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## Structure Reports

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

Jin-Long Hou

 College of Chemistry and Chemical Engineering, Qiqihar University, Qiqihar 161006, People's Republic of China  
 Correspondence e-mail: houjinlong09@163.com

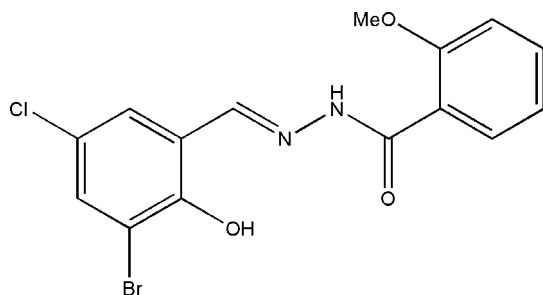
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 Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å;  $R$  factor = 0.033;  $wR$  factor = 0.062; data-to-parameter ratio = 11.3.

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  
 $\beta = 96.027(3)^\circ$   
 $V = 1524.4(3)$  Å<sup>3</sup>  
 $Z = 4$ 

 Mo  $K\alpha$  radiation  
 $\mu = 2.89$  mm<sup>-1</sup>  
 $T = 298$  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<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.28$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983), 671 Friedel pairs  
 Flack parameter: 0.068 (12)

**Table 1**

Hydrogen-bond geometry (Å, °).

<i>D</i> — <i>H</i> ⋯ <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ⋯ <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D</i> — <i>H</i> ⋯ <i>A</i>
O1—H1⋯N1	0.82	1.83	2.549 (4)	146
N2—H2⋯O3	0.895 (10)	1.92 (3)	2.623 (4)	134 (4)
C6—H6⋯O2 <sup>i</sup>	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*.

Financially support from Qiqihar University is gratefully acknowledged.

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.

## supporting information

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

***N'*-(3-Bromo-5-chloro-2-hydroxybenzylidene)-2-methoxybenzohydrazide****Jin-Long Hou****S1. 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 $\cdots$ N and N—H $\cdots$ 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 $\cdots$ O hydrogen bonds. The chains are further connected by aromatic  $\pi$ - $\pi$  stacking interactions: Cp1 $\cdots$ Cp2<sup>i</sup> = 3.583 (4) Å, perpendicular interplanar distance = 3.430 (4) Å, Cp1 $\cdots$ Cp2<sup>i</sup> 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].

**S2. 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.

**S3. 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 Å<sup>2</sup>. 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 $U_{\text{eq}}(\text{O})$ .

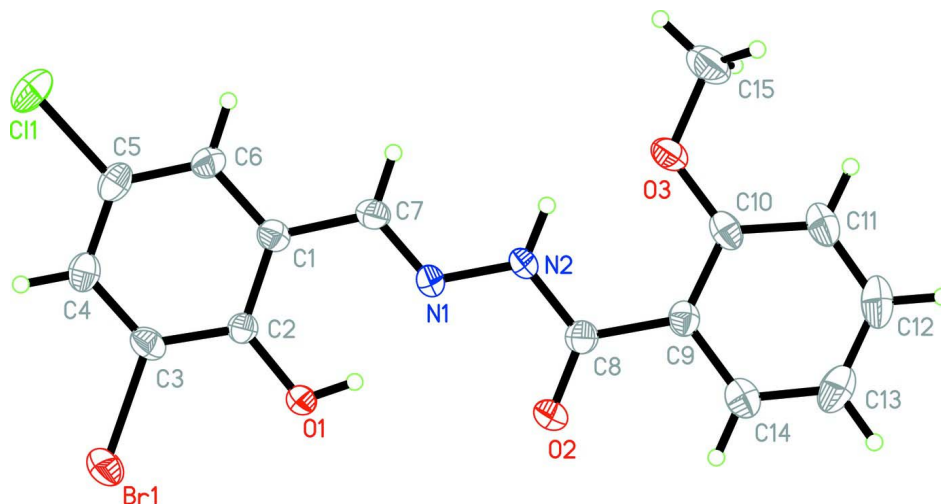


Figure 1

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

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

#### Crystal data

$C_{15}H_{12}BrClN_2O_3$

$M_r = 383.63$

Monoclinic, *Cc*

Hall symbol: *C* -2yc

$a = 10.883$  (1) Å

$b = 12.863$  (2) Å

$c = 10.950$  (1) Å

$\beta = 96.027$  (3)°

$V = 1524.4$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 768$

$D_x = 1.672$  Mg m<sup>-3</sup>

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

Cell parameters from 1920 reflections

$\theta = 2.4$ – $25.0$ °

$\mu = 2.89$  mm<sup>-1</sup>

$T = 298$  K

Block, yellow

$0.12 \times 0.12 \times 0.10$  mm

#### Data collection

Bruker SMART 1000 CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.709$ ,  $T_{\max} = 0.746$

4397 measured reflections

2323 independent reflections

1906 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\max} = 27.0$ °,  $\theta_{\min} = 2.5$ °

$h = -13 \rightarrow 12$

$k = -16 \rightarrow 16$

$l = -13 \rightarrow 13$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.062$

$S = 1.02$

2323 reflections

205 parameters

3 restraints

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

$w = 1/[\sigma^2(F_o^2) + (0.0041P)^2]$

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

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

$\Delta\rho_{\max} = 0.32$  e Å<sup>-3</sup>

$$\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack (1983), 671 Friedel  
pairs  
Absolute structure 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 ( $\text{\AA}^2$ )

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

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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 (Å, °)*

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 ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 $\cdots$ N1	0.82	1.83	2.549 (4)	146
N2—H2 $\cdots$ O3	0.90 (1)	1.92 (3)	2.623 (4)	134 (4)
C6—H6 $\cdots$ O2 <sup>i</sup>	0.93	2.45	3.315 (6)	154

Symmetry code: (i)  $x, -y+2, z-1/2$ .