

2-Bromo-5-methoxybenzohydrazide

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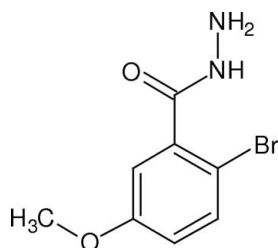
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.046; wR factor = 0.116; data-to-parameter ratio = 16.6.

In the title compound, $\text{C}_8\text{H}_9\text{BrN}_2\text{O}_2$, the amide bond is in a *cis* configuration. The $\text{N}-\text{N}-\text{C}=\text{O}$ group is planar [torsion angle $0.6(6)^\circ$] and forms a dihedral angle of $46.4(2)^\circ$ with the aromatic ring. The crystal packing is stabilized by two strong and one rather weak $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds.

Related literature

For related literature, see: Bhat *et al.* (1974); Cajocorius *et al.* (1977); Katrusiak (1993); Liu *et al.* (2006); Muir & Morris (2003); Narayana, Ashalatha *et al.* (2005); Narayana, Vijayaraj *et al.* (2005); Sarojini *et al.* (2007); Swain (1959).



Experimental

Crystal data

 $\text{C}_8\text{H}_9\text{BrN}_2\text{O}_2$ $M_r = 245.08$ Orthorhombic, $P2_12_12_1$ $a = 5.0150(5)$ Å $b = 11.4093(10)$ Å $c = 16.1736(14)$ Å $V = 925.42(15)$ Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 4.41$ mm⁻¹ $T = 173(2)$ K $0.32 \times 0.27 \times 0.23$ mm

Data collection

Stoe IPDSII two-circle diffractometer

Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995) $T_{\min} = 0.263$, $T_{\max} = 0.380$

7646 measured reflections

2135 independent reflections

2008 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.070$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.046$ $wR(F^2) = 0.116$ $S = 1.03$

2135 reflections

129 parameters

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\max} = 0.95$ e Å⁻³ $\Delta\rho_{\min} = -0.94$ e Å⁻³

Absolute structure: Flack (1983),

862 Friedel pairs

Flack parameter: $-0.014(17)$

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{O1}^{\text{i}}$	0.91 (6)	1.95 (6)	2.783 (5)	152 (5)
$\text{N2}-\text{H2A}\cdots\text{O2}^{\text{ii}}$	0.81 (6)	2.61 (6)	3.324 (5)	148 (6)
$\text{N2}-\text{H2B}\cdots\text{O2}^{\text{iii}}$	0.92 (6)	2.29 (6)	3.156 (5)	156 (5)

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

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: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2037).

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supplementary materials

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2-Bromo-5-methoxybenzohydrazide

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Comment

Hydrazides are useful precursors in the synthesis of several heterocyclic systems (Narayana, Vijayaraj *et al.*, 2005; Narayana, Ashalatha *et al.*, 2005). Some substituted hydrazides are reported to exhibit carcinostatic activity (Cajocorius *et al.*, 1977) against several types of tumors and also possess antimicrobial activity (Swain, 1959 & Liu *et al.*, 2006). They are also used as intermediates in many pharmaceutically important compounds. Structures of maleic hydrazide (Katrusiak, 1993), isonicotinic acid hydrazide (Bhat *et al.*, 1974) and *N,N*-dimethyl-*N'*-(*o*-fluorobenzoyl)hydrazide (Muir & Morris, 2003) have been reported. Recently the structure of 2-bromo-*N'*-isopropylidene-5-methoxybenzohydrazide was reported (Sarojini *et al.*, 2007). In view of the importance of hydrazides, a new hydrazide, (I), C₈H₉BrN₂O₂, has been synthesized and its crystal structure is reported.

Geometric parameters of the title compound are in the usual ranges. The amide bond is in a *cis* conformation. The N—N—C=O moiety is planar [torsion angle N2—N1—C7—O1 0.6 (6)°] and forms a dihedral angle of 46.4 (2)° with the aromatic ring. The crystal packing is stabilized by two strong and one rather weak N—H···O hydrogen bonds.

Experimental

A mixture of ethyl 2-bromo-5-methoxybenzoate (25.9 g, 0.1 mol) and 5.5 ml of hydrazine hydrate in 100 ml of ethanol was refluxed over water bath for 4 h. The precipitate formed was filtered and recrystallized from a mixture (8:2) of ethanol and toluene (m.p.:433–435 K). Analysis for C₈H₉BrN₂O₂: Found (Calculated): C: 39.14 (39.21); H: 3.66 (3.70); N: 11.39% (11.43%).

Refinement

H atoms were refined with fixed individual displacement parameters [$U(H) = 1.2 U_{eq}(C,N)$ or $U(H) = 1.5 U_{eq}(C_{methyl})$] using a riding model with C—H(aromatic) = 0.95 Å or C—H(methyl) = 0.98 Å, respectively. The methyl group was allowed to rotate but not to tip. The coordinates of the amino H atoms were refined.

Figures

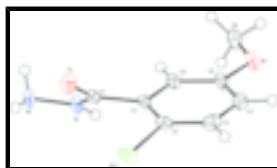


Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are plotted at the 50% probability level.

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Crystal data

$C_8H_9BrN_2O_2$

$M_r = 245.08$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 5.0150$ (5) Å

$b = 11.4093$ (10) Å

$c = 16.1736$ (14) Å

$V = 925.42$ (15) Å³

$Z = 4$

$F_{000} = 488$

$D_x = 1.759$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 6028 reflections

$\theta = 3.7$ – 27.1°

$\mu = 4.41$ mm⁻¹

$T = 173$ (2) K

Block, colourless

$0.32 \times 0.27 \times 0.23$ mm

Data collection

Stoe IPDSII two-circle diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 173$ (2) K

ω scans

Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)

$T_{\min} = 0.263$, $T_{\max} = 0.380$

7646 measured reflections

2135 independent reflections

2008 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.070$

$\theta_{\text{max}} = 27.6^\circ$

$\theta_{\text{min}} = 3.6^\circ$

$h = -6 \rightarrow 5$

$k = -14 \rightarrow 14$

$l = -21 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.116$

$S = 1.04$

2135 reflections

129 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0796P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\text{max}} = 0.95$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.94$ e Å⁻³

Extinction correction: SHELXL97 (Sheldrick, 1997),

$$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.025 (4)

Absolute structure: Flack (1983), 862 Friedel pairs

Flack parameter: -0.014 (17)

Special details

Experimental. ;

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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	1.19431 (9)	0.27433 (4)	0.41643 (3)	0.02729 (19)
O1	1.0833 (6)	0.5462 (3)	0.4178 (2)	0.0235 (6)
O2	0.4447 (7)	0.3871 (3)	0.13391 (18)	0.0249 (7)
N1	0.6358 (7)	0.5633 (3)	0.4286 (2)	0.0173 (7)
H1	0.471 (12)	0.537 (5)	0.414 (4)	0.021*
N2	0.6506 (8)	0.6559 (3)	0.4876 (2)	0.0207 (7)
H2A	0.694 (13)	0.714 (5)	0.462 (4)	0.025*
H2B	0.799 (13)	0.634 (5)	0.518 (3)	0.025*
C1	0.8142 (9)	0.4236 (3)	0.3314 (2)	0.0163 (7)
C2	0.9609 (9)	0.3205 (4)	0.3285 (3)	0.0211 (8)
C3	0.9408 (10)	0.2434 (4)	0.2620 (3)	0.0250 (9)
H3	1.0455	0.1740	0.2604	0.030*
C4	0.7651 (9)	0.2693 (4)	0.1979 (3)	0.0240 (9)
H4	0.7510	0.2179	0.1519	0.029*
C5	0.6095 (9)	0.3707 (4)	0.2009 (2)	0.0196 (8)
C6	0.6336 (8)	0.4478 (4)	0.2672 (2)	0.0168 (8)
H6	0.5279	0.5168	0.2690	0.020*
C7	0.8561 (9)	0.5152 (4)	0.3976 (2)	0.0165 (8)
C8	0.2815 (11)	0.4903 (4)	0.1332 (3)	0.0266 (10)
H8A	0.1511	0.4860	0.1782	0.040*
H8B	0.1878	0.4958	0.0801	0.040*
H8C	0.3941	0.5597	0.1407	0.040*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0261 (3)	0.0310 (3)	0.0248 (2)	0.00662 (19)	-0.00015 (18)	0.00917 (16)
O1	0.0107 (13)	0.0321 (15)	0.0278 (15)	-0.0018 (12)	0.0003 (14)	-0.0065 (14)
O2	0.0269 (18)	0.0347 (17)	0.0130 (13)	0.0016 (15)	-0.0039 (12)	-0.0064 (12)
N1	0.0085 (17)	0.0267 (17)	0.0167 (15)	-0.0009 (13)	-0.0030 (12)	-0.0070 (13)
N2	0.0200 (19)	0.0257 (18)	0.0163 (15)	-0.0004 (15)	-0.0033 (14)	-0.0070 (13)

supplementary materials

C1	0.0131 (18)	0.0242 (18)	0.0114 (15)	-0.0030 (17)	0.0014 (16)	0.0010 (13)
C2	0.022 (2)	0.0241 (19)	0.0177 (17)	-0.0023 (17)	0.0042 (16)	0.0059 (16)
C3	0.028 (2)	0.0171 (19)	0.030 (2)	0.0057 (16)	0.0073 (19)	0.0016 (16)
C4	0.025 (2)	0.0252 (19)	0.0213 (18)	-0.0005 (18)	0.0056 (16)	-0.0063 (16)
C5	0.017 (2)	0.028 (2)	0.0132 (16)	-0.0017 (17)	0.0026 (14)	-0.0052 (15)
C6	0.014 (2)	0.0214 (18)	0.0152 (17)	0.0000 (14)	0.0047 (14)	-0.0030 (14)
C7	0.015 (2)	0.0218 (18)	0.0132 (17)	0.0011 (15)	0.0011 (14)	0.0016 (13)
C8	0.025 (2)	0.034 (2)	0.0202 (18)	0.002 (2)	-0.0069 (18)	-0.0035 (16)

Geometric parameters (\AA , $^\circ$)

Br1—C2	1.916 (4)	C1—C7	1.511 (5)
O1—C7	1.237 (6)	C2—C3	1.393 (6)
O2—C5	1.376 (5)	C3—C4	1.393 (6)
O2—C8	1.434 (6)	C3—H3	0.9500
N1—C7	1.332 (5)	C4—C5	1.396 (6)
N1—N2	1.426 (5)	C4—H4	0.9500
N1—H1	0.91 (6)	C5—C6	1.391 (5)
N2—H2A	0.81 (6)	C6—H6	0.9500
N2—H2B	0.92 (6)	C8—H8A	0.9800
C1—C2	1.388 (6)	C8—H8B	0.9800
C1—C6	1.405 (6)	C8—H8C	0.9800
C5—O2—C8	117.5 (3)	C3—C4—H4	119.9
C7—N1—N2	121.0 (3)	C5—C4—H4	119.9
C7—N1—H1	121 (4)	O2—C5—C6	125.0 (4)
N2—N1—H1	118 (4)	O2—C5—C4	114.9 (4)
N1—N2—H2A	107 (4)	C6—C5—C4	120.1 (4)
N1—N2—H2B	101 (3)	C5—C6—C1	120.1 (4)
H2A—N2—H2B	106 (6)	C5—C6—H6	120.0
C2—C1—C6	118.9 (4)	C1—C6—H6	120.0
C2—C1—C7	122.5 (4)	O1—C7—N1	123.1 (4)
C6—C1—C7	118.5 (4)	O1—C7—C1	120.9 (4)
C1—C2—C3	121.6 (4)	N1—C7—C1	115.9 (4)
C1—C2—Br1	122.1 (3)	O2—C8—H8A	109.5
C3—C2—Br1	116.3 (3)	O2—C8—H8B	109.5
C2—C3—C4	119.1 (4)	H8A—C8—H8B	109.5
C2—C3—H3	120.5	O2—C8—H8C	109.5
C4—C3—H3	120.5	H8A—C8—H8C	109.5
C3—C4—C5	120.2 (4)	H8B—C8—H8C	109.5
C6—C1—C2—C3	2.7 (6)	O2—C5—C6—C1	-178.2 (4)
C7—C1—C2—C3	-172.7 (4)	C4—C5—C6—C1	-0.2 (6)
C6—C1—C2—Br1	-175.7 (3)	C2—C1—C6—C5	-1.9 (6)
C7—C1—C2—Br1	9.0 (6)	C7—C1—C6—C5	173.7 (4)
C1—C2—C3—C4	-1.4 (7)	N2—N1—C7—O1	0.6 (6)
Br1—C2—C3—C4	177.1 (3)	N2—N1—C7—C1	-176.0 (3)
C2—C3—C4—C5	-0.7 (7)	C2—C1—C7—O1	45.0 (6)
C8—O2—C5—C6	-1.4 (6)	C6—C1—C7—O1	-130.4 (4)
C8—O2—C5—C4	-179.5 (4)	C2—C1—C7—N1	-138.3 (4)
C3—C4—C5—O2	179.7 (4)	C6—C1—C7—N1	46.3 (5)

C3—C4—C5—C6

1.5 (7)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1···O1 ⁱ	0.91 (6)	1.95 (6)	2.783 (5)	152 (5)
N2—H2A···O2 ⁱⁱ	0.81 (6)	2.61 (6)	3.324 (5)	148 (6)
N2—H2B···O2 ⁱⁱⁱ	0.92 (6)	2.29 (6)	3.156 (5)	156 (5)

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, y+1/2, -z+1/2$; (iii) $-x+3/2, -y+1, z+1/2$.

Fig. 1

