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

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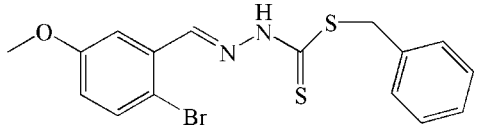
Key indicators: single-crystal X-ray study; $T$ = 294 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.034; $wR$ factor = 0.069; data-to-parameter ratio = 14.9.

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
$\alpha$ = 111.931 (5)°
$\beta$ = 91.725 (4)°
$\gamma$ = 99.771 (4)°
$V$ = 828.1 (6) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 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).

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

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# supplementary materials

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

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

**Z. Fan, Y.-L. Huang, Z. Wang, H.-Q. Guo and S. Shan**

## 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].

## 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. Re-crystallization was performed twice with absolute methanol to obtain colourless single crystals of the title compound.

## 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) = 1.5$U_{eq}$(C) for methyl H atoms and 1.2$U_{eq}$(C,*N*) for the others.

## Figures

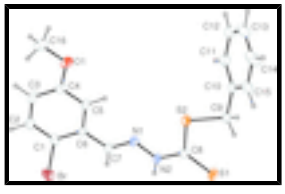


Fig. 1. The molecular structure of the title compound with 30% probability displacement (arbitrary spheres for H atoms).

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

*Crystal data*

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

*Data collection*

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

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.034$ | H-atom parameters constrained |
| $wR(F^2) = 0.069$ | $w = 1/[\sigma^2(F_o^2) + (0.0276P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.02$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 2988 reflections | $\Delta\rho_{max} = 0.25$ e Å$^{-3}$ |
| 201 parameters | $\Delta\rho_{min} = -0.30$ e Å$^{-3}$ |
| 0 restraints | Extinction correction: *SHELXL97*, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$ |
| Primary atom site location: structure-invariant direct methods | 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 (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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, °)*

| | | | |
|---|---|---|---|
| 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 |

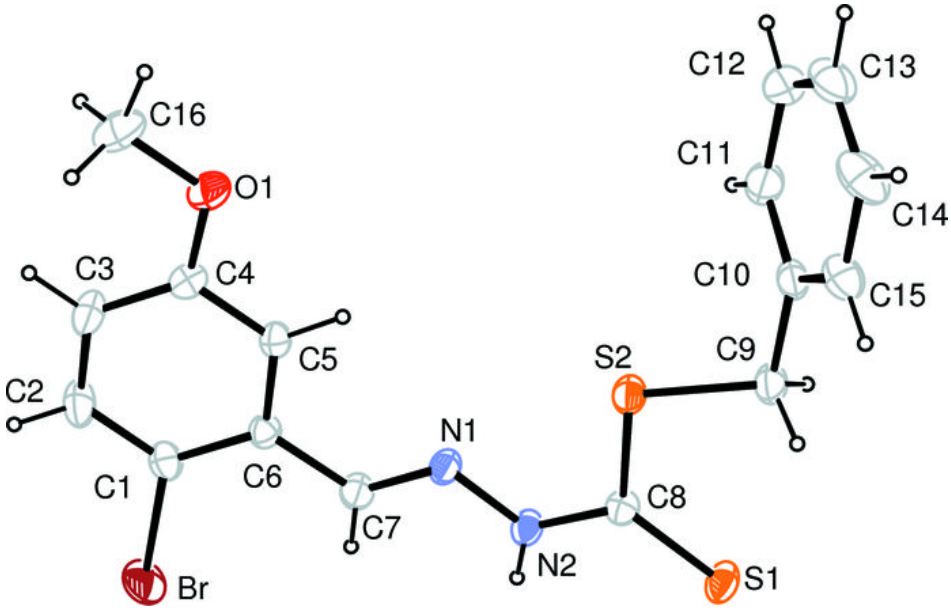
| | | | |
|---|---|---|---|
| C4—C5 | 1.382 (3) | C16—H16A | 0.9600 |
| C5—C6 | 1.385 (3) | C16—H16B | 0.9600 |
| C5—H5 | 0.9300 | C16—H16C | 0.9600 |
| C8—S2—C9 | 101.87 (12) | C10—C9—S2 | 107.86 (17) |
| C7—N1—N2 | 116.98 (19) | C10—C9—H9A | 110.1 |
| C8—N2—N1 | 119.40 (18) | S2—C9—H9A | 110.1 |
| 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, °)*

| *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 codes: (i) −*x*+2, −*y*+1, −*z*.

**Fig. 1**


C16
O1
C3
C4
C5
C2
C1
C6
Br
C7
N1
N2
S2
C8
S1
C9
C10
C11
C12
C13
C14
C15