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Benzyl 3-[(*E*)-2-nitrobenzylidene]dithiocarbazate

Shang Shan,* Yan-Lan Huang, Han-Qi Guo, Deng-Feng Li and Jian Sun

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

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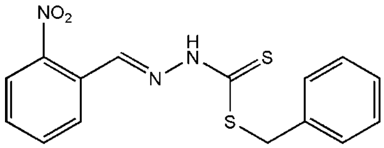
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.005 Å; R factor = 0.055; wR factor = 0.147; data-to-parameter ratio = 14.1.

The title compound, $C_{15}H_{13}N_3O_2S_2$, was obtained from a condensation reaction of benzyl dithiocarbazate and 2-nitrobenzaldehyde. In the molecule, the nearly planar dithiocarbazate fragment [r.m.s deviation = 0.0264 Å] is oriented at dihedral angles of 7.25 (17) and 74.09 (9)°with respect to the two benzene rings. The nitro group is twisted by a dihedral angle of 22.4 (7)° to the attached benzene ring. The nitrobenzene ring and dithiocarbazate fragment are located on the opposite sides of the C=N bond, showing an *E* configuration. In the crystal, molecules are linked *via* intermolecular N—H⋯S hydrogen bonds, forming centrosymmetric supramolecular dimers. Weak C—H⋯π interaction is also observed in the crystal structure.

Related literature

For applications 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.* (2006, 2008*a*,*b*, 2011). For the synthesis, see: Hu *et al.* (2001).



Experimental

Crystal data

$C_{15}H_{13}N_3O_2S_2$
M_r = 331.40
Monoclinic, $P2_1/c$
a = 4.673 (2) Å
b = 28.498 (6) Å
c = 11.735 (5) Å
β = 94.070 (4)°
V = 1558.8 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.35 mm^{-1}
T = 294 K
0.38 × 0.25 × 0.23 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.87, T_{max} = 0.94
6957 measured reflections
2814 independent reflections
1925 reflections with $I > 2\sigma(I)$
R_{int} = 0.041

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.147
S = 1.05
2814 reflections
199 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

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

Cg is the centroid of the C10–C15 ring.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2⋯S1^{i}	0.86	2.51	3.359 (3)	171
C9—H9B⋯Cg^{ii}	0.97	2.50	3.410 (4)	156

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

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 (No. M203027).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5268).

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supplementary materials

Acta Cryst. (2011). E**67**, o2107 [**doi:10.1107/S1600536811028686**]

Benzyl 3-[(*E*)-2-nitrobenzylidene]dithiocarbazate

S. Shan, Y.-L. Huang, H.-Q. Guo, D.-F. Li and **J. Sun**

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.

The molecular structure of the title compound is shown in Fig. 1. In the molecule the nearly planar dithiocarbazate fragment [r.m.s deviation 0.0264 Å] is oriented with respect to the two benzene rings at 7.25 (17) and 74.09 (9)°, respectively. The nitro group is twisted to the attached-benzene ring with a dihedral angle of 22.4 (7)°. The N1—C7 bond length of 1.272 (4) Å indicates a typical C═N double bonds. The nitrobenzene ring and dithiocarbazate fragment are located on the opposite positions of the C═N bonds, showing the E-configuration, which agrees with those found in related compounds (Shan *et al.*, 2006; Shan *et al.*, 2008*a*,*b*); Shan *et al.* 2011). In the crystal the molecules are linked to each other via intermolecular N—H···S hydrogen bonding to form the centro-symmetric supramolecular dimer (Table 1). Weak C—H···π interaction is also observed in the crystal structure.

Experimental

Benzyl dithiocarbazate was synthesized as described previously (Hu *et al.*, 2001). Benzyl dithiocarbazate (0.4 g, 2 mmol) and 2-nitrobenzaldehyde (0.3 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, yellow 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 single crystals of the title compound.

Refinement

H atoms were placed in calculated positions with C—H = 0.93 (aromatic), 0.97 (methylene) and N—H = 0.86 Å, and refined in riding mode with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C},N)$.

Figures

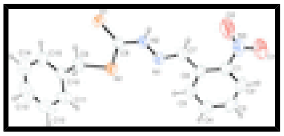


Fig. 1. The molecular structure of the title compound with 40% probability displacement (arbitrary spheres for H atoms).

Benzyl 3-[(*E*)-2-nitrobenzylidene]dithiocarbazate

Crystal data

$C_{15}H_{13}N_3O_2S_2$

$M_r = 331.40$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 4.673$ (2) Å

$b = 28.498$ (6) Å

$c = 11.735$ (5) Å

$\beta = 94.070$ (4)°

$V = 1558.8$ (10) Å^3

$Z = 4$

$F(000) = 688$

$D_x = 1.412$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2814 reflections

$\theta = 2.7$–25.2°

$\mu = 0.35$ mm^{-1}

$T = 294$ K

Needle, yellow

0.38 × 0.25 × 0.23 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer

Radiation source: fine-focus sealed tube

graphite

Detector resolution: 10.0 pixels mm^{-1}

ω scans

Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)

$T_{min} = 0.87$, $T_{max} = 0.94$

6957 measured reflections

2814 independent reflections

1925 reflections with $I > 2\sigma(I)$

$R_{int} = 0.041$

$\theta_{max} = 25.2°$, $\theta_{min} = 2.8°$

$h = -5 \rightarrow 5$

$k = -34 \rightarrow 33$

$l = -10 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.055$

$wR(F^2) = 0.147$

$S = 1.05$

2814 reflections

199 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

$w = 1/[\sigma^2(F_o^2) + (0.0677P)^2 + 0.3832P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.63$ e Å^{-3}

$\Delta\rho_{min} = -0.47$ 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.

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}
S1	0.1945 (2)	0.55533 (3)	0.40002 (8)	0.0502 (3)
S2	0.53350 (19)	0.50159 (3)	0.23425 (8)	0.0520 (3)
N1	0.3569 (6)	0.42391 (8)	0.3495 (2)	0.0448 (7)
N2	0.2412 (6)	0.46411 (8)	0.3892 (2)	0.0462 (7)
H2	0.1235	0.4627	0.4423	0.055*
N3	0.2496 (8)	0.29447 (12)	0.5248 (3)	0.0760 (10)
O1	0.1632 (9)	0.25714 (11)	0.5505 (3)	0.1173 (13)
O2	0.2227 (15)	0.32692 (14)	0.5852 (5)	0.201 (3)
C1	0.4074 (7)	0.29939 (11)	0.4221 (3)	0.0513 (9)
C2	0.5231 (9)	0.25869 (11)	0.3821 (4)	0.0663 (11)
H2A	0.4958	0.2303	0.4190	0.080*
C3	0.6797 (9)	0.26018 (13)	0.2870 (4)	0.0725 (12)
H3	0.7596	0.2329	0.2595	0.087*
C4	0.7165 (8)	0.30232 (13)	0.2332 (4)	0.0659 (11)
H4	0.8221	0.3036	0.1691	0.079*
C5	0.5979 (8)	0.34250 (11)	0.2739 (3)	0.0539 (9)
H5	0.6260	0.3707	0.2364	0.065*
C6	0.4374 (7)	0.34259 (10)	0.3691 (3)	0.0452 (8)
C7	0.3121 (7)	0.38673 (10)	0.4055 (3)	0.0495 (9)
H7	0.2018	0.3876	0.4684	0.059*
C8	0.3103 (7)	0.50609 (10)	0.3458 (3)	0.0406 (7)
C9	0.5817 (7)	0.56211 (11)	0.1951 (3)	0.0499 (9)
H9A	0.6092	0.5805	0.2646	0.060*
H9B	0.7566	0.5645	0.1556	0.060*
C10	0.3412 (6)	0.58388 (11)	0.1207 (3)	0.0422 (8)
C11	0.2337 (8)	0.56274 (14)	0.0219 (3)	0.0620 (10)
H11	0.3021	0.5334	0.0021	0.074*
C12	0.0259 (9)	0.58440 (18)	−0.0482 (4)	0.0754 (12)
H12	−0.0452	0.5698	−0.1151	0.091*
C13	−0.0762 (9)	0.62724 (17)	−0.0198 (4)	0.0783 (14)
H13	−0.2157	0.6419	−0.0677	0.094*
C14	0.0259 (8)	0.64873 (13)	0.0791 (4)	0.0731 (13)
H14	−0.0454	0.6778	0.0992	0.088*
C15	0.2341 (7)	0.62698 (11)	0.1483 (4)	0.0560 (10)
H15	0.3044	0.6417	0.2152	0.067*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0721 (6)	0.0349 (4)	0.0446 (5)	0.0042 (4)	0.0116 (4)	0.0001 (4)
S2	0.0618 (6)	0.0402 (4)	0.0561 (6)	0.0052 (4)	0.0197 (5)	0.0039 (4)
N1	0.0575 (16)	0.0352 (14)	0.0415 (16)	0.0028 (12)	0.0008 (14)	0.0020 (13)
N2	0.0601 (16)	0.0347 (14)	0.0451 (17)	0.0064 (12)	0.0132 (14)	0.0034 (13)
N3	0.107 (3)	0.0466 (19)	0.076 (3)	0.0025 (19)	0.019 (2)	0.0149 (19)
O1	0.170 (4)	0.076 (2)	0.110 (3)	−0.038 (2)	0.042 (3)	0.023 (2)
O2	0.406 (9)	0.068 (2)	0.152 (4)	0.020 (4)	0.178 (5)	0.029 (3)
C1	0.059 (2)	0.0388 (18)	0.055 (2)	−0.0062 (15)	−0.0015 (18)	0.0084 (17)
C2	0.080 (3)	0.0318 (17)	0.085 (3)	−0.0018 (17)	−0.009 (2)	0.008 (2)
C3	0.088 (3)	0.041 (2)	0.088 (3)	0.0135 (19)	0.006 (3)	−0.006 (2)
C4	0.081 (3)	0.055 (2)	0.063 (3)	0.0091 (19)	0.012 (2)	−0.002 (2)
C5	0.068 (2)	0.0364 (17)	0.057 (2)	0.0012 (16)	0.005 (2)	0.0052 (17)
C6	0.0516 (19)	0.0356 (16)	0.047 (2)	−0.0011 (14)	−0.0061 (17)	0.0048 (15)
C7	0.066 (2)	0.0368 (17)	0.046 (2)	−0.0010 (16)	0.0056 (18)	0.0076 (16)
C8	0.0456 (17)	0.0395 (16)	0.0358 (18)	0.0000 (13)	−0.0041 (15)	0.0037 (14)
C9	0.0454 (18)	0.0479 (18)	0.057 (2)	−0.0060 (15)	0.0100 (17)	0.0089 (17)
C10	0.0396 (17)	0.0466 (18)	0.041 (2)	−0.0072 (14)	0.0089 (15)	0.0093 (16)
C11	0.064 (2)	0.075 (2)	0.048 (2)	−0.001 (2)	0.014 (2)	−0.007 (2)
C12	0.073 (3)	0.111 (4)	0.041 (2)	−0.020 (3)	−0.001 (2)	0.003 (2)
C13	0.057 (2)	0.090 (3)	0.085 (4)	−0.010 (2)	−0.009 (2)	0.048 (3)
C14	0.067 (3)	0.047 (2)	0.103 (4)	−0.0021 (19)	−0.009 (3)	0.018 (2)
C15	0.060 (2)	0.0395 (18)	0.067 (3)	−0.0069 (16)	−0.006 (2)	0.0060 (18)

Geometric parameters (Å, °)

S1—C8	1.648 (3)	C5—C6	1.389 (5)
S2—C8	1.735 (3)	C5—H5	0.9300
S2—C9	1.803 (3)	C6—C7	1.464 (4)
N1—C7	1.272 (4)	C7—H7	0.9300
N1—N2	1.363 (3)	C9—C10	1.507 (5)
N2—C8	1.349 (4)	C9—H9A	0.9700
N2—H2	0.8600	C9—H9B	0.9700
N3—O2	1.178 (5)	C10—C11	1.370 (5)
N3—O1	1.185 (4)	C10—C15	1.374 (5)
N3—C1	1.464 (5)	C11—C12	1.374 (6)
C1—C2	1.376 (5)	C11—H11	0.9300
C1—C6	1.390 (4)	C12—C13	1.361 (6)
C2—C3	1.377 (6)	C12—H12	0.9300
C2—H2A	0.9300	C13—C14	1.368 (6)
C3—C4	1.373 (5)	C13—H13	0.9300
C3—H3	0.9300	C14—C15	1.370 (5)
C4—C5	1.373 (5)	C14—H14	0.9300
C4—H4	0.9300	C15—H15	0.9300
C8—S2—C9	102.38 (15)	C6—C7—H7	120.6

C7—N1—N2	116.1 (3)	N2—C8—S1	121.0 (2)
C8—N2—N1	120.3 (3)	N2—C8—S2	113.1 (2)
C8—N2—H2	119.8	S1—C8—S2	125.83 (18)
N1—N2—H2	119.8	C10—C9—S2	116.1 (2)
O2—N3—O1	119.9 (4)	C10—C9—H9A	108.3
O2—N3—C1	120.2 (4)	S2—C9—H9A	108.3
O1—N3—C1	119.8 (4)	C10—C9—H9B	108.3
C2—C1—C6	122.6 (4)	S2—C9—H9B	108.3
C2—C1—N3	115.7 (3)	H9A—C9—H9B	107.4
C6—C1—N3	121.7 (3)	C11—C10—C15	118.3 (3)
C1—C2—C3	119.6 (4)	C11—C10—C9	121.5 (3)
C1—C2—H2A	120.2	C15—C10—C9	120.1 (3)
C3—C2—H2A	120.2	C10—C11—C12	120.7 (4)
C4—C3—C2	119.4 (4)	C10—C11—H11	119.7
C4—C3—H3	120.3	C12—C11—H11	119.7
C2—C3—H3	120.3	C13—C12—C11	120.1 (4)
C5—C4—C3	120.2 (4)	C13—C12—H12	119.9
C5—C4—H4	119.9	C11—C12—H12	119.9
C3—C4—H4	119.9	C12—C13—C14	120.2 (4)
C4—C5—C6	122.4 (3)	C12—C13—H13	119.9
C4—C5—H5	118.8	C14—C13—H13	119.9
C6—C5—H5	118.8	C13—C14—C15	119.4 (4)
C5—C6—C1	115.8 (3)	C13—C14—H14	120.3
C5—C6—C7	119.1 (3)	C15—C14—H14	120.3
C1—C6—C7	125.1 (3)	C14—C15—C10	121.3 (4)
N1—C7—C6	118.8 (3)	C14—C15—H15	119.3
N1—C7—H7	120.6	C10—C15—H15	119.3

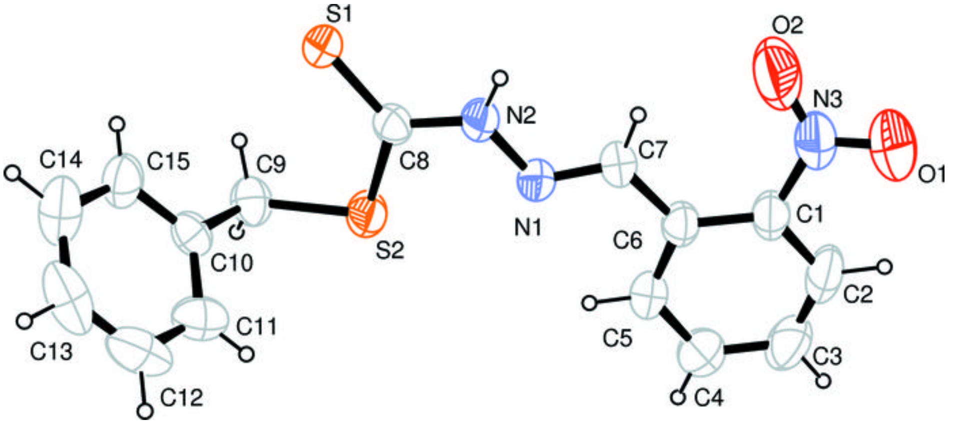
Hydrogen-bond geometry (Å, °)

Cg is the centroid of the C10–C15 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···S1^{i}	0.86	2.51	3.359 (3)	171
C9—H9B···Cg^{ii}	0.97	2.50	3.410 (4)	156

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

Fig. 1


S1
O2
N2
N3
C14
C15
C9
C8
C7
O1
N1
C6
C1
C10
S2
C2
C5
C11
C13
C3
C12
C4