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***N'*-(3-Bromo-5-chloro-2-hydroxybenzylidene)-2-methoxybenzohydrazide**

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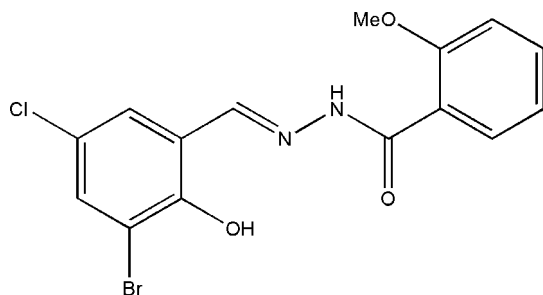
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.033; wR factor = 0.062; data-to-parameter ratio = 11.3.

The title compound, $\text{C}_{15}\text{H}_{12}\text{BrClN}_2\text{O}_3$, was obtained by the condensation reaction between 3-bromo-5-chloro-2-hydroxybenzaldehyde and 2-methoxybenzohydrazide. The molecule is essentially planar, with a dihedral angle between the two benzene rings of $4.7(2)^\circ$, and displays an *E* configuration about the $\text{C}=\text{N}$ double bond. The molecular conformation is stabilized by intramolecular $\text{O}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds. In the crystal structure, molecules are linked into zigzag chains running parallel to the *c* axis by intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds. The chains are further connected through aromatic $\pi-\pi$ stacking interactions with centroid-centroid distances of $3.583(4)$ Å.

Related literature

For the biological properties of hydrazone compounds, see: Cukurovali *et al.* (2006); Karthikeyan *et al.* (2006); Kucukguzel *et al.* (2006). For the crystal structures of related hydrazone compounds, see: Mohd Lair *et al.* (2009); Fun *et al.* (2008); Zhang *et al.* (2009); Khaledi *et al.* (2008). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$\text{C}_{15}\text{H}_{12}\text{BrClN}_2\text{O}_3$
 $M_r = 383.63$

Monoclinic, *Cc*
 $a = 10.883(1)$ Å

$b = 12.863(2)$ Å
 $c = 10.950(1)$ Å
 $\beta = 96.027(3)^\circ$
 $V = 1524.4(3)$ Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 2.89$ mm⁻¹
 $T = 298$ K
 $0.12 \times 0.12 \times 0.10$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.709$, $T_{\max} = 0.746$

4397 measured reflections
2323 independent reflections
1906 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.062$
 $S = 1.02$
2323 reflections
205 parameters
3 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.32$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³
Absolute structure: Flack (1983), 671 Friedel pairs
Flack parameter: 0.068 (12)

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1 \cdots N1	0.82	1.83	2.549 (4)	146
N2—H2 \cdots O3	0.895 (10)	1.92 (3)	2.623 (4)	134 (4)
C6—H6 \cdots O2 ⁱ	0.93	2.45	3.315 (6)	154

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; 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: RZ2301).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bruker (1998). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cukurovali, A., Yilmaz, I., Gur, S. & Kazaz, C. (2006). *Eur. J. Med. Chem.* **41**, 201–207.
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
Fun, H.-K., Patil, P. S., Rao, J. N., Kalluraya, B. & Chantrapromma, S. (2008). *Acta Cryst.* **E64**, o1707.
Karthikeyan, M. S., Prasad, D. J., Poojary, B., Bhat, K. S., Holla, B. S. & Kumari, N. S. (2006). *Bioorg. Med. Chem.* **14**, 7482–7489.
Khaledi, H., Mohd Ali, H. & Ng, S. W. (2008). *Acta Cryst.* **E64**, o2481.
Kucukguzel, G., Kocatepe, A., De Clercq, E., Sahi, F. & Gulluce, M. (2006). *Eur. J. Med. Chem.* **41**, 353–359.
Mohd Lair, N., Mohd Ali, H. & Ng, S. W. (2009). *Acta Cryst.* **E65**, o189.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Zhang, M.-J., Yin, L.-Z., Wang, D.-C., Deng, X.-M. & Liu, J.-B. (2009). *Acta Cryst.* **E65**, o508.

supplementary materials

Acta Cryst. (2009). E65, o851 [doi:10.1107/S1600536809010198]

N'-(3-Bromo-5-chloro-2-hydroxybenzylidene)-2-methoxybenzohydrazide

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Comment

Hydrazones derived from the condensation reactions of hydrazides with aldehydes show excellent biological properties (Cukurovali *et al.*, 2006; Karthikeyan *et al.*, 2006; Kucukguzel *et al.*, 2006). In the last two years, several hydrazone compounds have been structurally characterized (Mohd Lair *et al.*, 2009; Fun *et al.*, 2008; Zhang *et al.*, 2009; Khaledi *et al.*, 2008). In this paper, the synthesis and crystal structure of the title compound, derived from the condensation reaction of 3-bromo-5-chloro-2-hydroxybenzaldehyde and 2-methoxybenzohydrazide, is reported.

The molecular structure of the title compound is shown in Fig. 1. The molecule is essentially planar (mean deviation 0.010 (4) Å) and displays an *E* configuration about the C=N double bond. All bond lengths are within normal ranges (Allen *et al.*, 1987). The molecular conformation is stabilized by intramolecular O—H···N and N—H···O hydrogen bonds (Table 1). In the crystal structure, the molecules are linked into zig-zag chains running parallel to the *c* axis by intermolecular C—H···O hydrogen bonds. The chains are further connected by aromatic π - π stacking interactions: Cp1···Cp2ⁱ = 3.583 (4) Å, perpendicular interplanar distance = 3.430 (4) Å, Cp1···Cp2ⁱ offset = 1.037 (3) Å [Cp1 and Cp2 are the centroids of the C9–C14 and C1–C6 aromatic rings, respectively]. Symmetry code: (i) $-1/2+x, -1/2+y, z$.

Experimental

3-Bromo-5-chloro-2-hydroxybenzaldehyde (1.0 mmol, 235.5 mg) and 2-methoxybenzohydrazide (1.0 mmol, 166.2 mg) were mixed and refluxed with stirring for two hours. Yellow single crystals were formed after slow evaporation of the solution in air for a week.

Refinement

H2 was located in a difference Fourier map and refined isotropically, with the N–H distance restrained to 0.90 (1) Å, and with the $U_{\text{iso}}(\text{H})$ value fixed at 0.08 Å². All other H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C–H = 0.93–0.96 Å, O–H = 0.82 Å, and with $U_{\text{iso}}(\text{H})$ set at 1.2 $U_{\text{eq}}(\text{C})$ or 1.5 $U_{\text{eq}}(\text{O})$.

Figures

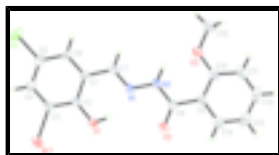


Fig. 1. Molecular structure with displacement ellipsoids drawn at 30% probability for non-H atoms.

***N'*-(3-Bromo-5-chloro-2-hydroxybenzylidene)-2-methoxybenzohydrazide**

Crystal data

$C_{15}H_{12}BrClN_2O_3$	$F_{000} = 768$
$M_r = 383.63$	$D_x = 1.672 \text{ Mg m}^{-3}$
Monoclinic, <i>Cc</i>	Mo <i>K</i> α radiation
Hall symbol: C -2yc	$\lambda = 0.71073 \text{ \AA}$
$a = 10.883 (1) \text{ \AA}$	Cell parameters from 1920 reflections
$b = 12.863 (2) \text{ \AA}$	$\theta = 2.4\text{--}25.0^\circ$
$c = 10.950 (1) \text{ \AA}$	$\mu = 2.89 \text{ mm}^{-1}$
$\beta = 96.027 (3)^\circ$	$T = 298 \text{ K}$
$V = 1524.4 (3) \text{ \AA}^3$	Block, yellow
$Z = 4$	$0.12 \times 0.12 \times 0.10 \text{ mm}$

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	2323 independent reflections
Radiation source: fine-focus sealed tube	1906 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.028$
$T = 298 \text{ K}$	$\theta_{\text{max}} = 27.0^\circ$
ω scans	$\theta_{\text{min}} = 2.5^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -13 \rightarrow 12$
$T_{\text{min}} = 0.709$, $T_{\text{max}} = 0.746$	$k = -16 \rightarrow 16$
4397 measured reflections	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.033$	$w = 1/[\sigma^2(F_o^2) + (0.0041P)^2]$
$wR(F^2) = 0.062$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2323 reflections	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
205 parameters	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
3 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 671 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.068 (12)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.87674 (5)	1.27290 (3)	0.55418 (4)	0.05914 (15)
Cl1	0.79439 (11)	1.45929 (8)	0.10011 (11)	0.0630 (3)
O3	0.5131 (3)	0.7894 (2)	-0.0042 (3)	0.0538 (9)
O2	0.6516 (3)	0.8295 (2)	0.3590 (3)	0.0546 (9)
C8	0.6188 (3)	0.8209 (3)	0.2494 (4)	0.0396 (9)
N2	0.6245 (3)	0.9033 (2)	0.1728 (3)	0.0418 (8)
N1	0.6674 (3)	0.9949 (2)	0.2236 (3)	0.0392 (7)
O1	0.7599 (3)	1.09258 (19)	0.4140 (2)	0.0444 (6)
H1	0.7332	1.0421	0.3738	0.067*
C7	0.6737 (3)	1.0742 (3)	0.1564 (4)	0.0415 (9)
H7	0.6477	1.0713	0.0728	0.050*
C2	0.7652 (3)	1.1748 (3)	0.3396 (3)	0.0344 (8)
C6	0.7306 (4)	1.2597 (3)	0.1403 (5)	0.0390 (11)
H6	0.7025	1.2577	0.0571	0.047*
C9	0.5699 (4)	0.7207 (3)	0.1948 (4)	0.0383 (9)
C1	0.7228 (3)	1.1710 (3)	0.2134 (3)	0.0370 (9)
C5	0.7799 (3)	1.3492 (3)	0.1920 (4)	0.0447 (10)
C3	0.8145 (3)	1.2676 (3)	0.3864 (4)	0.0420 (9)
C4	0.8216 (4)	1.3547 (3)	0.3147 (4)	0.0444 (10)
H4	0.8541	1.4163	0.3487	0.053*
C10	0.5176 (3)	0.7058 (3)	0.0733 (4)	0.0433 (10)
C11	0.4706 (4)	0.6082 (3)	0.0378 (4)	0.0528 (11)
H11	0.4330	0.5987	-0.0417	0.063*
C15	0.4532 (5)	0.7794 (4)	-0.1255 (4)	0.0696 (15)
H15A	0.3678	0.7624	-0.1219	0.104*
H15B	0.4922	0.7252	-0.1678	0.104*
H15C	0.4593	0.8438	-0.1687	0.104*
C14	0.5754 (4)	0.6344 (4)	0.2755 (4)	0.0486 (12)
H14	0.6094	0.6422	0.3565	0.058*
C13	0.5317 (4)	0.5407 (4)	0.2359 (5)	0.0645 (13)
H13	0.5374	0.4845	0.2896	0.077*
C12	0.4787 (4)	0.5271 (4)	0.1169 (5)	0.0661 (13)
H12	0.4485	0.4622	0.0911	0.079*

supplementary materials

H2 0.597 (4) 0.897 (4) 0.0932 (14) 0.080*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0772 (3)	0.0527 (2)	0.0443 (2)	-0.0058 (3)	-0.00881 (19)	-0.0139 (3)
Cl1	0.0775 (8)	0.0393 (6)	0.0743 (8)	0.0053 (5)	0.0180 (6)	0.0199 (6)
O3	0.066 (2)	0.059 (2)	0.0339 (18)	-0.0160 (16)	-0.0040 (16)	-0.0048 (16)
O2	0.080 (2)	0.049 (2)	0.0320 (18)	-0.0123 (16)	-0.0084 (16)	-0.0009 (14)
C8	0.041 (2)	0.038 (2)	0.040 (2)	0.0012 (17)	0.0042 (18)	-0.0006 (19)
N2	0.058 (2)	0.0367 (19)	0.0294 (17)	-0.0104 (15)	-0.0027 (15)	-0.0052 (15)
N1	0.0491 (18)	0.0338 (18)	0.0338 (17)	-0.0084 (14)	0.0003 (14)	-0.0040 (14)
O1	0.0669 (17)	0.0337 (16)	0.0304 (14)	-0.0053 (13)	-0.0056 (13)	-0.0023 (12)
C7	0.049 (2)	0.044 (2)	0.031 (2)	0.0010 (18)	-0.0001 (17)	-0.0006 (18)
C2	0.041 (2)	0.028 (2)	0.034 (2)	0.0049 (15)	0.0012 (17)	-0.0020 (16)
C6	0.042 (2)	0.037 (3)	0.038 (3)	0.0041 (18)	0.0027 (19)	0.0063 (18)
C9	0.040 (2)	0.036 (2)	0.041 (2)	-0.0012 (16)	0.0115 (18)	-0.0041 (18)
C1	0.0378 (19)	0.037 (2)	0.036 (2)	0.0046 (17)	0.0020 (17)	-0.0033 (17)
C5	0.045 (2)	0.031 (2)	0.059 (3)	0.0068 (18)	0.013 (2)	0.006 (2)
C3	0.045 (2)	0.045 (2)	0.035 (2)	0.0050 (18)	-0.0012 (18)	-0.0095 (19)
C4	0.050 (2)	0.029 (2)	0.055 (3)	0.0033 (16)	0.008 (2)	-0.0042 (18)
C10	0.038 (2)	0.050 (3)	0.043 (2)	-0.0062 (17)	0.0095 (18)	-0.0154 (19)
C11	0.053 (3)	0.052 (3)	0.055 (3)	-0.015 (2)	0.012 (2)	-0.018 (2)
C15	0.073 (3)	0.089 (4)	0.044 (3)	-0.023 (3)	-0.005 (2)	-0.011 (3)
C14	0.045 (2)	0.052 (3)	0.049 (3)	-0.006 (2)	0.008 (2)	-0.010 (2)
C13	0.071 (3)	0.043 (3)	0.083 (4)	-0.004 (2)	0.025 (3)	0.012 (3)
C12	0.067 (3)	0.044 (3)	0.090 (4)	-0.014 (2)	0.020 (3)	-0.018 (3)

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

Br1—C3	1.891 (4)	C6—H6	0.9300
Cl1—C5	1.754 (4)	C9—C10	1.404 (6)
O3—C10	1.367 (5)	C9—C14	1.417 (6)
O3—C15	1.423 (5)	C5—C4	1.374 (6)
O2—C8	1.221 (4)	C3—C4	1.375 (6)
C8—N2	1.357 (5)	C4—H4	0.9300
C8—C9	1.494 (5)	C10—C11	1.396 (5)
N2—N1	1.364 (4)	C11—C12	1.353 (7)
N2—H2	0.895 (10)	C11—H11	0.9300
N1—C7	1.265 (4)	C15—H15A	0.9600
O1—C2	1.341 (4)	C15—H15B	0.9600
O1—H1	0.8200	C15—H15C	0.9600
C7—C1	1.468 (5)	C14—C13	1.350 (6)
C7—H7	0.9300	C14—H14	0.9300
C2—C3	1.384 (5)	C13—C12	1.379 (7)
C2—C1	1.411 (5)	C13—H13	0.9300
C6—C5	1.367 (6)	C12—H12	0.9300
C6—C1	1.402 (6)		

C10—O3—C15	119.4 (4)	C4—C3—C2	122.2 (4)
O2—C8—N2	120.6 (4)	C4—C3—Br1	119.3 (3)
O2—C8—C9	121.8 (4)	C2—C3—Br1	118.5 (3)
N2—C8—C9	117.6 (4)	C5—C4—C3	118.9 (4)
C8—N2—N1	117.3 (3)	C5—C4—H4	120.5
C8—N2—H2	120 (3)	C3—C4—H4	120.5
N1—N2—H2	123 (3)	O3—C10—C11	123.1 (4)
C7—N1—N2	119.8 (3)	O3—C10—C9	117.7 (3)
C2—O1—H1	109.5	C11—C10—C9	119.1 (4)
N1—C7—C1	118.4 (3)	C12—C11—C10	121.2 (4)
N1—C7—H7	120.8	C12—C11—H11	119.4
C1—C7—H7	120.8	C10—C11—H11	119.4
O1—C2—C3	119.6 (3)	O3—C15—H15A	109.5
O1—C2—C1	122.5 (3)	O3—C15—H15B	109.5
C3—C2—C1	117.9 (3)	H15A—C15—H15B	109.5
C5—C6—C1	119.6 (4)	O3—C15—H15C	109.5
C5—C6—H6	120.2	H15A—C15—H15C	109.5
C1—C6—H6	120.2	H15B—C15—H15C	109.5
C10—C9—C14	118.1 (4)	C13—C14—C9	120.6 (4)
C10—C9—C8	126.1 (4)	C13—C14—H14	119.7
C14—C9—C8	115.9 (4)	C9—C14—H14	119.7
C6—C1—C2	119.8 (4)	C14—C13—C12	121.0 (5)
C6—C1—C7	119.3 (4)	C14—C13—H13	119.5
C2—C1—C7	120.9 (3)	C12—C13—H13	119.5
C6—C5—C4	121.5 (4)	C11—C12—C13	119.9 (4)
C6—C5—C11	119.8 (4)	C11—C12—H12	120.0
C4—C5—C11	118.6 (3)	C13—C12—H12	120.0

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1 \cdots N1	0.82	1.83	2.549 (4)	146
N2—H2 \cdots O3	0.895 (10)	1.92 (3)	2.623 (4)	134 (4)
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Fig. 1

