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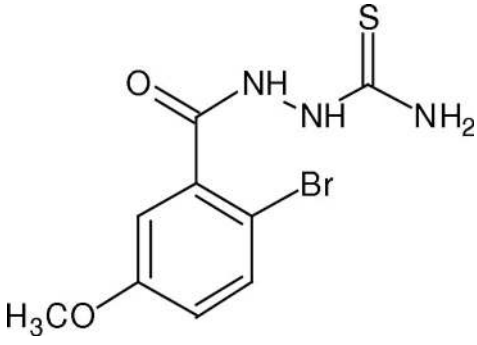
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.004 Å; R factor = 0.030; wR factor = 0.071; data-to-parameter ratio = 13.9.

The geometric parameters of the title molecule, $C_9H_{10}BrN_3O_2S$, are in the usual ranges. The mean plane of the thiourea group is almost parallel to the plane of the benzene ring [dihedral angle = 8.40 (12)°]. Only the torsion angles about the $C_{carbonyl}-C_{aromatic}$ bond and the N—N bond differ significantly from 0 or 180°. The crystal packing is stabilized by N—H···O and N—H···S hydrogen bonds.

Related literature

For related crystal structures, see: Chattopadhyay *et al.* (1987, 1989, 1991); Fonari *et al.* (2003); Jian *et al.* (2005); Sarojini *et al.* (2007). For related literature, see: Ren *et al.* (2000); Onderwater *et al.* (2004); Rodriguez-Fernandez *et al.* (2005); Zhou *et al.* (2003); Stankovic & Vukovic (1996); Trochimczuk & Kolarz (2000); Castro *et al.* (2003); Kearney *et al.* (1998); Nie *et al.* (2004).



Experimental

Crystal data

$C_9H_{10}BrN_3O_2S$
M_r = 304.17
Monoclinic, $P2_1/c$
a = 15.6156 (17) Å
b = 7.7312 (15) Å
c = 9.8876 (9) Å
β = 98.531 (8)°
V = 1180.5 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.65 mm^{-1}
T = 173 (2) K
0.27 × 0.25 × 0.24 mm

Data collection

Stoe IPDSII two-circle diffractometer
Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)
T_{min} = 0.439, T_{max} = 0.475 (expected range = 0.385–0.417)
10501 measured reflections
2266 independent reflections
1931 reflections with $I > 2\sigma(I)$
R_{int} = 0.063

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.071
S = 1.05
2266 reflections
163 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.56 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.85 (4)	2.06 (3)	2.825 (3)	148 (4)
N2—H2···S1^{ii}	0.81 (3)	2.55 (3)	3.351 (2)	171 (3)
N3—H3*A*···O1^{iii}	0.86 (4)	2.25 (4)	3.068 (3)	159 (3)
N3—H3*B*···S1^{iv}	0.84 (4)	2.95 (4)	3.570 (3)	132 (3)

Symmetry codes: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+1, -y, -z+1$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2477).

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supplementary materials

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1-(2-Bromo-5-methoxybenzoyl)thiosemicarbazide

B. K. Sarojini, B. Narayana, K. Veena, H. S. Yathirajan and M. Bolte

Comment

Thiourea and its derivatives have been the focus of attention in recent years in view of their interesting physicochemical properties and broad range of applications in several chemical disciplines. Certain thiourea molecules have antiviral activity and might be characterized as prospective inhibitors of many enzymes, particularly, HIV-1 reverse transcriptase (Ren *et al.*, 2000; Onderwater *et al.*, 2004). As antibacterial and antifungal agents, they have been used in agriculture (Rodriguez-Fernandez *et al.*, 2005). In technical applications, dithioamide compounds are known to be prospective nonlinear optical materials (Zhou *et al.*, 2003), corrosion inhibitors for copper and iron in acidic media (Stankovic *et al.*, 1996) and functionalization agents for production of chemically modified resins (Trochimczuk *et al.*, 2000). Thiourea derivatives have been also reported as potential receptors and ionophores for heavy metal cations (Castro *et al.*, 2003), building blocks in the synthesis of heterocyclic compounds (Kearney *et al.*, 1998). Finally, the strong hydrogen-bonding donor capability of the –N(H)—C(=S)—N(H)- group has been widely exploited in supramolecular chemistry, where it has been used as a building block for anion receptors (Nie *et al.*, 2004). A new carbothioamide, $C_9H_{10}BrN_3O_2S$, has been synthesized and its crystal structure is reported herein.

Geometric parameters of the title molecule (Fig. 1) are in the usual ranges. The plane of the thiourea moiety is almost co-parallel to the plane of the aromatic ring [dihedral angle = 8.40 (12)°]. Only the torsion angles about the $C_{carbonyl}$—$C_{aromatic}$ bond [N1—C1—C11—C12 = 114.0 (3)°] and N—N bond [C1—N1—N2—C2 = −100.9 (3)°] differ significantly from 0 or 180°. The crystal packing is stabilized by N—H···O and N—H···S hydrogen bonds.

Experimental

2-Bromo-5-methoxybenzohydrazide (1.98 g, 0.0081 mol) was refluxed with potassium thiocyanate (1.4 g, 0.0142 mol) in 20 ml of water and 1.6 ml of conc. HCl for 4 h. The reaction mixture was then cooled to room temperature and stirred overnight. The precipitated product was then filtered, washed with water, dried and recrystallized from a mixture of dimethylformamide and methylethylketone (1:1) (m.p.: 472–474 K). Analysis for $C_9H_{10}BrN_3O_2S$: Found (Calculated): C:35.46 (35.54); H: 3.27 (3.31); N:13.72 (13.81): S: 10.43% (10.54%).

Refinement

H atoms were found in a difference map, but those bonded to C atom were refined using a riding model with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C) for $C_{aromatic}$ and C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C) for C_{methyl}. The methyl group was allowed to rotate but not to tip. The H atoms bonded to N were refined isotropically.

Figures

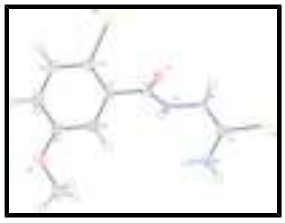

Fig. 1. The molecular structure with the atom numbering; displacement ellipsoids are at the 50% probability level.

1-(2-Bromo-5-methoxybenzoyl)thiosemicarbazide

Crystal data

$C_9H_{10}BrN_3O_2S$	F_{000} = 608
M_r = 304.17	D_x = 1.711 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 10030 reflections
a = 15.6156 (17) Å	θ = 3.7–25.9º
b = 7.7312 (15) Å	μ = 3.65 mm^{-1}
c = 9.8876 (9) Å	T = 173 (2) K
β = 98.531 (8)º	Block, colourless
V = 1180.5 (3) Å^3	0.27 × 0.25 × 0.24 mm
Z = 4	

Data collection

Stoe IPDSII two-circle diffractometer	2266 independent reflections
Radiation source: fine-focus sealed tube	1931 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.063
T = 173(2) K	θ_{max} = 25.8º
ω scans	θ_{min} = 3.7º
Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)	h = −19→17
T_{min} = 0.439, T_{max} = 0.475	k = −9→8
10501 measured reflections	l = −12→12

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)]$ = 0.030	$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 0.1127P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.071	$(\Delta/\sigma)_{max} < 0.001$

S = 1.05	$\Delta\rho_{max}$ = 0.52 e Å^{-3}
2266 reflections	$\Delta\rho_{min}$ = −0.56 e Å^{-3}
163 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0071 (8)
Secondary atom site location: difference Fourier map	

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 $F^2 > 2\text{sigma}(F^2)$ 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}
Br1	0.85433 (2)	0.12212 (4)	0.47258 (3)	0.03109 (12)
S1	0.39720 (4)	0.17481 (10)	0.55281 (7)	0.02750 (18)
O1	0.65985 (12)	0.3225 (2)	0.41909 (16)	0.0221 (4)
O2	0.86654 (13)	0.8137 (3)	0.75887 (19)	0.0295 (5)
N1	0.64664 (14)	0.2785 (3)	0.6421 (2)	0.0181 (4)
H1	0.669 (3)	0.269 (5)	0.726 (4)	0.043 (10)*
N2	0.56775 (14)	0.1932 (3)	0.6095 (2)	0.0185 (4)
H2	0.570 (2)	0.103 (4)	0.569 (3)	0.026 (8)*
N3	0.49439 (18)	0.4348 (3)	0.6639 (2)	0.0267 (5)
H3A	0.447 (2)	0.491 (5)	0.660 (3)	0.033 (9)*
H3B	0.543 (3)	0.476 (5)	0.695 (3)	0.038 (10)*
C1	0.69051 (16)	0.3331 (3)	0.5411 (2)	0.0161 (5)
C2	0.49182 (17)	0.2770 (3)	0.6114 (2)	0.0181 (5)
C11	0.77712 (16)	0.4120 (3)	0.5912 (2)	0.0164 (5)
C12	0.85456 (17)	0.3356 (3)	0.5681 (2)	0.0195 (5)
C13	0.93357 (17)	0.4171 (4)	0.6103 (2)	0.0237 (6)
H13	0.9860	0.3632	0.5955	0.028*
C14	0.93542 (18)	0.5765 (4)	0.6738 (3)	0.0257 (6)
H14	0.9893	0.6326	0.7019	0.031*
C15	0.85812 (17)	0.6559 (3)	0.6970 (2)	0.0210 (5)
C16	0.77910 (16)	0.5724 (3)	0.6580 (2)	0.0181 (5)
H16	0.7269	0.6240	0.6765	0.022*
C17	0.7887 (2)	0.9056 (4)	0.7737 (3)	0.0307 (6)
H17A	0.7513	0.9115	0.6850	0.046*
H17B	0.8033	1.0231	0.8066	0.046*

H17C	0.7582	0.8451	0.8395	0.046*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.03588 (19)	0.02696 (17)	0.03174 (16)	0.00653 (14)	0.00934 (11)	−0.00653 (11)
S1	0.0147 (3)	0.0272 (4)	0.0387 (4)	0.0010 (3)	−0.0021 (3)	−0.0109 (3)
O1	0.0232 (10)	0.0288 (10)	0.0133 (8)	−0.0023 (8)	−0.0001 (7)	−0.0017 (7)
O2	0.0228 (10)	0.0300 (11)	0.0351 (10)	−0.0058 (9)	0.0021 (8)	−0.0124 (9)
N1	0.0157 (11)	0.0247 (12)	0.0137 (9)	−0.0040 (9)	0.0014 (8)	0.0004 (8)
N2	0.0139 (11)	0.0196 (11)	0.0222 (10)	−0.0028 (9)	0.0035 (8)	−0.0043 (9)
N3	0.0187 (13)	0.0253 (13)	0.0352 (12)	0.0015 (11)	0.0013 (10)	−0.0121 (10)
C1	0.0174 (12)	0.0159 (12)	0.0151 (10)	0.0022 (10)	0.0030 (9)	0.0000 (9)
C2	0.0199 (13)	0.0214 (13)	0.0129 (10)	0.0004 (11)	0.0017 (9)	0.0007 (9)
C11	0.0181 (12)	0.0195 (13)	0.0117 (10)	−0.0005 (10)	0.0026 (9)	0.0032 (8)
C12	0.0231 (13)	0.0213 (13)	0.0148 (10)	0.0023 (10)	0.0048 (9)	0.0026 (9)
C13	0.0154 (13)	0.0356 (16)	0.0209 (11)	0.0033 (11)	0.0051 (10)	0.0061 (10)
C14	0.0153 (13)	0.0371 (16)	0.0239 (12)	−0.0037 (12)	0.0005 (10)	0.0011 (11)
C15	0.0193 (13)	0.0256 (14)	0.0178 (10)	−0.0025 (11)	0.0014 (9)	0.0015 (10)
C16	0.0165 (13)	0.0230 (13)	0.0151 (10)	−0.0009 (10)	0.0035 (9)	−0.0008 (9)
C17	0.0310 (16)	0.0282 (16)	0.0338 (14)	−0.0035 (13)	0.0080 (12)	−0.0126 (12)

Geometric parameters (Å, °)

Br1—C12	1.901 (3)	C1—C11	1.499 (3)
S1—C2	1.700 (3)	C11—C12	1.395 (4)
O1—C1	1.233 (3)	C11—C16	1.403 (3)
O2—C15	1.363 (3)	C12—C13	1.393 (4)
O2—C17	1.434 (4)	C13—C14	1.382 (4)
N1—C1	1.359 (3)	C13—H13	0.9500
N1—N2	1.392 (3)	C14—C15	1.403 (4)
N1—H1	0.85 (4)	C14—H14	0.9500
N2—C2	1.354 (3)	C15—C16	1.395 (4)
N2—H2	0.81 (3)	C16—H16	0.9500
N3—C2	1.324 (3)	C17—H17A	0.9800
N3—H3A	0.86 (4)	C17—H17B	0.9800
N3—H3B	0.84 (4)	C17—H17C	0.9800
C15—O2—C17	117.6 (2)	C13—C12—Br1	118.54 (19)
C1—N1—N2	120.13 (19)	C11—C12—Br1	120.74 (19)
C1—N1—H1	124 (3)	C14—C13—C12	119.8 (2)
N2—N1—H1	114 (3)	C14—C13—H13	120.1
C2—N2—N1	121.1 (2)	C12—C13—H13	120.1
C2—N2—H2	122 (2)	C13—C14—C15	120.2 (2)
N1—N2—H2	115 (2)	C13—C14—H14	119.9
C2—N3—H3A	118 (2)	C15—C14—H14	119.9
C2—N3—H3B	118 (2)	O2—C15—C16	124.1 (2)
H3A—N3—H3B	124 (3)	O2—C15—C14	115.9 (2)
O1—C1—N1	122.2 (2)	C16—C15—C14	120.0 (2)

O1—C1—C11	123.4 (2)	C15—C16—C11	119.7 (2)
N1—C1—C11	114.32 (19)	C15—C16—H16	120.1
N3—C2—N2	118.1 (2)	C11—C16—H16	120.1
N3—C2—S1	122.4 (2)	O2—C17—H17A	109.5
N2—C2—S1	119.45 (19)	O2—C17—H17B	109.5
C12—C11—C16	119.5 (2)	H17A—C17—H17B	109.5
C12—C11—C1	122.4 (2)	O2—C17—H17C	109.5
C16—C11—C1	118.1 (2)	H17A—C17—H17C	109.5
C13—C12—C11	120.7 (2)	H17B—C17—H17C	109.5
C1—N1—N2—C2	−100.9 (3)	C1—C11—C12—Br1	−1.0 (3)
N2—N1—C1—O1	5.9 (4)	C11—C12—C13—C14	−1.1 (4)
N2—N1—C1—C11	−176.1 (2)	Br1—C12—C13—C14	176.76 (18)
N1—N2—C2—N3	−9.6 (3)	C12—C13—C14—C15	0.6 (4)
N1—N2—C2—S1	172.75 (17)	C17—O2—C15—C16	−5.7 (4)
O1—C1—C11—C12	−68.1 (3)	C17—O2—C15—C14	174.8 (2)
N1—C1—C11—C12	114.0 (3)	C13—C14—C15—O2	−179.3 (2)
O1—C1—C11—C16	108.9 (3)	C13—C14—C15—C16	1.1 (4)
N1—C1—C11—C16	−69.1 (3)	O2—C15—C16—C11	178.2 (2)
C16—C11—C12—C13	−0.1 (3)	C14—C15—C16—C11	−2.3 (3)
C1—C11—C12—C13	176.8 (2)	C12—C11—C16—C15	1.8 (3)
C16—C11—C12—Br1	−177.87 (17)	C1—C11—C16—C15	−175.2 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.85 (4)	2.06 (3)	2.825 (3)	148 (4)
N2—H2···S1^{ii}	0.81 (3)	2.55 (3)	3.351 (2)	171 (3)
N3—H3A···O1^{iii}	0.86 (4)	2.25 (4)	3.068 (3)	159 (3)
N3—H3B···S1^{iv}	0.84 (4)	2.95 (4)	3.570 (3)	132 (3)

Symmetry codes: (i) *x*, −*y*+1/2, *z*+1/2; (ii) −*x*+1, −*y*, −*z*+1; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) −*x*+1, *y*+1/2, −*z*+3/2.

Fig. 1