6—C5	120.46 (18)	C13—N15—H15A	118.8 (13)
C1—C6—H6	119.8	C13—N15—H15B	121.9 (13)
C5—C6—H6	119.8	H15A—N15—H15B	119.1 (18)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N9—H9···O11^{i}	0.843 (18)	2.172 (18)	2.9891 (18)	163.3 (16)
N12—H12···O8	0.882 (19)	1.919 (19)	2.6171 (17)	135.0 (17)
N15—H15*A*···O11	0.91 (2)	1.99 (2)	2.684 (2)	132.0 (17)
N15—H15*B*···S14^{ii}	0.85 (2)	2.58 (2)	3.4295 (17)	171.3 (17)

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