

# *N'*-(5-Bromo-2-hydroxybenzylidene)-4-nitrobenzohydrazide methanol monosolvate

Wei-Hua Liu, Shuang-Ju Song and Jing-Jun Ma\*

Hebei Key Laboratory of Bioinorganic Chemistry, College of Sciences, Agricultural University of Hebei, Baoding 071001, People's Republic of China

Correspondence e-mail: majingjun71@yahoo.cn

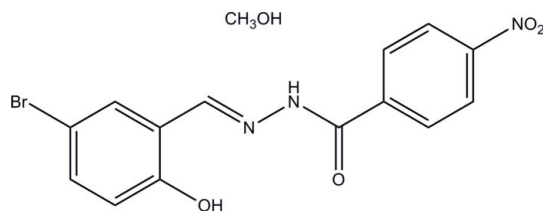
Received 23 July 2011; accepted 25 July 2011

Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.049;  $wR$  factor = 0.101; data-to-parameter ratio = 15.5.

In the title compound,  $\text{C}_{14}\text{H}_{10}\text{BrN}_3\text{O}_4 \cdot \text{CH}_4\text{O}$ , the benzohydrazide molecule is nearly planar [maximum deviation = 0.110 (2) Å]. The mean planes of the two benzene rings make a dihedral angle of 8.4 (3)°. In the benzohydrazide molecule, there is an intramolecular O—H...N hydrogen bond and the NH group is hydrogen bonded to the methanol solvent molecule. In the crystal, intermolecular O—H...O hydrogen bonds involving the methanol solvent molecule link the benzohydrazide molecules to form chains which propagate along the  $a$  axis.

## Related literature

For the biological activities of benzohydrazide compounds, see: El-Sayed *et al.* (2011); Horiuchi *et al.* (2009). For coordination compounds of benzohydrazide compounds, see: El-Dissouky *et al.* (2010); Zhang *et al.* (2010). For standard bond distances, see: Allen *et al.* (1987). For related structures, see: Suleiman Gwaram *et al.* (2010); Dai & Mao (2010); Ban (2010).



## Experimental

### Crystal data

$\text{C}_{14}\text{H}_{10}\text{BrN}_3\text{O}_4 \cdot \text{CH}_4\text{O}$

$M_r = 396.20$

Monoclinic,  $P2_1/n$

$a = 6.660$  (2) Å

$b = 19.068$  (3) Å

$c = 12.730$  (2) Å

$\beta = 93.222$  (2)°

$V = 1614.1$  (6) Å<sup>3</sup>

$Z = 4$

Mo  $K\alpha$  radiation

$\mu = 2.58$  mm<sup>-1</sup>

$T = 298$  K

0.17 × 0.13 × 0.12 mm

### Data collection

Bruker SMART 1K CCD area-detector diffractometer

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.668$ ,  $T_{\max} = 0.747$

8673 measured reflections

3442 independent reflections

1824 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.062$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.101$

$S = 0.95$

3442 reflections

222 parameters

1 restraint

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.31$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.43$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$                             | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|----------|-------------|-------------|---------------|
| $\text{N2}-\text{H2}\cdots\text{O5}$      | 0.89 (1) | 2.00 (2)    | 2.875 (4)   | 166 (4)       |
| $\text{O1}-\text{H1}\cdots\text{N1}$      | 0.82     | 2.03        | 2.737 (4)   | 143           |
| $\text{O1}-\text{H1}\cdots\text{O5}^i$    | 0.82     | 2.51        | 2.952 (4)   | 115           |
| $\text{O5}-\text{H5}\cdots\text{O2}^{ii}$ | 0.82     | 1.90        | 2.710 (4)   | 171           |

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

Data collection: SMART (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); 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.

This project was sponsored by the Nature Development Foundation of Hebei Province (grant No. B2011204051), the Development Foundation of the Department of Education of Hebei Province (grant No. 2010137) and the Research Development Foundation of the Agricultural University of Hebei.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2299).

## References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orphen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Ban, H.-Y. (2010). *Acta Cryst. E66*, o3240.
- Bruker (2007). SMART and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Dai, C.-H. & Mao, F.-L. (2010). *Acta Cryst. E66*, o2942.
- El-Dissouky, A., Al-Fulaij, O., Awad, M. K. & Rizk, S. (2010). *J. Coord. Chem.* **63**, 330–345.
- El-Sayed, M. A. A., Abdel-Aziz, N. I., Abdel-Aziz, A. A. M., El-Azab, A. S., Asiri, Y. A. & ElTahir, K. E. H. (2011). *Bioorg. Med. Chem.* **19**, 3416–3424.
- Horiuchi, T., Nagata, M., Kitagawa, M., Akahane, K. & Uoto, K. (2009). *Bioorg. Med. Chem.* **17**, 7850–7860.
- Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst. A64*, 112–122.
- Suleiman Gwaram, N., Khaledi, H., Mohd Ali, H., Robinson, W. T. & Abdulla, M. A. (2010). *Acta Cryst. E66*, o721.
- Zhang, S.-P., Wei, Y. & Shao, S.-C. (2010). *Acta Cryst. E66*, m1635.

**supplementary materials**

*Acta Cryst.* (2011). E67, o2198 [ doi:10.1107/S1600536811030108 ]

## *N'*-(5-Bromo-2-hydroxybenzylidene)-4-nitrobenzohydrazide methanol monosolvate

W.-H. Liu, S.-J. Song and J.-J. Ma

### Comment

Benzohydrazide compounds are well known for their biological activities (El-Sayed *et al.*, 2011; Horiuchi *et al.*, 2009). In addition, benzohydrazide compounds have also been used as versatile ligands in coordination chemistry (El-Dissouky *et al.*, 2010, Zhang *et al.*, 2010). As a contribution to a structural study on hydrazone compounds, we present here the crystal structure of the title compound, that was obtained as the product of the reaction of 5-bromosalicylaldehyde with 4-nitrobenzohydrazide in methanol.

The title compound contains a benzohydrazide molecule and a methanol solvent molecule of crystallization (Fig. 1). In the benzohydrazide molecule there is an intramolecular O-H $\cdots$ N hydrogen bond and NH group is hydrogen bonded to the methanol solvate molecule. The bond distances (Allen *et al.*, 1987) and angles are within normal ranges and agree well with the corresponding bond distances and angles reported in closely related compounds (Suleiman Gwaram *et al.*, 2010; Dai & Mao, 2010; Ban, 2010). The benzohydrazide molecule is nearly planar [maximum deviation of 0.110 (2) Å], with the mean planes of the two benzene rings making a dihedral angle of 8.4 (3)°.

In the crystal, intermolecular O—H $\cdots$ O hydrogen bonds involving the methanol solvate molecule link the benzohydrazide molecules to form chains which propagate along along the *a* axis direction (Table 1, Fig. 2).

### Experimental

To a methanol solution (20 ml) of 5-bromosalicylaldehyde (0.1 mmol, 20.1 mg) and 4-nitrobenzohydrazide (0.1 mmol, 18.1 mg), a few drops of acetic acid were added. The mixture was refluxed for 1 h and then cooled to room temperature. The white crystalline solid was collected by filtration, washed with cold methanol and dried in air. Single crystals, suitable for X-ray diffraction, were obtained by slow evaporation of a methanol solution of the product in air.

### Refinement

The NH H-atom was located in a difference Fourier map and was refined with a distance restraint, N-H = 0.90 (1) Å, and  $U_{\text{iso}}(\text{H}) = 0.08 \text{ \AA}^2$ . The OH and C-bound H atoms were positioned geometrically and refined using a riding model: O-H = 0.82 Å, C—H = 0.93 and 0.96 Å, for CH and CH<sub>3</sub> H-atoms, respectively, with  $U_{\text{iso}}(\text{H}) = k \times U_{\text{eq}}(\text{O,C})$  where  $k = 1.5$  for OH and CH<sub>3</sub> H-atoms and  $k = 1.2$  for all other H-atoms.

### Figures

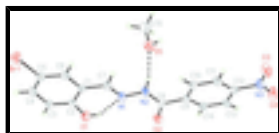


Fig. 1. The molecular structure of the title compound, with the numbering scheme and displacement ellipsoids drawn at the 30% probability level. The N-H $\cdots$ O and O-H $\cdots$ N hydrogen bonds are shown as dashed lines.

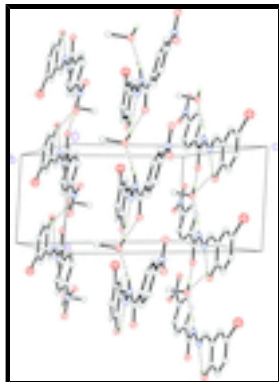


Fig. 2. The crystal packing of the title compound, showing the N-H...O and O-H...O hydrogen-bonds (dashed lines) forming the chains propagating in [100]. H-atoms not involved in the hydrogen bonding have been omitted for clarity.

***N'*-(5-Bromo-2-hydroxybenzylidene)-4-nitrobenzohydrazide methanol monosolvate**

*Crystal data*

$C_{14}H_{10}BrN_3O_4 \cdot CH_4O$

$M_r = 396.20$

Monoclinic,  $P2_1/n$

$a = 6.660$  (2) Å

$b = 19.068$  (3) Å

$c = 12.730$  (2) Å

$\beta = 93.222$  (2)°

$V = 1614.1$  (6) Å<sup>3</sup>

$Z = 4$

$F(000) = 800$

$D_x = 1.630$  Mg m<sup>-3</sup>

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

Cell parameters from 1199 reflections

$\theta = 2.6$ – $24.7$ °

$\mu = 2.58$  mm<sup>-1</sup>

$T = 298$  K

Block, yellow

$0.17 \times 0.13 \times 0.12$  mm

*Data collection*

Bruker SMART 1K CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

$\omega$  scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.668$ ,  $T_{\max} = 0.747$

8673 measured reflections

3442 independent reflections

1824 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.062$

$\theta_{\max} = 27.0$ °,  $\theta_{\min} = 2.1$ °

$h = -8 \rightarrow 8$

$k = -22 \rightarrow 24$

$l = -10 \rightarrow 16$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.101$

$S = 0.95$

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

$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2]$

3442 reflections  
222 parameters  
1 restraint

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.31 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$$

*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 | 0.68607 (7) | 0.04160 (2)  | 0.91805 (4) | 0.06305 (19)                     |
| N1  | 0.9844 (5)  | 0.36314 (16) | 0.8690 (2)  | 0.0446 (9)                       |
| N2  | 0.8848 (5)  | 0.42751 (16) | 0.8642 (3)  | 0.0451 (9)                       |
| H2  | 0.7512 (18) | 0.427 (2)    | 0.853 (3)   | 0.080*                           |
| N3  | 0.5371 (7)  | 0.74331 (19) | 0.8890 (3)  | 0.0577 (10)                      |
| O1  | 1.2966 (4)  | 0.26998 (14) | 0.8658 (3)  | 0.0627 (9)                       |
| H1  | 1.2483      | 0.3094       | 0.8694      | 0.094*                           |
| O2  | 1.1708 (4)  | 0.49115 (14) | 0.8668 (2)  | 0.0563 (8)                       |
| O3  | 0.3577 (5)  | 0.73870 (16) | 0.9023 (3)  | 0.0786 (10)                      |
| O4  | 0.6261 (5)  | 0.79787 (17) | 0.8773 (3)  | 0.0821 (11)                      |
| O5  | 0.4668 (4)  | 0.40586 (15) | 0.8042 (3)  | 0.0661 (9)                       |
| H5  | 0.3706      | 0.4278       | 0.8249      | 0.099*                           |
| C1  | 0.9471 (6)  | 0.23839 (19) | 0.8828 (3)  | 0.0391 (10)                      |
| C2  | 1.1502 (6)  | 0.2216 (2)   | 0.8756 (3)  | 0.0433 (10)                      |
| C3  | 1.2093 (6)  | 0.1525 (2)   | 0.8787 (3)  | 0.0572 (12)                      |
| H3  | 1.3443      | 0.1414       | 0.8733      | 0.069*                           |
| C4  | 1.0715 (7)  | 0.0993 (2)   | 0.8896 (3)  | 0.0581 (12)                      |
| H4  | 1.1133      | 0.0528       | 0.8907      | 0.070*                           |
| C5  | 0.8718 (6)  | 0.1156 (2)   | 0.8989 (3)  | 0.0448 (10)                      |
| C6  | 0.8105 (6)  | 0.18444 (19) | 0.8959 (3)  | 0.0424 (10)                      |
| H6  | 0.6755      | 0.1951       | 0.9026      | 0.051*                           |
| C7  | 0.8712 (6)  | 0.3099 (2)   | 0.8769 (3)  | 0.0450 (10)                      |
| H7  | 0.7334      | 0.3171       | 0.8791      | 0.054*                           |
| C8  | 0.9875 (6)  | 0.4882 (2)   | 0.8666 (3)  | 0.0411 (10)                      |
| C9  | 0.8637 (5)  | 0.55344 (18) | 0.8725 (3)  | 0.0384 (9)                       |
| C10 | 0.6648 (6)  | 0.55357 (19) | 0.8983 (3)  | 0.0483 (11)                      |
| H10 | 0.6010      | 0.5113       | 0.9112      | 0.058*                           |
| C11 | 0.5605 (6)  | 0.6152 (2)   | 0.9052 (3)  | 0.0518 (11)                      |

## supplementary materials

---

|      |            |              |            |             |
|------|------------|--------------|------------|-------------|
| H11  | 0.4274     | 0.6148       | 0.9239     | 0.062*      |
| C12  | 0.6532 (6) | 0.6769 (2)   | 0.8845 (3) | 0.0445 (10) |
| C13  | 0.8513 (6) | 0.6794 (2)   | 0.8602 (3) | 0.0504 (11) |
| H13  | 0.9144     | 0.7221       | 0.8488     | 0.060*      |
| C14  | 0.9540 (6) | 0.61711 (19) | 0.8530 (3) | 0.0468 (11) |
| H14  | 1.0871     | 0.6178       | 0.8346     | 0.056*      |
| C15  | 0.4336 (8) | 0.3910 (2)   | 0.6962 (4) | 0.0810 (16) |
| H15A | 0.5205     | 0.4196       | 0.6565     | 0.122*      |
| H15B | 0.2960     | 0.4008       | 0.6747     | 0.122*      |
| H15C | 0.4618     | 0.3424       | 0.6838     | 0.122*      |

### Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$    | $U^{22}$    | $U^{33}$   | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|-------------|-------------|------------|--------------|--------------|--------------|
| Br1 | 0.0601 (3)  | 0.0462 (3)  | 0.0829 (4) | -0.0063 (2)  | 0.0049 (2)   | 0.0158 (3)   |
| N1  | 0.042 (2)   | 0.0374 (19) | 0.054 (2)  | 0.0118 (16)  | -0.0029 (17) | 0.0009 (16)  |
| N2  | 0.0325 (18) | 0.0361 (18) | 0.066 (3)  | 0.0090 (17)  | -0.0054 (18) | -0.0002 (17) |
| N3  | 0.074 (3)   | 0.045 (2)   | 0.054 (3)  | 0.017 (2)    | 0.002 (2)    | 0.0011 (18)  |
| O1  | 0.0411 (17) | 0.0452 (16) | 0.102 (3)  | -0.0002 (14) | 0.0036 (17)  | 0.0050 (18)  |
| O2  | 0.0337 (17) | 0.0477 (16) | 0.087 (2)  | 0.0049 (13)  | 0.0019 (15)  | -0.0032 (15) |
| O3  | 0.066 (2)   | 0.071 (2)   | 0.100 (3)  | 0.0291 (19)  | 0.012 (2)    | -0.0011 (19) |
| O4  | 0.103 (3)   | 0.0429 (19) | 0.101 (3)  | 0.0126 (19)  | 0.007 (2)    | 0.0085 (18)  |
| O5  | 0.0413 (18) | 0.064 (2)   | 0.092 (3)  | 0.0117 (15)  | -0.0014 (17) | -0.0201 (18) |
| C1  | 0.040 (2)   | 0.040 (2)   | 0.037 (3)  | 0.0072 (18)  | 0.0015 (19)  | -0.0007 (18) |
| C2  | 0.040 (2)   | 0.039 (2)   | 0.051 (3)  | 0.0014 (19)  | -0.005 (2)   | 0.0023 (19)  |
| C3  | 0.038 (2)   | 0.042 (2)   | 0.091 (4)  | 0.010 (2)    | -0.002 (2)   | 0.002 (2)    |
| C4  | 0.057 (3)   | 0.037 (2)   | 0.080 (4)  | 0.007 (2)    | 0.001 (3)    | 0.007 (2)    |
| C5  | 0.043 (3)   | 0.041 (2)   | 0.050 (3)  | -0.0022 (19) | 0.001 (2)    | 0.009 (2)    |
| C6  | 0.038 (2)   | 0.039 (2)   | 0.051 (3)  | -0.0006 (18) | 0.002 (2)    | 0.001 (2)    |
| C7  | 0.040 (2)   | 0.042 (2)   | 0.053 (3)  | 0.006 (2)    | 0.004 (2)    | -0.002 (2)   |
| C8  | 0.040 (3)   | 0.039 (2)   | 0.043 (3)  | 0.003 (2)    | -0.005 (2)   | -0.0016 (19) |
| C9  | 0.037 (2)   | 0.035 (2)   | 0.044 (3)  | 0.0050 (17)  | 0.0002 (19)  | 0.0004 (18)  |
| C10 | 0.046 (3)   | 0.036 (2)   | 0.064 (3)  | -0.0013 (19) | 0.007 (2)    | -0.006 (2)   |
| C11 | 0.038 (2)   | 0.048 (3)   | 0.070 (3)  | 0.006 (2)    | 0.009 (2)    | -0.008 (2)   |
| C12 | 0.054 (3)   | 0.039 (2)   | 0.040 (3)  | 0.012 (2)    | -0.004 (2)   | -0.0030 (19) |
| C13 | 0.052 (3)   | 0.037 (2)   | 0.062 (3)  | 0.002 (2)    | 0.002 (2)    | 0.007 (2)    |
| C14 | 0.037 (2)   | 0.039 (2)   | 0.064 (3)  | 0.0001 (19)  | 0.002 (2)    | 0.005 (2)    |
| C15 | 0.090 (4)   | 0.070 (3)   | 0.083 (5)  | -0.004 (3)   | 0.006 (3)    | 0.001 (3)    |

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

|        |            |        |           |
|--------|------------|--------|-----------|
| Br1—C5 | 1.901 (4)  | C4—C5  | 1.377 (5) |
| N1—C7  | 1.271 (4)  | C4—H4  | 0.9300    |
| N1—N2  | 1.395 (4)  | C5—C6  | 1.375 (5) |
| N2—C8  | 1.343 (5)  | C6—H6  | 0.9300    |
| N2—H2  | 0.894 (10) | C7—H7  | 0.9300    |
| N3—O4  | 1.211 (4)  | C8—C9  | 1.497 (5) |
| N3—O3  | 1.219 (4)  | C9—C10 | 1.383 (5) |
| N3—C12 | 1.486 (5)  | C9—C14 | 1.384 (5) |

|           |           |               |           |
|-----------|-----------|---------------|-----------|
| O1—C2     | 1.353 (4) | C10—C11       | 1.370 (5) |
| O1—H1     | 0.8200    | C10—H10       | 0.9300    |
| O2—C8     | 1.222 (4) | C11—C12       | 1.362 (5) |
| O5—C15    | 1.409 (5) | C11—H11       | 0.9300    |
| O5—H5     | 0.8200    | C12—C13       | 1.373 (5) |
| C1—C6     | 1.390 (5) | C13—C14       | 1.377 (5) |
| C1—C2     | 1.398 (5) | C13—H13       | 0.9300    |
| C1—C7     | 1.456 (5) | C14—H14       | 0.9300    |
| C2—C3     | 1.375 (5) | C15—H15A      | 0.9600    |
| C3—C4     | 1.379 (5) | C15—H15B      | 0.9600    |
| C3—H3     | 0.9300    | C15—H15C      | 0.9600    |
| C7—N1—N2  | 115.0 (3) | C1—C7—H7      | 118.4     |
| C8—N2—N1  | 121.1 (3) | O2—C8—N2      | 123.1 (4) |
| C8—N2—H2  | 121 (3)   | O2—C8—C9      | 121.0 (4) |
| N1—N2—H2  | 117 (3)   | N2—C8—C9      | 115.9 (3) |
| O4—N3—O3  | 124.7 (4) | C10—C9—C14    | 118.2 (3) |
| O4—N3—C12 | 117.9 (4) | C10—C9—C8     | 123.4 (3) |
| O3—N3—C12 | 117.4 (4) | C14—C9—C8     | 118.3 (3) |
| C2—O1—H1  | 109.5     | C11—C10—C9    | 120.9 (4) |
| C15—O5—H5 | 109.5     | C11—C10—H10   | 119.6     |
| C6—C1—C2  | 118.7 (3) | C9—C10—H10    | 119.6     |
| C6—C1—C7  | 118.2 (3) | C12—C11—C10   | 119.5 (4) |
| C2—C1—C7  | 123.1 (4) | C12—C11—H11   | 120.3     |
| O1—C2—C3  | 116.7 (3) | C10—C11—H11   | 120.3     |
| O1—C2—C1  | 123.7 (3) | C11—C12—C13   | 121.7 (4) |
| C3—C2—C1  | 119.6 (4) | C11—C12—N3    | 119.1 (4) |
| C2—C3—C4  | 121.1 (4) | C13—C12—N3    | 119.2 (4) |
| C2—C3—H3  | 119.5     | C12—C13—C14   | 118.2 (4) |
| C4—C3—H3  | 119.5     | C12—C13—H13   | 120.9     |
| C5—C4—C3  | 119.6 (4) | C14—C13—H13   | 120.9     |
| C5—C4—H4  | 120.2     | C13—C14—C9    | 121.5 (4) |
| C3—C4—H4  | 120.2     | C13—C14—H14   | 119.2     |
| C6—C5—C4  | 120.0 (4) | C9—C14—H14    | 119.2     |
| C6—C5—Br1 | 121.2 (3) | O5—C15—H15A   | 109.5     |
| C4—C5—Br1 | 118.9 (3) | O5—C15—H15B   | 109.5     |
| C5—C6—C1  | 121.0 (4) | H15A—C15—H15B | 109.5     |
| C5—C6—H6  | 119.5     | O5—C15—H15C   | 109.5     |
| C1—C6—H6  | 119.5     | H15A—C15—H15C | 109.5     |
| N1—C7—C1  | 123.1 (4) | H15B—C15—H15C | 109.5     |
| N1—C7—H7  | 118.4     |               |           |

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

| $D-H\cdots A$                   | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------------|----------|-------------|-------------|---------------|
| N2—H2 $\cdots$ O5               | 0.89 (1) | 2.00 (2)    | 2.875 (4)   | 166 (4)       |
| O1—H1 $\cdots$ N1               | 0.82     | 2.03        | 2.737 (4)   | 143           |
| O1—H1 $\cdots$ O5 <sup>i</sup>  | 0.82     | 2.51        | 2.952 (4)   | 115           |
| O5—H5 $\cdots$ O2 <sup>ii</sup> | 0.82     | 1.90        | 2.710 (4)   | 171           |

# supplementary materials

---

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

Fig. 1

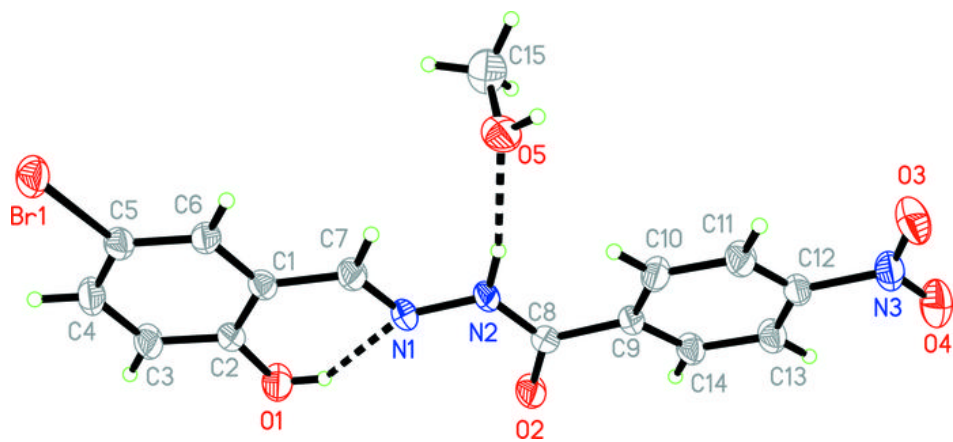




Fig. 2

