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## Structure Reports

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## 2'-(3-Bromo-5-chloro-2-hydroxybenzylidene)isonicotinohydrazide methanol solvate

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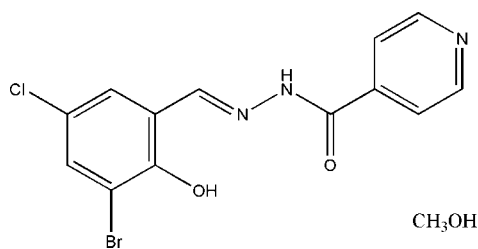
Received 25 June 2008; accepted 27 June 2008

 Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.039;  $wR$  factor = 0.093; data-to-parameter ratio = 15.9.

The title Schiff base compound,  $\text{C}_{13}\text{H}_9\text{BrClN}_3\text{O}_2 \cdot \text{CH}_4\text{O}$ , was derived from the condensation reaction of 3-bromo-5-chlorosalicylaldehyde with isonicotinohydrazide. The dihedral angle between the benzene and pyridine rings is  $5.9$  ( $2^\circ$ ). In the crystal structure, molecules are linked through  $\text{N}-\text{H} \cdots \text{O}$ ,  $\text{O}-\text{H} \cdots \text{O}$ , and  $\text{O}-\text{H} \cdots \text{Br}$  intermolecular hydrogen bonds, forming dimers and chains. There is also an intramolecular  $\text{O}-\text{H} \cdots \text{N}$  hydrogen bond.

## Related literature

For related structures, see: Tang, (2006); Tang, (2007a,b,c,d). For reference structural data, see: Allen *et al.* (1987).



## Experimental

## Crystal data

 $\text{C}_{13}\text{H}_9\text{BrClN}_3\text{O}_2 \cdot \text{CH}_4\text{O}$ 
 $M_r = 386.63$ 

 Triclinic,  $P\bar{1}$ 
 $a = 7.531$  (1) Å

 $b = 8.735$  (1) Å

 $c = 12.130$  (2) Å

 $\alpha = 80.853$  ( $2^\circ$ )

 $\beta = 77.781$  ( $2^\circ$ )

 $\gamma = 86.721$  ( $2^\circ$ )  
 $V = 769.73$  (19) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation

 $\mu = 2.86$  mm<sup>-1</sup>  
 $T = 298$  (2) K  
 $0.32 \times 0.32 \times 0.30$  mm

## Data collection

 Bruker SMART CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.461$ ,  $T_{\max} = 0.481$   
 (expected range = 0.407–0.424)

 4529 measured reflections  
 3254 independent reflections  
 2438 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.018$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.039$   
 $wR(F^2) = 0.093$   
 $S = 1.01$   
 3254 reflections  
 205 parameters  
 1 restraint

 H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.44$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.36$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N2}-\text{H2} \cdots \text{O3}^{\text{i}}$	0.890 (10)	2.005 (15)	2.876 (4)	166 (4)
$\text{O3}-\text{H3} \cdots \text{Br1}$	0.82	3.05	3.641 (3)	131
$\text{O3}-\text{H3} \cdots \text{O1}$	0.82	2.62	3.268 (4)	137
$\text{O3}-\text{H3} \cdots \text{O1}^{\text{ii}}$	0.82	2.55	3.114 (4)	127
$\text{O1}-\text{H1} \cdots \text{N1}$	0.82	1.87	2.590 (3)	146

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

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); 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: SHELXL97.

Financial support from the Jiaying University research fund is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2582).

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## supporting information

*Acta Cryst.* (2008). E64, o1381 [doi:10.1107/S1600536808019648]

## 2'-(3-Bromo-5-chloro-2-hydroxybenzylidene)isonicotinohydrazide methanol solvate

Chun-Bao Tang

### S1. Comment

Recently, the author has reported the structures of several Schiff base compounds (Tang, 2006; Tang, 2007a,b,c,d) and, in continuation of work in this area, reports herein the crystal structure of the title new Schiff base compound, (I).

In the title compound (Fig. 1), the dihedral angle between the benzene ring and the pyridine ring is  $5.9(2)^\circ$ . The torsion angles C1—C7—N1—N2, C7—N1—N2—C8, and N1—N2—C8—C9 are  $0.4(2)$ ,  $2.3(2)$ , and  $1.9(2)^\circ$ , respectively. All the bond lengths are within normal values (Allen *et al.*, 1987).

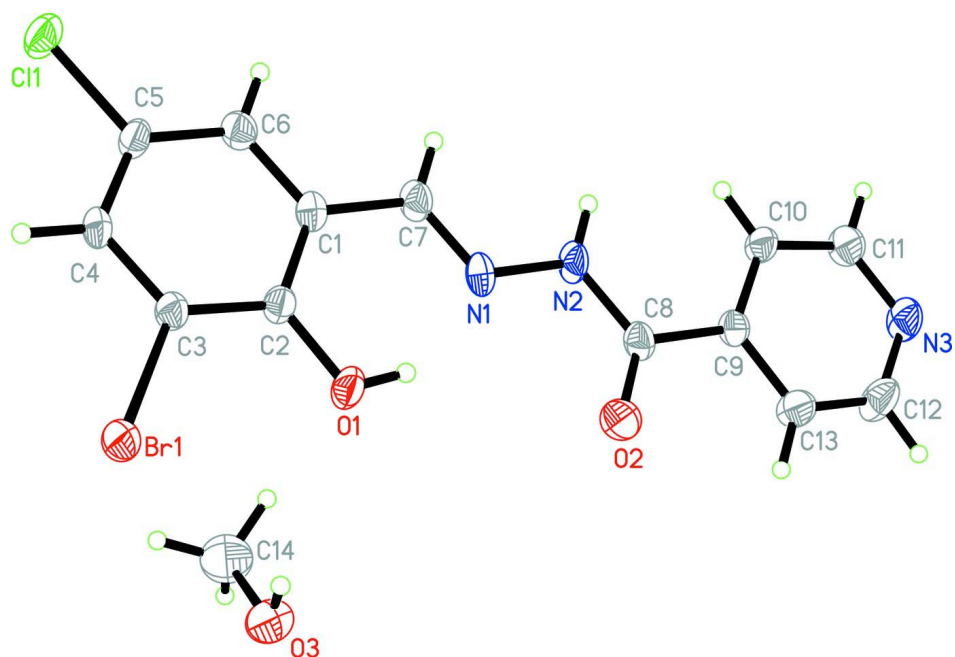
In the crystal structure of the compound, molecules are linked through N—H $\cdots$ O, O—H $\cdots$ O, and O—H $\cdots$ Br intermolecular hydrogen bonds (Table 1), forming dimers (Fig. 2).

### S2. Experimental

3-Bromo-5-chlorosalicylaldehyde (0.1 mmol, 23.5 mg) and isonicotinohydrazide (0.1 mmol, 13.7 mg) were dissolved in a methanol solution (20 ml). The mixture was stirred at reflux for 10 min to give a clear colourless solution. Colourless block-like crystals of the compound were formed by slow evaporation of the solvent over several days.

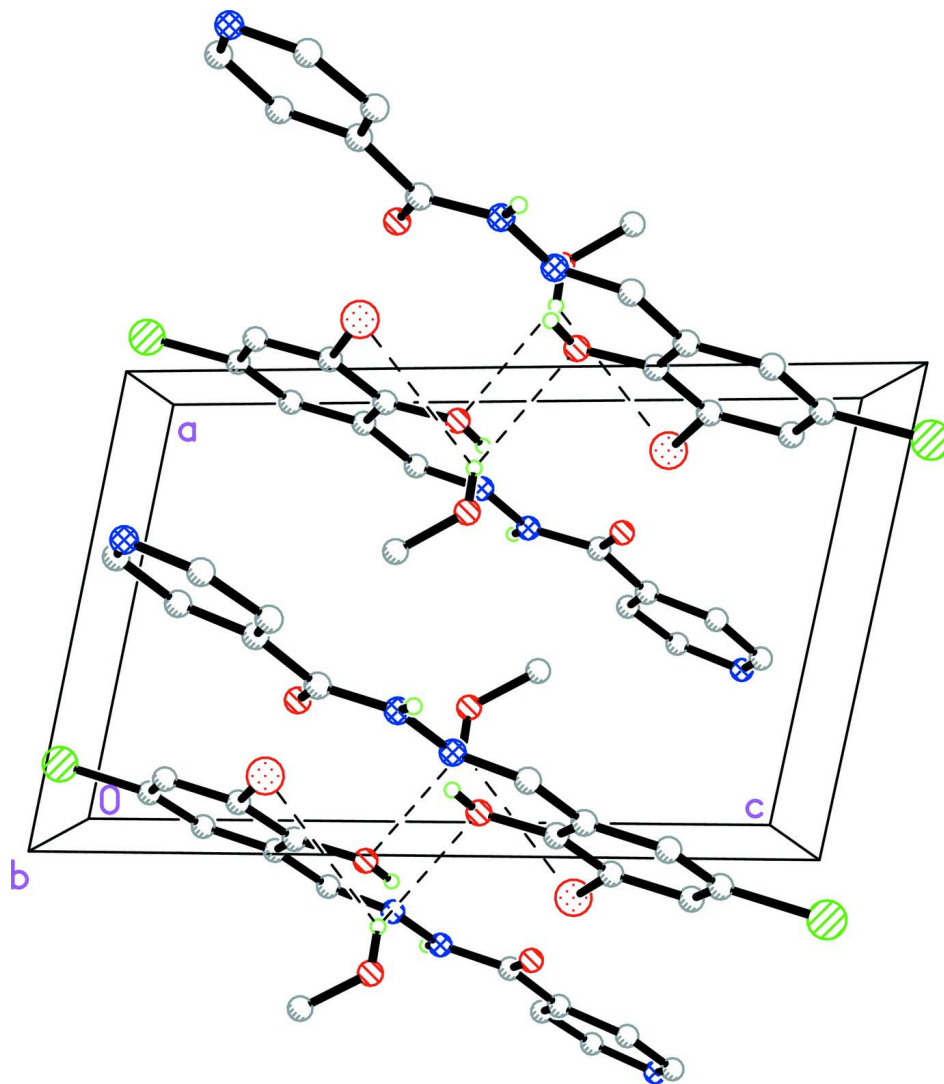
### S3. Refinement

H2 was located from a difference Fourier map and refined isotropically, with  $U_{\text{iso}}$  restrained to  $0.08\text{\AA}^2$ . Other H atoms were constrained to ideal geometries, with  $d(\text{C—H}) = 0.93\text{--}0.96\text{\AA}$ ,  $d(\text{O—H}) = 0.82\text{\AA}$ , and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ,  $1.5U_{\text{eq}}(\text{C14, O1 and O3})$ .



**Figure 1**

The molecular structure of the compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.



**Figure 2**

Molecular packing of (I) with hydrogen bonds drawn as dashed lines.

**2'-(3-Bromo-5-chloro-2-hydroxybenzylidene)isonicotinohydrazide methanol solvate**

*Crystal data*

$C_{13}H_9BrClN_3O_2 \cdot CH_4O$

$M_r = 386.63$

Triclinic,  $P\bar{1}$

Hall symbol:  $-P\ 1$

$a = 7.531\ (1)\ \text{\AA}$

$b = 8.735\ (1)\ \text{\AA}$

$c = 12.130\ (2)\ \text{\AA}$

$\alpha = 80.853\ (2)^\circ$

$\beta = 77.781\ (2)^\circ$

$\gamma = 86.721\ (2)^\circ$

$V = 769.73\ (19)\ \text{\AA}^3$

$Z = 2$

$F(000) = 388$

$D_x = 1.668\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1404 reflections

$\theta = 2.5\text{--}24.3^\circ$

$\mu = 2.86\ \text{mm}^{-1}$

$T = 298\ \text{K}$

Block, colourless

$0.32 \times 0.32 \times 0.30\ \text{mm}$

*Data collection*

Bruker SMART CCD area-detector  
diffractometer  
Radiation source: fine-focus sealed tube  
Graphite monochromator  
 $\omega$  scans  
Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 1996)  
 $T_{\min} = 0.461$ ,  $T_{\max} = 0.481$

4529 measured reflections  
3254 independent reflections  
2438 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.018$   
 $\theta_{\text{max}} = 27.0^\circ$ ,  $\theta_{\text{min}} = 2.4^\circ$   
 $h = -9 \rightarrow 9$   
 $k = -11 \rightarrow 10$   
 $l = -15 \rightarrow 13$

*Refinement*

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.039$   
 $wR(F^2) = 0.093$   
 $S = 1.01$   
3254 reflections  
205 parameters  
1 restraint  
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  
 $w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 0.2117P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.44 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.36 \text{ e } \text{\AA}^{-3}$

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	1.13987 (5)	0.60600 (4)	0.27243 (3)	0.04953 (14)
Cl1	1.14281 (14)	0.21720 (11)	-0.04331 (7)	0.0585 (3)
O1	0.9336 (4)	0.3429 (3)	0.42960 (18)	0.0492 (6)
H1	0.8805	0.2694	0.4718	0.074*
O2	0.6850 (4)	0.1108 (3)	0.6960 (2)	0.0613 (7)
O3	0.7162 (4)	0.6702 (3)	0.4708 (2)	0.0648 (7)
H3	0.8129	0.6213	0.4678	0.097*
N1	0.7910 (4)	0.0712 (3)	0.4821 (2)	0.0422 (7)
N2	0.7009 (4)	-0.0439 (3)	0.5622 (2)	0.0435 (7)
N3	0.3580 (4)	-0.3481 (4)	0.9325 (3)	0.0541 (8)
C1	0.9409 (4)	0.1661 (4)	0.2938 (3)	0.0376 (7)
C2	0.9789 (4)	0.3099 (3)	0.3219 (2)	0.0356 (7)
C3	1.0695 (4)	0.4184 (3)	0.2357 (3)	0.0371 (7)
C4	1.1193 (4)	0.3917 (3)	0.1240 (3)	0.0383 (7)
H4	1.1788	0.4670	0.0674	0.046*

C5	1.0792 (4)	0.2518 (4)	0.0983 (3)	0.0388 (7)
C6	0.9935 (4)	0.1387 (4)	0.1807 (3)	0.0406 (8)
H6	0.9703	0.0439	0.1615	0.049*
C7	0.8466 (4)	0.0454 (4)	0.3797 (3)	0.0423 (8)
H7	0.8271	-0.0499	0.3599	0.051*
C8	0.6508 (4)	-0.0112 (4)	0.6708 (3)	0.0392 (7)
C9	0.5474 (4)	-0.1341 (3)	0.7577 (3)	0.0353 (7)
C10	0.5137 (5)	-0.2802 (4)	0.7393 (3)	0.0432 (8)
H10	0.5524	-0.3098	0.6675	0.052*
C11	0.4218 (5)	-0.3815 (4)	0.8288 (3)	0.0533 (9)
H11	0.4032	-0.4806	0.8155	0.064*
C12	0.3884 (5)	-0.2064 (5)	0.9486 (3)	0.0601 (10)
H12	0.3433	-0.1788	1.0204	0.072*
C13	0.4825 (5)	-0.0977 (4)	0.8658 (3)	0.0507 (9)
H13	0.5023	-0.0005	0.8825	0.061*
C14	0.6322 (7)	0.6375 (5)	0.3861 (4)	0.0809 (14)
H14A	0.5114	0.6820	0.3967	0.121*
H14B	0.6264	0.5272	0.3902	0.121*
H14C	0.7007	0.6808	0.3127	0.121*
H2	0.689 (6)	-0.136 (2)	0.543 (3)	0.080*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.0660 (3)	0.0388 (2)	0.0409 (2)	-0.01820 (16)	0.00010 (16)	-0.00617 (14)
Cl1	0.0847 (7)	0.0584 (5)	0.0301 (4)	-0.0171 (5)	0.0016 (4)	-0.0118 (4)
O1	0.0672 (17)	0.0464 (14)	0.0289 (12)	-0.0191 (12)	0.0035 (11)	-0.0019 (10)
O2	0.088 (2)	0.0386 (13)	0.0523 (15)	-0.0236 (13)	0.0019 (13)	-0.0050 (11)
O3	0.073 (2)	0.0651 (18)	0.0574 (17)	-0.0025 (15)	-0.0088 (15)	-0.0168 (14)
N1	0.0448 (16)	0.0384 (15)	0.0373 (16)	-0.0112 (12)	-0.0042 (12)	0.0104 (12)
N2	0.0547 (18)	0.0384 (15)	0.0331 (15)	-0.0216 (14)	-0.0030 (13)	0.0063 (12)
N3	0.059 (2)	0.0546 (19)	0.0415 (17)	-0.0192 (15)	0.0025 (14)	0.0047 (14)
C1	0.0376 (18)	0.0377 (17)	0.0344 (17)	-0.0055 (14)	-0.0053 (14)	0.0028 (13)
C2	0.0383 (18)	0.0375 (17)	0.0292 (16)	-0.0064 (14)	-0.0041 (13)	-0.0017 (13)
C3	0.0421 (19)	0.0339 (16)	0.0331 (16)	-0.0103 (14)	-0.0024 (14)	-0.0028 (13)
C4	0.0418 (19)	0.0351 (17)	0.0322 (16)	-0.0098 (14)	0.0003 (14)	0.0048 (13)
C5	0.0451 (19)	0.0439 (18)	0.0256 (15)	-0.0084 (15)	-0.0029 (14)	-0.0028 (13)
C6	0.046 (2)	0.0361 (17)	0.0405 (18)	-0.0097 (14)	-0.0095 (15)	-0.0049 (14)
C7	0.047 (2)	0.0376 (17)	0.0394 (19)	-0.0157 (15)	-0.0047 (15)	0.0022 (14)
C8	0.0424 (19)	0.0341 (17)	0.0374 (18)	-0.0089 (14)	-0.0042 (14)	0.0037 (14)
C9	0.0334 (17)	0.0346 (16)	0.0349 (17)	-0.0086 (13)	-0.0030 (13)	0.0014 (13)
C10	0.052 (2)	0.0387 (18)	0.0335 (17)	-0.0125 (15)	0.0030 (15)	-0.0025 (14)
C11	0.062 (2)	0.0433 (19)	0.049 (2)	-0.0178 (18)	0.0004 (18)	0.0006 (16)
C12	0.068 (3)	0.072 (3)	0.035 (2)	-0.022 (2)	0.0059 (18)	-0.0078 (18)
C13	0.061 (2)	0.0446 (19)	0.043 (2)	-0.0167 (17)	0.0042 (17)	-0.0090 (16)
C14	0.095 (4)	0.077 (3)	0.078 (3)	-0.012 (3)	-0.025 (3)	-0.019 (3)

## Geometric parameters (Å, °)

Br1—C3	1.897 (3)	C4—C5	1.373 (4)
Cl1—C5	1.753 (3)	C4—H4	0.9300
O1—C2	1.351 (3)	C5—C6	1.370 (4)
O1—H1	0.8200	C6—H6	0.9300
O2—C8	1.209 (4)	C7—H7	0.9300
O3—C14	1.388 (5)	C8—C9	1.503 (4)
O3—H3	0.8200	C9—C10	1.377 (4)
N1—C7	1.276 (4)	C9—C13	1.380 (4)
N1—N2	1.380 (3)	C10—C11	1.374 (4)
N2—C8	1.363 (4)	C10—H10	0.9300
N2—H2	0.890 (10)	C11—H11	0.9300
N3—C11	1.320 (5)	C12—C13	1.373 (5)
N3—C12	1.323 (5)	C12—H12	0.9300
C1—C6	1.400 (4)	C13—H13	0.9300
C1—C2	1.412 (4)	C14—H14A	0.9600
C1—C7	1.457 (4)	C14—H14B	0.9600
C2—C3	1.383 (4)	C14—H14C	0.9600
C3—C4	1.380 (4)		
C2—O1—H1	109.5	N1—C7—H7	120.2
C14—O3—H3	109.5	C1—C7—H7	120.2
C7—N1—N2	118.9 (3)	O2—C8—N2	122.1 (3)
C8—N2—N1	116.0 (3)	O2—C8—C9	121.6 (3)
C8—N2—H2	124 (3)	N2—C8—C9	116.3 (3)
N1—N2—H2	120 (3)	C10—C9—C13	117.2 (3)
C11—N3—C12	115.9 (3)	C10—C9—C8	125.7 (3)
C6—C1—C2	119.4 (3)	C13—C9—C8	117.0 (3)
C6—C1—C7	118.9 (3)	C11—C10—C9	118.7 (3)
C2—C1—C7	121.6 (3)	C11—C10—H10	120.6
O1—C2—C3	119.5 (3)	C9—C10—H10	120.6
O1—C2—C1	122.3 (3)	N3—C11—C10	124.7 (3)
C3—C2—C1	118.2 (3)	N3—C11—H11	117.6
C4—C3—C2	122.3 (3)	C10—C11—H11	117.6
C4—C3—Br1	118.4 (2)	N3—C12—C13	124.1 (3)
C2—C3—Br1	119.3 (2)	N3—C12—H12	118.0
C5—C4—C3	118.6 (3)	C13—C12—H12	118.0
C5—C4—H4	120.7	C12—C13—C9	119.3 (3)
C3—C4—H4	120.7	C12—C13—H13	120.4
C6—C5—C4	121.6 (3)	C9—C13—H13	120.4
C6—C5—Cl1	119.6 (2)	O3—C14—H14A	109.5
C4—C5—Cl1	118.8 (2)	O3—C14—H14B	109.5
C5—C6—C1	119.9 (3)	H14A—C14—H14B	109.5
C5—C6—H6	120.1	O3—C14—H14C	109.5
C1—C6—H6	120.1	H14A—C14—H14C	109.5
N1—C7—C1	119.6 (3)	H14B—C14—H14C	109.5

*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>
N2—H2...O3 <sup>i</sup>	0.89 (1)	2.01 (2)	2.876 (4)	166 (4)
O3—H3...Br1	0.82	3.05	3.641 (3)	131
O3—H3...O1	0.82	2.62	3.268 (4)	137
O3—H3...O1 <sup>ii</sup>	0.82	2.55	3.114 (4)	127
O1—H1...N1	0.82	1.87	2.590 (3)	146

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