Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Benzyl (*E*)-3-(2-bromo-5-methoxybenzylidene)dithiocarbazate

Zheng Fan,[a] Yan-Lan Huang,[b] Zhao Wang,[b] Han-Qi Guo[b] and Shang Shan[b]*

[a]College of Biological and Environmental Engineering, Zhejiang University of Technology, People's Republic of China, and [b]College of Chemical Engineering and Materials Science, Zhejiang University of Technology, People's Republic of China
Correspondence e-mail: shanshang@mail.hz.zj.cn

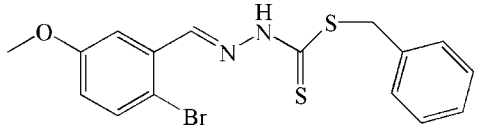
Received 7 October 2011; accepted 15 October 2011

Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.004 Å; R factor = 0.034; wR factor = 0.069; data-to-parameter ratio = 14.9.

The title compound, $C_{16}H_{15}BrN_2OS_2$, was obtained from the condensation reaction of benzyl dithiocarbazate and 2-bromo-5-methoxylbenzaldehyde. In the molecule, the bromomethoxyphenyl ring and dithiocarbazate fragment are located on the opposite sides of the C=N double bond, showing the *E* conformation. The dithiocarbazate fragment is approximately planar (r.m.s deviation 0.0187 Å); its mean plane is oriented with respect to the bromomethoxyphenyl and phenyl rings at 7.60 (12) and 60.08 (9)°, respectively. In the crystal, inversion dimers linked by pairs of N—H···S hydrogen bonds occur. A short Br···Br contact of 3.5526 (12) Å is observed in the crystal structure.

Related literature

For the potential application of hydrazone and its derivatives in the biological field, see: Okabe *et al.* (1993); Hu *et al.* (2001). For related structures, see: Shan *et al.* (2008*a*,*b*). For the synthesis, see: Hu *et al.* (2001).



Experimental

Crystal data

$C_{16}H_{15}BrN_2OS_2$
M_r = 395.33
Triclinic, $P\overline{1}$
a = 6.260 (3) Å
b = 11.889 (5) Å
c = 12.235 (5) Å
α = 111.931 (5)°
β = 91.725 (4)°
γ = 99.771 (4)°
V = 828.1 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.74 mm^{-1}
T = 294 K
0.32 × 0.28 × 0.19 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.56, T_{max} = 0.72
5637 measured reflections
2988 independent reflections
2379 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.069
S = 1.02
2988 reflections
201 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···S1^{i}	0.86	2.56	3.402 (3)	167

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The work was supported by the Natural Science Foundation of Zhejiang Province, China (grant No. M203027).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5353).

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Hu, W., Sun, N. & Yang, Z. (2001). *Chem. J. Chin. Univ.* **22**, 2014–2017.
Okabe, N., Nakamura, T. & Fukuda, H. (1993). *Acta Cryst.* C**49**, 1678–1680.
Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC, The Woodlands, Texas, USA.
Shan, S., Tian, Y.-L., Wang, S.-H., Wang, W.-L. & Xu, Y.-L. (2008*a*). *Acta Cryst.* E**64**, o1014.
Shan, S., Tian, Y.-L., Wang, S.-H., Wang, W.-L. & Xu, Y.-L. (2008*b*). *Acta Cryst.* E**64**, o1024.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2011). E**67**, o3015 [doi:10.1107/S1600536811042826]

Benzyl (*E*)-3-(2-bromo-5-methoxybenzylidene)dithiocarbazate

Zheng Fan, Yan-Lan Huang, Zhao Wang, Han-Qi Guo and Shang Shan

S1. Comment

Hydrazone and its derivatives have shown the potential application in the biological field (Okabe *et al.*, 1993; Hu *et al.*, 2001). As part of the ongoing investigation on anti-cancer compounds, the title compound has recently been prepared in our laboratory and its crystal structure is presented here.

In the molecules, the methoxylphenyl ring and dithiocarbazate fragment are located on the opposite sides of the C═N double bond, showing the E-configuration. The dithiocarbazate fragment is approximately planar [r.m.s deviation 0.0187 Å]; the mean plane of dithiocarbazate is oriented with respect to the methoxylphenyl and phenyl rings at 7.60 (12) and 60.08 (9)°, similar to those found in related structures (Shan *et al.* 2008*a*, 2008*b*). Intermolecular N—H···S hydrogen bonding is observed in the crystal structure (Table 1). The short Br···Br^{i} contact of 3.5526 (12) Å is also present in the crystal structure [symmetry code: (i) 1-x,-y,-z].

S2. Experimental

Benzyl dithiocarbazate was synthesized as described previously (Hu *et al.*, 2001). Benzyl dithiocarbazate (0.40 g, 2 mmol) and 2-bromo-5-methoxybenzaldehyde (0.43 g, 2 mmol) were dissolved in ethanol (20 ml), then acetic acid (0.2 ml) was added to the ethanol solution with stirring. The mixture solution was refluxed for 6 h. After cooling to room temperature, microcrystals appeared. The microcrystals were separated from the solution and washed with cold water three times. Recrystallization was performed twice with absolute methanol to obtain colourless single crystals of the title compound.

S3. Refinement

H atoms were placed in calculated positions with C—H = 0.93–0.97 Å and N—H = 0.86 Å, and refined in riding mode with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C,*N*) for the others.

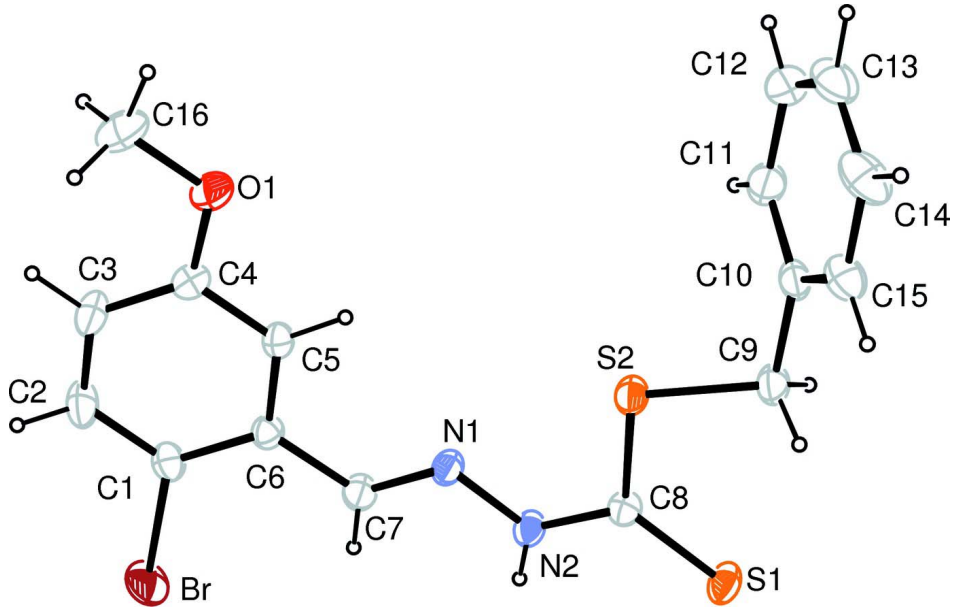


Figure 1

The molecular structure of the title compound with 30% probability displacement (arbitrary spheres for H atoms).

Benzyl (*E*)-3-(2-bromo-5-methoxybenzylidene)dithiocarbazate

Crystal data

$C_{16}H_{15}BrN_2OS_2$
$M_r = 395.33$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 6.260$ (3) Å
$b = 11.889$ (5) Å
$c = 12.235$ (5) Å
$\alpha = 111.931$ (5)°
$\beta = 91.725$ (4)°
$\gamma = 99.771$ (4)°
$V = 828.1$ (6) Å^3
$Z = 2$
$F(000) = 400$
$D_x = 1.586$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2988 reflections
$\theta = 3.3$–25.2°
$\mu = 2.74$ mm^{-1}
$T = 294$ K
Block, yellow
0.32 × 0.28 × 0.19 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.0 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.56$, $T_{max} = 0.72$
5637 measured reflections
2988 independent reflections
2379 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 25.2°$, $\theta_{min} = 3.3°$
$h = -5 \rightarrow 7$
$k = -14 \rightarrow 11$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.069$
$S = 1.02$
2988 reflections
201 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
$w = 1/[\sigma^2(F_o^2) + (0.0276P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Extinction correction: *SHELXL97*, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0123 (11)

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}
Br	0.33444 (5)	0.11365 (3)	0.04397 (2)	0.05700 (14)
S1	1.10460 (10)	0.70610 (6)	0.10224 (6)	0.0458 (2)
S2	0.72189 (10)	0.76733 (6)	0.24288 (6)	0.0423 (2)
N1	0.5742 (3)	0.51783 (19)	0.15272 (15)	0.0336 (5)
N2	0.7654 (3)	0.54749 (19)	0.10904 (16)	0.0356 (5)
H2	0.8197	0.4905	0.0580	0.043*
O1	−0.0891 (3)	0.51964 (18)	0.35686 (15)	0.0501 (5)
C1	0.1988 (4)	0.2431 (2)	0.13964 (19)	0.0366 (6)
C2	0.0116 (5)	0.2108 (3)	0.1861 (2)	0.0487 (8)
H2A	−0.0459	0.1278	0.1682	0.058*
C3	−0.0907 (4)	0.2999 (3)	0.2586 (2)	0.0465 (7)
H3	−0.2169	0.2778	0.2900	0.056*
C4	−0.0045 (4)	0.4226 (3)	0.2843 (2)	0.0370 (6)
C5	0.1811 (4)	0.4548 (2)	0.23569 (19)	0.0341 (6)
H5	0.2356	0.5378	0.2518	0.041*
C6	0.2875 (4)	0.3660 (2)	0.16346 (19)	0.0314 (6)
C7	0.4884 (4)	0.4042 (2)	0.11732 (19)	0.0356 (6)
H7	0.5525	0.3453	0.0623	0.043*
C8	0.8663 (4)	0.6654 (2)	0.14642 (18)	0.0319 (6)
C9	0.8899 (4)	0.9158 (2)	0.2670 (2)	0.0414 (7)
H9A	1.0306	0.9241	0.3078	0.050*
H9B	0.9132	0.9233	0.1918	0.050*
C10	0.7736 (4)	1.0146 (2)	0.3410 (2)	0.0380 (6)
C11	0.5706 (5)	1.0236 (3)	0.3006 (2)	0.0489 (8)
H11	0.5048	0.9677	0.2267	0.059*
C12	0.4647 (5)	1.1145 (3)	0.3690 (3)	0.0587 (8)
H12	0.3299	1.1210	0.3404	0.070*
C13	0.5599 (6)	1.1955 (3)	0.4797 (3)	0.0624 (9)
H13	0.4869	1.2552	0.5269	0.075*

C14	0.7606 (6)	1.1886 (3)	0.5205 (2)	0.0636 (9)
H14	0.8250	1.2441	0.5948	0.076*
C15	0.8682 (5)	1.0989 (3)	0.4509 (2)	0.0487 (7)
H15	1.0059	1.0953	0.4786	0.058*
C16	−0.2653 (5)	0.4938 (3)	0.4202 (2)	0.0604 (9)
H16A	−0.3916	0.4475	0.3655	0.091*
H16B	−0.2973	0.5700	0.4744	0.091*
H16C	−0.2260	0.4464	0.4636	0.091*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.0715 (2)	0.03141 (19)	0.0601 (2)	0.01393 (14)	0.01395 (15)	0.00643 (14)
S1	0.0383 (4)	0.0355 (4)	0.0532 (4)	0.0005 (3)	0.0211 (3)	0.0069 (3)
S2	0.0413 (4)	0.0289 (4)	0.0511 (4)	0.0051 (3)	0.0214 (3)	0.0084 (3)
N1	0.0292 (10)	0.0319 (13)	0.0367 (10)	0.0026 (9)	0.0078 (9)	0.0109 (9)
N2	0.0333 (11)	0.0297 (13)	0.0390 (11)	0.0034 (9)	0.0146 (9)	0.0083 (9)
O1	0.0423 (11)	0.0511 (13)	0.0580 (11)	0.0155 (9)	0.0225 (9)	0.0181 (9)
C1	0.0422 (15)	0.0286 (15)	0.0355 (13)	0.0030 (12)	0.0031 (11)	0.0101 (11)
C2	0.0553 (17)	0.0332 (17)	0.0505 (15)	−0.0061 (14)	0.0095 (14)	0.0140 (13)
C3	0.0389 (15)	0.0474 (19)	0.0507 (15)	−0.0051 (13)	0.0116 (13)	0.0214 (14)
C4	0.0309 (13)	0.0432 (17)	0.0362 (13)	0.0080 (12)	0.0038 (11)	0.0142 (12)
C5	0.0311 (13)	0.0265 (14)	0.0412 (13)	0.0006 (11)	0.0028 (11)	0.0113 (11)
C6	0.0302 (13)	0.0300 (15)	0.0313 (11)	0.0030 (11)	0.0013 (10)	0.0102 (10)
C7	0.0378 (14)	0.0294 (15)	0.0347 (12)	0.0050 (11)	0.0092 (11)	0.0070 (11)
C8	0.0327 (13)	0.0329 (15)	0.0276 (11)	0.0047 (11)	0.0044 (10)	0.0096 (10)
C9	0.0414 (15)	0.0293 (15)	0.0476 (14)	0.0016 (12)	0.0134 (12)	0.0097 (12)
C10	0.0443 (15)	0.0262 (15)	0.0444 (14)	0.0047 (12)	0.0165 (12)	0.0146 (12)
C11	0.0441 (16)	0.0421 (18)	0.0547 (16)	0.0045 (13)	0.0117 (13)	0.0133 (13)
C12	0.0470 (17)	0.054 (2)	0.084 (2)	0.0160 (15)	0.0236 (17)	0.0319 (18)
C13	0.085 (2)	0.043 (2)	0.068 (2)	0.0282 (17)	0.0390 (19)	0.0228 (16)
C14	0.102 (3)	0.0402 (19)	0.0437 (16)	0.0218 (18)	0.0107 (17)	0.0072 (14)
C15	0.0603 (18)	0.0353 (17)	0.0466 (15)	0.0094 (14)	0.0060 (14)	0.0113 (13)
C16	0.0449 (16)	0.085 (3)	0.0553 (16)	0.0222 (16)	0.0221 (14)	0.0258 (16)

Geometric parameters (Å, º)

Br—C1	1.902 (3)	C6—C7	1.465 (3)
S1—C8	1.658 (3)	C7—H7	0.9300
S2—C8	1.745 (2)	C9—C10	1.505 (4)
S2—C9	1.808 (3)	C9—H9A	0.9700
N1—C7	1.267 (3)	C9—H9B	0.9700
N1—N2	1.370 (3)	C10—C15	1.381 (3)
N2—C8	1.333 (3)	C10—C11	1.385 (4)
N2—H2	0.8600	C11—C12	1.382 (4)
O1—C4	1.368 (3)	C11—H11	0.9300
O1—C16	1.424 (3)	C12—C13	1.378 (4)
C1—C2	1.377 (4)	C12—H12	0.9300

C1—C6	1.387 (4)	C13—C14	1.365 (5)
C2—C3	1.372 (4)	C13—H13	0.9300
C2—H2A	0.9300	C14—C15	1.384 (4)
C3—C4	1.378 (4)	C14—H14	0.9300
C3—H3	0.9300	C15—H15	0.9300
C4—C5	1.382 (3)	C16—H16A	0.9600
C5—C6	1.385 (3)	C16—H16B	0.9600
C5—H5	0.9300	C16—H16C	0.9600

C8—S2—C9	101.87 (12)	C10—C9—S2	107.86 (17)
C7—N1—N2	116.98 (19)	C10—C9—H9A	110.1
C8—N2—N1	119.40 (18)	S2—C9—H9A	110.1
C8—N2—H2	120.3	C10—C9—H9B	110.1
N1—N2—H2	120.3	S2—C9—H9B	110.1
C4—O1—C16	118.1 (2)	H9A—C9—H9B	108.4
C2—C1—C6	121.2 (2)	C15—C10—C11	118.5 (2)
C2—C1—Br	117.7 (2)	C15—C10—C9	120.4 (2)
C6—C1—Br	121.16 (18)	C11—C10—C9	121.0 (2)
C3—C2—C1	120.6 (3)	C12—C11—C10	120.8 (3)
C3—C2—H2A	119.7	C12—C11—H11	119.6
C1—C2—H2A	119.7	C10—C11—H11	119.6
C2—C3—C4	119.3 (2)	C13—C12—C11	119.7 (3)
C2—C3—H3	120.3	C13—C12—H12	120.2
C4—C3—H3	120.3	C11—C12—H12	120.2
O1—C4—C3	124.7 (2)	C14—C13—C12	120.3 (3)
O1—C4—C5	115.2 (2)	C14—C13—H13	119.8
C3—C4—C5	120.0 (2)	C12—C13—H13	119.8
C4—C5—C6	121.3 (2)	C13—C14—C15	119.9 (3)
C4—C5—H5	119.3	C13—C14—H14	120.1
C6—C5—H5	119.3	C15—C14—H14	120.1
C5—C6—C1	117.6 (2)	C10—C15—C14	120.8 (3)
C5—C6—C7	119.6 (2)	C10—C15—H15	119.6
C1—C6—C7	122.8 (2)	C14—C15—H15	119.6
N1—C7—C6	119.7 (2)	O1—C16—H16A	109.5
N1—C7—H7	120.1	O1—C16—H16B	109.5
C6—C7—H7	120.1	H16A—C16—H16B	109.5
N2—C8—S1	121.55 (17)	O1—C16—H16C	109.5
N2—C8—S2	113.22 (17)	H16A—C16—H16C	109.5
S1—C8—S2	125.23 (15)	H16B—C16—H16C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···S1^{i}	0.86	2.56	3.402 (3)	167

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