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2-Bromo-*N*′-[(2*Z*)-butan-2-ylidene]-5-methoxybenzohydrazide

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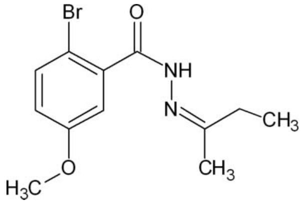
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.004 Å; R factor = 0.044; wR factor = 0.122; data-to-parameter ratio = 16.4.

In the title compound, $C_{12}H_{15}BrN_2O_2$, the dihedral angle between the benzene ring and the mean plane of the amide grouping is 77.7 (8)°. In the crystal, inversion dimers linked by pairs of N—H···O hydrogen bonds occur, and the packing is further supported by C—H···O and C—H···Br interactions and weak π–π ring stacking interactions.

Related literature

Hydrazides and their corresponding Schiff bases are useful precursors in the synthesis of several heterocyclic systems, see: Narayana *et al.* (2005; 2005*a*). For the biological activity of substituted hydrazides, see: Cajocorius *et al.* (1977). Hydrazides are intermediates in the production of many pharmaceutically important compounds, see: Liu *et al.* (2006). For related structures, see: Butcher *et al.* (2007); Hou (2009); Li & Ban (2009); Sarojini *et al.* (2007*a*,*b*,*c*,*d*). For the MOPAC AM1 calculations, see: Schmidt & Polik (2007).



Experimental

Crystal data

$C_{12}H_{15}BrN_2O_2$
M_r = 299.17
Monoclinic, $P2_1/c$
a = 8.0942 (1) Å
b = 14.2475 (2) Å
c = 11.2974 (2) Å
β = 91.1519 (13)°
V = 1302.58 (3) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 4.25 mm^{-1}
T = 200 K
0.56 × 0.47 × 0.35 mm

Data collection

Oxford Diffraction Gemini R CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
T_{min} = 0.452, T_{max} = 1.000
7962 measured reflections
2577 independent reflections
2484 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.122
S = 1.07
2577 reflections
157 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.73 e Å^{-3}
$\Delta\rho_{min}$ = −1.07 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7*B*···O2[i]	0.98	2.60	3.561 (4)	166
C10—H10*A*···Br[ii]	0.98	3.07	3.949 (5)	151
C10—H10*A*···O2[iii]	0.98	2.55	3.231 (4)	127
C11—H11*A*···O1[iv]	0.99	2.55	3.373 (4)	141
N1—H1*A*···O2[iii]	0.88	2.07	2.932 (3)	165

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

Data collection: *CrysAlis Pro* (Oxford Diffraction, 2007); cell refinement: *CrysAlis Pro*; data reduction: *CrysAlis Pro*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DS2010).

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Acta Cryst. (2009). E**65**, o2968–o2969 Jasinski *et al.* • $C_{12}H_{15}BrN_2O_2$ **o2969**

supplementary materials

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2-Bromo-*N*'-[(2*Z*)-butan-2-ylidene]-5-methoxybenzohydrazide

J. P. Jasinski, R. J. Butcher, L. P. Suchitra, H. S. Yathirajan and **B. Narayana**

Comment

Hydrazides and the corresponding Schiff bases are useful precursors in the synthesis of several heterocyclic systems (Narayana *et al.* 2005; 2005*a*). Some substituted hydrazides are reported to exhibit carcinostatic activity against several types of tumors (Cajocorius *et al.* 1977) and also possess antimicrobial activity. It is also used as an intermediate in many pharmaceutically important compounds (Liu *et al.* 2006). In continuation with our studies on the structures of hydrazides and their Schiff bases (Sarojini *et al.* 2007*a*, 2007*b*, 2007*c*, 2007d; Butcher *et al.* 2007) a new Schiff base, (I), $C_{12}H_15BrN_2O_2$, has been synthesized and its crystal structure is now reported.

In the title compound, $C_{12}H_15BrN_2O_2$, (Fig. 1), the 2-bromo and 5-methoxy groups are in the plane of the benzene ring. The dihedral angle between the mean planes of the carbonyl group (–C6—C8(O2)—N1—N2-) and benzene ring is 77.7 (8)°. The C1—C6—C8—O2 and C1—C6—C8—N1 torsion angles (-101.1 (3)° & -103.7 (3)°) support this observation. Crystal packing is supported by a collection of intermediate N1—H1A—O2 (*-x,-y + 2,-z + 1*) intermolecular interactions (see Table 1) which produces a cooperative network of infinite O—H···O—H···O—H chains arranged diagonally along the (101) plane of the unit cell (Fig. 2). In addition, weak intermolecular C10—H10A···O2 (*-x,-y + 2,-z + 1*), C11—H11A···O1 (*-x + 1, y - 1/2,-z + 1/2*), C7—H7B···O2 (*-x,-y + 2,-z*) and C10—H10A···Br (*x,-y + 3/2,z1/2*) interactions (Table 1) along with *Cg*1···*Cg*1 π-π ring stacking interactions at 3.869 (1)Å (*2 - x,1 - y,1 - z*; slippage = 1.43 (2) Å, where *Cg*1 = C1—C6), collectively, slightly influence crystal packing in this crystalline environment.

After a MOPAC AM1 computational calculation (Schmidt, 2007), the dihedral angle between the mean planes of the carbonyl group (–C6—C8(O2)—N1—N2-) and benzene ring becomes 84.0 (8)°, significantly greater that the 77.7 (8)° seen in the crystal. This supports the observation of a collective action of the intermediate and weak hydrogen bond interactions along with weak intermolecular π-π stacking interactions which influence crystal packing stability.

Experimental

A mixture of 2-bromo-5-methoxybenzohydrazide (2.45 g, 0.01 mol) and ethyl methyl ketone(1.44 g, 0.02 mol) in 20 ml of ethanol containing a drop of dilute sulfuric acid was refluxed for about 2 h (Scheme 2). On cooling, the solid separated was filtered and recrystallized from ethyl methyl ketone. M.P.: 385 K. Analysis for $C_{12}H_{15}BrN_2O_2$: Found (Calculated): C: 48.14 (48.18); H: 5.02 (5.05%); N: 9.31 (9.36%).

Refinement

All of the H atoms were placed in their calculated positions and then refined using the riding model with N—H = 0.88, C—H = 0.95–0.99 Å, and with $U_{iso}(H) = 1.2–1.5\ U_{eq}(C,N)$.

Figures

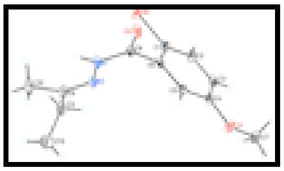

Fig. 1. Molecular structure of $C_{12}H_15BrN_2O_2$ showing atom labeling scheme and 50% probability displacement ellipsoids.

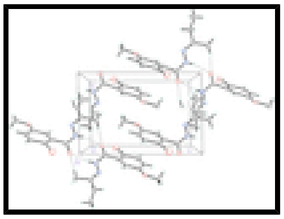

Fig. 2. Packing diagram of the title compound, (I), viewed down the *b* axis. Dashed lines indicate intermediate intermolecular N—H···O and C—H···O interactions which produces a network of infinite O—H···O—H···O—H chains arranged diagonally along the (101) plane of the unit cell.

2-Bromo-*N*'-[(2*Z*)-butan-2-ylidene]-5-methoxybenzohydrazide

Crystal data

$C_{12}H_{15}BrN_2O_2$	F_{000} = 608
M_r = 299.17	D_x = 1.526 Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, λ = 1.54184 Å
Hall symbol: -P 2ybc	Cell parameters from 8517 reflections
a = 8.09420 (10) Å	θ = 5.0–73.4°
b = 14.2475 (2) Å	μ = 4.25 mm^{-1}
c = 11.2974 (2) Å	*T* = 200 K
β = 91.1519 (13)°	Chunk, colorless
V = 1302.58 (3) Å^3	0.56 × 0.47 × 0.35 mm
Z = 4	

Data collection

Oxford Diffraction Gemini R CCD diffractometer	2577 independent reflections
Radiation source: fine-focus sealed tube	2484 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.023
Detector resolution: 10.5081 pixels mm^{-1}	θ_{max} = 73.6°
T = 200 K	θ_{min} = 5.0°
φ and ω scans	*h* = −10→9
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2007)	*k* = −16→17
T_{min} = 0.452, T_{max} = 1.000	*l* = −9→13
7962 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
$R[F^2 > 2\sigma(F^2)] = 0.044$	H-atom parameters constrained
$wR(F^2) = 0.122$	$w = 1/[\sigma^2(F_o^2) + (0.0673P)^2 + 1.7115P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
2577 reflections	$\Delta\rho_{max} = 0.73$ e Å^{-3}
157 parameters	$\Delta\rho_{min} = -1.07$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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	−0.00062 (5)	0.75926 (3)	0.23886 (3)	0.05362 (18)
O1	0.3113 (3)	1.07458 (17)	−0.03054 (18)	0.0478 (6)
O2	−0.0433 (2)	1.01275 (15)	0.35066 (16)	0.0358 (5)
N1	0.1775 (3)	0.93324 (16)	0.42004 (18)	0.0306 (5)
H1A	0.1550	0.9465	0.4941	0.037*
N2	0.3148 (3)	0.87860 (17)	0.39363 (19)	0.0318 (5)
C1	0.0954 (3)	0.85866 (18)	0.1528 (2)	0.0305 (5)
C2	0.1316 (4)	0.8445 (2)	0.0351 (2)	0.0361 (6)
H2A	0.1073	0.7858	−0.0012	0.043*
C3	0.2033 (3)	0.9154 (2)	−0.0303 (2)	0.0316 (6)
H3A	0.2285	0.9056	−0.1111	0.038*
C4	0.2379 (3)	1.00067 (19)	0.0234 (2)	0.0294 (5)
C5	0.1981 (3)	1.01479 (18)	0.1415 (2)	0.0285 (5)
H5A	0.2195	1.0739	0.1775	0.034*
C6	0.1282 (3)	0.94403 (17)	0.2066 (2)	0.0244 (5)
C7	0.3619 (4)	1.0618 (3)	−0.1501 (3)	0.0525 (9)
H7A	0.4202	1.1181	−0.1766	0.079*
H7B	0.2644	1.0512	−0.2012	0.079*
H7C	0.4357	1.0075	−0.1544	0.079*
C8	0.0802 (3)	0.96538 (18)	0.3318 (2)	0.0258 (5)
C9	0.4048 (3)	0.8504 (2)	0.4794 (2)	0.0357 (6)
C10	0.3829 (5)	0.8738 (3)	0.6083 (3)	0.0624 (12)

H10A	0.2676	0.8632	0.6295	0.094*
H10B	0.4118	0.9397	0.6221	0.094*
H10C	0.4551	0.8336	0.6570	0.094*
C11	0.5478 (4)	0.7880 (3)	0.4479 (3)	0.0485 (8)
H11A	0.5308	0.7253	0.4835	0.058*
H11B	0.5486	0.7800	0.3609	0.058*
C12	0.7109 (5)	0.8246 (4)	0.4882 (5)	0.0764 (13)
H12A	0.7969	0.7786	0.4702	0.115*
H12B	0.7097	0.8357	0.5738	0.115*
H12C	0.7339	0.8837	0.4472	0.115*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.0949 (4)	0.0345 (2)	0.0315 (2)	−0.01786 (16)	0.00182 (18)	0.00284 (12)
O1	0.0666 (14)	0.0508 (13)	0.0261 (11)	−0.0214 (11)	0.0079 (9)	−0.0005 (9)
O2	0.0396 (10)	0.0467 (12)	0.0210 (9)	0.0198 (8)	−0.0009 (7)	−0.0063 (8)
N1	0.0373 (11)	0.0386 (12)	0.0159 (10)	0.0145 (9)	0.0007 (8)	−0.0042 (8)
N2	0.0371 (11)	0.0346 (12)	0.0238 (11)	0.0125 (9)	0.0026 (9)	−0.0023 (9)
C1	0.0452 (14)	0.0245 (12)	0.0219 (12)	0.0002 (10)	0.0004 (10)	−0.0003 (10)
C2	0.0576 (17)	0.0292 (13)	0.0212 (13)	0.0033 (12)	−0.0032 (11)	−0.0081 (10)
C3	0.0397 (13)	0.0395 (15)	0.0157 (11)	0.0066 (11)	0.0019 (9)	−0.0066 (10)
C4	0.0322 (12)	0.0352 (14)	0.0206 (12)	−0.0005 (10)	−0.0021 (10)	−0.0007 (10)
C5	0.0342 (12)	0.0283 (12)	0.0230 (12)	0.0015 (10)	−0.0020 (9)	−0.0070 (10)
C6	0.0281 (11)	0.0275 (12)	0.0175 (11)	0.0092 (9)	−0.0018 (8)	−0.0033 (9)
C7	0.0564 (19)	0.076 (2)	0.0250 (15)	−0.0218 (17)	0.0066 (13)	0.0033 (15)
C8	0.0327 (12)	0.0255 (12)	0.0192 (11)	0.0047 (9)	−0.0004 (9)	−0.0039 (9)
C9	0.0391 (14)	0.0418 (15)	0.0263 (13)	0.0132 (12)	0.0014 (10)	0.0018 (11)
C10	0.060 (2)	0.104 (3)	0.0233 (15)	0.040 (2)	−0.0041 (14)	0.0002 (17)
C11	0.0513 (18)	0.0549 (19)	0.0393 (17)	0.0250 (15)	0.0012 (13)	0.0036 (15)
C12	0.050 (2)	0.100 (4)	0.079 (3)	0.016 (2)	0.004 (2)	0.004 (3)

Geometric parameters (Å, °)

Br—C1	1.894 (3)	C5—H5A	0.9500
O1—C4	1.359 (3)	C6—C8	1.506 (3)
O1—C7	1.431 (4)	C7—H7A	0.9800
O2—C8	1.228 (3)	C7—H7B	0.9800
N1—C8	1.338 (3)	C7—H7C	0.9800
N1—N2	1.394 (3)	C9—C10	1.507 (4)
N1—H1A	0.8800	C9—C11	1.508 (4)
N2—C9	1.266 (4)	C10—H10A	0.9800
C1—C2	1.382 (4)	C10—H10B	0.9800
C1—C6	1.383 (3)	C10—H10C	0.9800
C2—C3	1.386 (4)	C11—C12	1.482 (6)
C2—H2A	0.9500	C11—H11A	0.9900
C3—C4	1.383 (4)	C11—H11B	0.9900
C3—H3A	0.9500	C12—H12A	0.9800
C4—C5	1.393 (4)	C12—H12B	0.9800

C5—C6	1.376 (4)	C12—H12C	0.9800

C4—O1—C7	117.4 (2)	H7A—C7—H7C	109.5
C8—N1—N2	119.4 (2)	H7B—C7—H7C	109.5
C8—N1—H1A	120.3	O2—C8—N1	121.9 (2)
N2—N1—H1A	120.3	O2—C8—C6	120.0 (2)
C9—N2—N1	117.5 (2)	N1—C8—C6	118.2 (2)
C2—C1—C6	120.6 (2)	N2—C9—C10	126.3 (3)
C2—C1—Br	118.8 (2)	N2—C9—C11	116.0 (3)
C6—C1—Br	120.59 (19)	C10—C9—C11	117.6 (3)
C1—C2—C3	120.3 (2)	C9—C10—H10A	109.5
C1—C2—H2A	119.9	C9—C10—H10B	109.5
C3—C2—H2A	119.9	H10A—C10—H10B	109.5
C4—C3—C2	119.4 (2)	C9—C10—H10C	109.5
C4—C3—H3A	120.3	H10A—C10—H10C	109.5
C2—C3—H3A	120.3	H10B—C10—H10C	109.5
O1—C4—C3	124.8 (2)	C12—C11—C9	113.8 (3)
O1—C4—C5	115.4 (2)	C12—C11—H11A	108.8
C3—C4—C5	119.8 (2)	C9—C11—H11A	108.8
C6—C5—C4	120.8 (2)	C12—C11—H11B	108.8
C6—C5—H5A	119.6	C9—C11—H11B	108.8
C4—C5—H5A	119.6	H11A—C11—H11B	107.7
C5—C6—C1	119.1 (2)	C11—C12—H12A	109.5
C5—C6—C8	118.1 (2)	C11—C12—H12B	109.5
C1—C6—C8	122.7 (2)	H12A—C12—H12B	109.5
O1—C7—H7A	109.5	C11—C12—H12C	109.5
O1—C7—H7B	109.5	H12A—C12—H12C	109.5
H7A—C7—H7B	109.5	H12B—C12—H12C	109.5
O1—C7—H7C	109.5		

C8—N1—N2—C9	179.2 (3)	Br—C1—C6—C5	179.97 (19)
C6—C1—C2—C3	0.8 (4)	C2—C1—C6—C8	175.6 (2)
Br—C1—C2—C3	−179.4 (2)	Br—C1—C6—C8	−4.2 (3)
C1—C2—C3—C4	−0.2 (4)	N2—N1—C8—O2	179.0 (3)
C7—O1—C4—C3	−2.5 (4)	N2—N1—C8—C6	−2.5 (4)
C7—O1—C4—C5	177.0 (3)	C5—C6—C8—O2	74.8 (3)
C2—C3—C4—O1	178.4 (3)	C1—C6—C8—O2	−101.1 (3)
C2—C3—C4—C5	−1.0 (4)	C5—C6—C8—N1	−103.7 (3)
O1—C4—C5—C6	−177.9 (2)	C1—C6—C8—N1	80.4 (3)
C3—C4—C5—C6	1.6 (4)	N1—N2—C9—C10	−3.0 (5)
C4—C5—C6—C1	−0.9 (4)	N1—N2—C9—C11	177.4 (3)
C4—C5—C6—C8	−177.0 (2)	N2—C9—C11—C12	122.5 (4)
C2—C1—C6—C5	−0.3 (4)	C10—C9—C11—C12	−57.1 (5)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7B···O2^{i}	0.98	2.60	3.561 (4)	166
C10—H10A···Br^{ii}	0.98	3.07	3.949 (5)	151
C10—H10A···O2^{iii}	0.98	2.55	3.231 (4)	127

C11—H11A···O1^{iv}	0.99	2.55	3.373 (4)	141
N1—H1A···O2^{iii}	0.88	2.07	2.932 (3)	165

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

Fig. 1

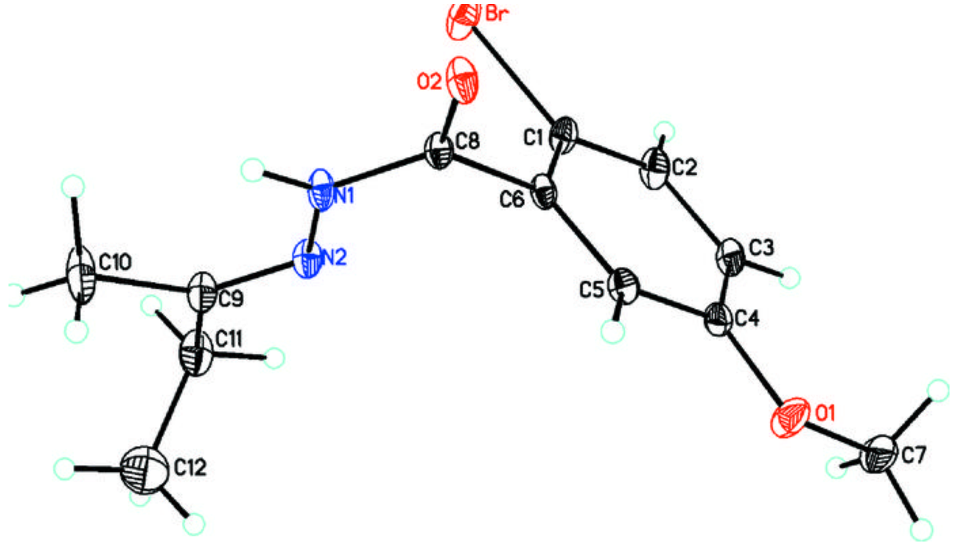

Fig. 2