Syntheses and crystal structures of benzyl N’-[(E)-2-hydroxybenzylidene]hydrazinecarboxylate and benzyl N’-[(E)-5-bromo-2-hydroxybenzylidene]-hydrazinecarboxylate

Vinaya,* Yeriyur B. Basavaraju,* Beliyaiah Lakshmana,* Hemmige S. Yathirajan** and Sean Parkinb

*Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysuru-570 006, India, and **Department of Chemistry, University of Kentucky, Lexington, KY, 40506-0055, USA. *Correspondence e-mail: yathirajan@hotmail.com

Benzyl N’-[(E)-2-hydroxybenzylidene]hydrazinecarboxylate, C_{15}H_{14}N_{2}O_{3} (I) and benzyl N’-[(E)-5-bromo-2-hydroxybenzylidene]hydrazinecarboxylate (II), C_{15}H_{13}BrN_{2}O_{3}, have been synthesized by the reaction of either 2-hydroxybenzaldehyde or 5-bromo-2-hydroxybenzaldehyde with benzyl carbazate, respectively. Both the compounds crystallize in the monoclinic crystal system with space groups $Pn$ ($Z = 1$, I) and $P2_1/c$ ($Z = 2$, II). Molecular conformations in each structure are similar, and both structures feature strong intramolecular O—H···N hydrogen bonds, which form $S(6)$ ring motifs. There are also strong N—H···O and weak C—H···O hydrogen bonds in both structures, but their modes of packing within their respective crystals are markedly different. Some comparisons are made with the structures of a few related compounds.

1. Chemical context

Hydroxybenzylidine hydrazines exhibit a wide spectrum of biological activities (Sersen et al., 2017). Benzaldehydehydrazone derivatives have received considerable attention for several decades as a result of their pharmacological activity (Parashar et al., 1988) and photochromic properties (Hadjoudis et al., 1987). Benzaldehydehydrazone derivatives are also important intermediates in the synthesis of 1,3,4-oxadiazoles, which are versatile compounds with many useful properties (Borg et al., 1999). Synthesis and biological activities of new hydrazide derivatives (Özdemir et al., 2009) and biological activities of hydrazone derivatives (Rollas & Küçükgüzel, 2007) have been reported. In view of the importance of benzylidine hydrazines and benzaldehydehydrazone derivatives in general, this paper reports the crystal structures of the title compounds, C_{15}H_{14}N_{2}O_{3} (I), and C_{15}H_{13}BrN_{2}O_{3} (II).
2. Structural commentary

The molecular structures of benzyl N'-(E)-2-hydroxybenzylidene]hydrazinecarboxylate (I) (Fig. 1) and benzyl N'-(E)-5-bromo-2-hydroxybenzylidene]hydrazinecarboxylate (II) (Fig. 2) each consist of a central N'-methylidenemethoxy-carboxyl core flanked by a benzyl group attached to the singly bonded oxygen and a 2-hydroxyphenyl (I) or 5-bromo-2-hydroxyphenyl (II) attached to the methylidene. There are no unusual bond lengths or angles in either structure. The molecules have strong intramolecular O—H⋯N hydrogen bonds (Tables 1 and 2), forming S(6) ring motifs (Etter et al., 1990). The asymmetric unit of I contains a single molecule while that of II contains two (labelled A and B in Fig. 2). In each case, the [(hydroxyphenyl)methylidene]carboxyhdrazide moieties are essentially planar [r.m.s. deviations 0.0429 Å (I), 0.0905 Å (IIA), 0.0692 Å (IIB)]. These form dihedral angles of 79.92 (3)°, 79.74 (4)°, and 74.27 (4)° to the benzyl groups of I, IIA, and IIB, respectively. Indeed, the V-shaped conformations of IIA, and IIB are strikingly similar, with I only deviating to any appreciable degree at the benzyl group, as evidenced by an overlay of the three molecules (Fig. 3). The conformation of I differs from IIA and IIB primarily by the torsion angles about bonds O2—C9 and C9—C10 (Table 3).

3. Supramolecular features

In addition to the strong O—H⋯N intramolecular hydrogen bonds in I and II, the structures both feature strong N—H⋯O and weaker C—H⋯O intermolecular hydrogen bonds. These interactions are summarized in Tables 1 and 2. The packing modes are, however, quite different.

In I, the V-shaped (Fig. 3) molecules stack into columns along [100] (Fig. 4). These columns interact with n-glide-related columns via the strong N2—H2N⋯O1 (symmetry codes as per Table 1) hydrogen bonds to give C(7) chains (Etter et al., 1990) and with different n-glide-related columns via the bifurcated C6—H6⋯O3 and C7—H7⋯O3 (Table 1) hydrogen bonds. In combination, these interactions produce layers that extend in the ac plane (Fig. 5), which in turn stack along [010].

Table 1

| D—H⋯A | D—H | H⋯A | D⋯A | D—H⋯A |
|-------|-----|-----|-----|-------|
| O1—H1—O1⋯N1 | 0.90 (3) | 1.73 (3) | 2.546 (2) | 148 (2) |
| N2—H2⋯O1 | 0.87 (2) | 1.97 (2) | 2.8225 (19) | 168 (2) |
| C7—H7⋯O3 | 0.95 | 2.43 | 3.271 (2) | 147 |

Symmetry codes: (i) \( x, -y + 1, z + \frac{1}{2} \); (ii) \( x, y + \frac{1}{2}, -z + \frac{1}{2} \); (iii) \( -x, y - \frac{1}{2}, -z + \frac{1}{2} \).
In II, the independent molecules (A and B) make hydrogen bonds to 2_1-screw-related copies of themselves via strong (N2—H2⋅⋅⋅O1) and weak (C3—H3⋅⋅⋅O2 and C6—H6⋅⋅⋅O3) hydrogen bonds (Table 2), forming R$_2^2$(8) and R$_3^3$(13) ring motifs (Etter et al., 1990), leading to adjacent pairs of ribbons that extend along [010] (Fig. 6). The 5-bromo-2-hydroxyphenyl and benzyl groups of II A and II B have notably different environments. For example, inversion-related (−x, −y, −z) pairs of II A molecules have close contacts of 3.3379 (9) Å between their Br1A atoms and the centroid of the inversion-related C10A–C15A ring. There is no corresponding close contact for the II B molecule (Fig. 7).
The differences in packing are also apparent in the atom–atom contact coverages, as quantified by CrystalExplorer (Spackman et al., 2021) fingerprint diagrams (Figs. 8 and 9).

4. Database survey

A search of the Cambridge Structure Database (CSD, v5.43 with updates as of June 2022; Groom et al., 2016) for a search fragment consisting of the structure of I, but with the two aromatic rings replaced by ‘any group’ gave 340 hits. A fragment including the benzyl group attached to the equivalent of O2 in I gave 105 hits, while a fragment including a phenyl ring at C7 gave 37 hits. A fragment consisting of I but without the phenolic OH group gave just four hits: HIXQIQ (Dong & Wang, 2014), QA VFA Y (Shen et al., 2022), GEZTUD (Chang et al., 2018) and PIVKUD (Zhang et al., 2019). In HIXQIQ, a 5-chloro-2-hydroxy-2-(methoxycarbonyl)-2,3-dihydro-1H-inden-1-ylidene) group is attached to the hydrazine. QA VFA Y features a four-membered 1,2-diazete ring, with the phenyl group fluorinated at its 4-position. Structures GEZTUD and PIVKUD each feature pyrazole rings; the former having a 2,2,2-trifluoroethyl group attached to the pyrazole and a methyl at the 4-position of the phenyl ring, and the latter having a 3,4,5-trimethoxyphenyl attached to its pyrazole ring.

New Schiff bases derived from benzyl carbazate with alkyl and heteroaryl ketones and crystal structures of benzyl 2-cyclopentylidenehydrazinecarboxylate (JENFAM, (E)-benzyl 2-[1-(pyridin-3-yl)ethylidene]hydrazine-1-carboxylate (JENFEQ), (E)-benzyl2-[1-(pyridin-4-yl)ethylidene]hydrazinecarboxylate (JENFIU) (Nithya et al., 2017) have also been reported. A selection of other structures similar to I and II deposited in the CSD are listed in Table 4.

| CSD refcode   | R    | R'   | R''  | Reference                  |
|---------------|------|------|------|----------------------------|
| HODLOC        | H    | methyl | Sun & Cheng (2008)          |
| QOFLAZ        | H    | ethyl  | Gao (2008)                  |
| KODUVU        | H    | methyl | Cheng (2008c)               |
| XOGVEV        | methyl | methyl | Cheng (2008b)               |
| XOGXEX        | H    | ethyl  | Cheng (2008c)               |
| XOGXIB        | H    | methyl | Cheng (2008f)               |
| AZOTAL        | H    | methyl | Li et al. (2011)            |
| AWUJAE        | H    | ethyl  | Hu et al. (2011)            |
| WEFTRUX       | H    | methyl | Lv et al. (2017)            |

5-chloro-2-hydroxy-2-(methoxycarbonyl)-2,3-dihydro-1H-inden-1-ylidene) group is attached to the hydrazine. QA VFA Y features a four-membered 1,2-diazete ring, with the phenyl group fluorinated at its 4-position. Structures GEZTUD and PIVKUD each feature pyrazole rings; the former having a 2,2,2-trifluoroethyl group attached to the pyrazole and a methyl at the 4-position of the phenyl ring, and the latter having a 3,4,5-trimethoxyphenyl attached to its pyrazole ring.

Figure 8
Fingerprint plots obtained from a Hirshfeld surface analysis for I using CrystalExplorer, separated into (a) H···H (47.4% coverage), (b) C···H/ H···C (24.4%), (c) O···H/H···O (17.5%), (d) C···C (4.2%). All other contacts are negligible.

Figure 9
Fingerprint plots obtained from a Hirshfeld surface analysis for II using CrystalExplorer, separated into (a) H···H (33.8% coverage), (b) C···H/ H···C (23.8%), (c) O···H/H···O (15.4%), (d) Br···H/H···Br (12.6%). All other contacts are negligible.
5. Synthesis and crystallization

Preparation of I and II followed similar synthetic routes. Either 2-hydroxybenzaldehyde (1.2 g, 0.01 mol) (for I) or 5-bromo-2-hydroxybenzaldehyde (2.0 g, 0.01 mol) (for II) and benzyl carbazate (1.66 g, 0.01 mol) were dissolved in methanol (25 ml) and stirred for 3 h at room temperature. The resulting solids were filtered off and recrystallized from ethanol to give I and II with yields of 80% in both cases. The general reaction scheme is summarized in Fig. 10. Single crystals suitable for X-ray analysis for both I and II were obtained by slow evaporation of methanolic solutions at room temperature (m.p.: 400–402 K for I and 468–470 K for II).

6. Crystal handling, data collection, and refinement

Crystals of I and II were each secured on the tips of fine glass fibres held in copper mounting pins. The crystal of I was mounted directly into a cold-nitrogen stream. Data for both samples (Cu Ka for I and Mo Ka for II) were collected with the crystals held at 90.0 (2) K. Determination of the absolute structure for I was inconclusive via traditional full-matrix refinement of Flack’s parameter [x = −0.08 (18); Flack & Bernardinelli, 1999], but Hooft’s Bayesian approach [y = 0.00 (8); Hooft et al. (2008), as calculated using PLATON (Spek, 2020)] and Parsons’ quotient method [z = 0.04 (10); Parsons et al., 2013] give credence to the assignment. Refinement progress was checked using PLATON (Spek, 2020) and by an R-tensor (Parkin, 2000). Crystal data, data collection, and refinement statistics are summarized in Table 5. Carbon-bound hydrogen atoms were included using riding models, with C−H distances constrained to 0.95 Å for Csp³H and 0.99 Å for R₂CH₂-N—H.
and O—H hydrogen-atom coordinates were refined. $U_{iso}(H)$ parameters were set to values of either $1.2U_{eq}(C—H, N—H)$ or $1.5U_{eq}(O—H)$ of the attached atom.

Acknowledgements

One of the authors (V) is grateful to the DST–PURSE Project, Vijnana Bhavana, UOM for providing research facilities.

Funding information

HSY thanks UGC for a BSR Faculty fellowship for three years. Funding for this research was provided by: NSF (MRI CHE1625732) and the University of Kentucky (Bruker D8 Venture diffractometer).

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Syntheses and crystal structures of benzyl N’-[(E)-2-hydroxybenzylidene]hydrazinecarboxylate and benzyl N’-[(E)-5-bromo-2-hydroxybenzylidene]hydrazinecarboxylate

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Computing details

For both structures, data collection: APEX3 (Bruker, 2016); cell refinement: APEX3 (Bruker, 2016); data reduction: APEX3 (Bruker, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2019/2 (Sheldrick, 2015b); molecular graphics: XP in SHELXTL (Sheldrick, 2008); software used to prepare material for publication: CIFIX (Parkin, 2013) and publCIF (Westrip, 2010).

Benzyl N’-[(E)-2-hydroxybenzylidene]hydrazinecarboxylate (I)

Crystal data

\[C_{15}H_{14}N_2O_3\]  
\(M_r = 270.28\)  
Monoclinic, \(Pn\)  
\(a = 4.5017 (12) \ \text{Å}\)  
\(b = 14.047 (4) \ \text{Å}\)  
\(c = 10.567 (3) \ \text{Å}\)  
\(\beta = 96.300 (15) ^\circ\)  
\(V = 664.2 (3) \ \text{Å}^3\)  
\(Z = 2\)

Data collection

Bruker D8 Venture dual source diffractometer  
Radiation source: microsource  
Detector resolution: 7.41 pixels mm\(^{-1}\)  
\(\varphi\) and \(\omega\) scans  
Absorption correction: multi-scan  
(SADABS; Krause et al., 2015)  
\(T_{\text{min}} = 0.589, T_{\text{max}} = 0.958\)

Refinement

Refinement on \(F^2\)  
Least-squares matrix: full  
\(R[F^2 > 2\sigma(F^2)] = 0.024\)  
\(wR(F^2) = 0.063\)  
\(S = 1.04\)  
2511 reflections  
187 parameters  
2 restraints

Primary atom site location: structure-invariant direct methods  
Secondary atom site location: difference Fourier map  
Hydrogen site location: mixed  
H atoms treated by a mixture of independent and constrained refinement

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\[ w = \frac{1}{\sigma^2(F_0^2) + (0.0283 P)^2 + 0.0531 P} \]
where 
\[ P = (F_0^2 + 2F_c^2)/3 \]

\( (\Delta/\sigma)_{\text{max}} < 0.001 \)
\( \Delta \rho_{\text{max}} = 0.13 \text{ e Å}^{-3} \)
\( \Delta \rho_{\text{min}} = -0.13 \text{ e Å}^{-3} \)

**Absolute structure:** Flack \( x \) determined using 1054 quotients \( [(I^+)-I]/[(I^-+I)] \) (Parsons et al., 2013)

**Absolute structure parameter:** 0.04 (10)

**Special details**

**Experimental.** The crystal was mounted using polyisobutene oil on the tip of a fine glass fibre, which was fastened in a copper mounting pin with electrical solder. It was flash-cooled in liquid nitrogen and mounted into the cold gas stream of a liquid-nitrogen based cryostat using specially designed tongs (Parkin & Hope, 1998).

Diffraction data were collected with the crystal at 90K, which is standard practice in this laboratory for the majority of flash-cooled crystals.

**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 progress was checked using Platon (Spek, 2020) and by an \( R \)-tensor (Parkin, 2000). The final model was further checked with the IUCr utility checkCIF.

**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\( \text{Å}^2 \))**

|       | \( x \)    | \( y \)    | \( z \)    | \( U_{\text{iso}} \) or \( U_{\text{eq}} \) |
|-------|------------|------------|------------|------------------|
| O1    | 0.7525 (3) | 0.44387 (9)| 0.34649 (11)| 0.0268 (3)       |
| H1O   | 0.631 (6)  | 0.4786 (18)| 0.391 (3)  | 0.040*           |
| O2    | -0.0407 (3)| 0.67535 (9)| 0.56997 (11)| 0.0243 (3)       |
| O3    | 0.2021 (3) | 0.64243 (9)| 0.39780 (11)| 0.0248 (3)       |
| N1    | 0.4688 (3) | 0.49495 (10)| 0.53076 (13)| 0.0202 (3)      |
| N2    | 0.2728 (3) | 0.55477 (11)| 0.58048 (13)| 0.0214 (3)     |
| H2N   | 0.242 (5)  | 0.5508 (15)| 0.660 (2)  | 0.026*           |
| C1    | 0.7887 (3) | 0.36137 (13)| 0.54751 (15)| 0.0205 (3)       |
| C2    | 0.8612 (4) | 0.37060 (12)| 0.42217 (16)| 0.0221 (4)       |
| C3    | 1.0493 (4) | 0.30492 (14)| 0.37311 (16)| 0.0275 (4)       |
| H3    | 1.101603   | 0.312160   | 0.288959   | 0.033*           |
| C4    | 1.1602 (4) | 0.22882 (14)| 0.44739 (19)| 0.0300 (4)       |
| H4    | 1.284895   | 0.183155   | 0.413092   | 0.036*           |
| C5    | 1.0907 (4) | 0.21882 (14)| 0.57132 (18)| 0.0289 (4)       |
| H5    | 1.168389   | 0.166681   | 0.621816   | 0.035*           |
| C6    | 0.9082 (4) | 0.28486 (13)| 0.62116 (15)| 0.0244 (4)       |
| H6    | 0.863238   | 0.278254   | 0.706480   | 0.029*           |
| C7    | 0.5866 (4) | 0.42754 (12)| 0.60123 (15)| 0.0204 (3)       |
| H7    | 0.542993   | 0.420844   | 0.686734   | 0.025*           |
| C8    | 0.1509 (4) | 0.62582 (12)| 0.50506 (15)| 0.0196 (3)       |
| C9    | -0.1607 (4)| 0.76046 (13)| 0.50546 (17)| 0.0251 (4)       |
| H9A   | -0.343944  | 0.780464   | 0.542188   | 0.030*           |
| H9B   | -0.215620  | 0.746317   | 0.414103   | 0.030*           |
| C10   | 0.0630 (4) | 0.83981 (12)| 0.51860 (17)| 0.0231 (4)       |
| C11   | 0.1698 (4) | 0.87256 (14)| 0.63955 (19)| 0.0311 (4)       |
| H11   | 0.100670   | 0.844554   | 0.712731   | 0.037*           |
| C12   | 0.3763 (5) | 0.94578 (15)| 0.6533 (2)  | 0.0401 (5)       |
| H12   | 0.448310   | 0.967698   | 0.736024   | 0.048*           |
Atomic displacement parameters (Å²)

|  | U¹¹ | U²² | U³³ | U¹² | U¹³ | U²³ |
|---|-----|-----|-----|-----|-----|-----|
| O1 | 0.0369 (8) | 0.0313 (7) | 0.0138 (5) | 0.0058 (5) | 0.0090 (5) | 0.0020 (5) |
| O2 | 0.0269 (6) | 0.0267 (6) | 0.0202 (6) | 0.0045 (5) | 0.0066 (5) | 0.0022 (5) |
| O3 | 0.0317 (6) | 0.0292 (6) | 0.0137 (5) | 0.0005 (5) | 0.0040 (4) | 0.0007 (5) |
| N1 | 0.0235 (7) | 0.0242 (7) | 0.0132 (6) | 0.0005 (5) | 0.0041 (5) | 0.0019 (5) |
| N2 | 0.0259 (8) | 0.0276 (8) | 0.0117 (6) | 0.0044 (6) | 0.0064 (5) | 0.0001 (5) |
| C1 | 0.0217 (8) | 0.0251 (8) | 0.0148 (7) | −0.0008 (6) | 0.0029 (6) | −0.0008 (6) |
| C2 | 0.0246 (8) | 0.0262 (9) | 0.0154 (7) | −0.0010 (7) | 0.0025 (6) | −0.0011 (7) |
| C3 | 0.0322 (10) | 0.0338 (10) | 0.0172 (8) | 0.0015 (7) | 0.0062 (7) | −0.0041 (7) |
| C4 | 0.0304 (10) | 0.0316 (10) | 0.0285 (9) | 0.0069 (8) | 0.0053 (7) | −0.0079 (8) |
| C5 | 0.0313 (9) | 0.0284 (9) | 0.0265 (9) | 0.0061 (7) | 0.0009 (7) | 0.0018 (7) |
| C6 | 0.0268 (8) | 0.0290 (9) | 0.0174 (8) | 0.0020 (7) | 0.0024 (7) | 0.0011 (6) |
| C7 | 0.0233 (8) | 0.0269 (8) | 0.0114 (7) | −0.0004 (6) | 0.0035 (6) | 0.0001 (6) |
| C8 | 0.0212 (8) | 0.0231 (8) | 0.0144 (8) | −0.0021 (6) | 0.0019 (6) | −0.0019 (6) |
| C9 | 0.0216 (8) | 0.0278 (9) | 0.0256 (8) | 0.0037 (7) | 0.0009 (7) | 0.0018 (7) |
| C10 | 0.0194 (7) | 0.0252 (9) | 0.0243 (8) | 0.0063 (6) | 0.0009 (6) | −0.0018 (7) |
| C11 | 0.0254 (9) | 0.0386 (11) | 0.0290 (9) | 0.0068 (8) | 0.0010 (7) | −0.0067 (8) |
| C12 | 0.0287 (10) | 0.0389 (11) | 0.0503 (13) | 0.0061 (8) | −0.0067 (9) | −0.0187 (9) |
| C13 | 0.0240 (9) | 0.0252 (10) | 0.0741 (16) | 0.0034 (8) | −0.0039 (10) | −0.0034 (10) |
| C14 | 0.0279 (10) | 0.0339 (11) | 0.0552 (12) | 0.0039 (8) | 0.0042 (9) | 0.0155 (10) |
| C15 | 0.0251 (9) | 0.031 (1) | 0.0290 (9) | 0.0055 (7) | 0.0012 (7) | 0.0053 (7) |

Geometric parameters (Å, °)

|  | O1—C2 | 1.361 (2) | C5—H5 | 0.9500 |
|---|-------|---------|-------|--------|
| O1—H1O | 0.90 (3) | C6—H6 | 0.9500 |
| O2—C8 | 1.352 (2) | C7—H7 | 0.9500 |
| O2—C9 | 1.451 (2) | C9—C10 | 1.498 (2) |
| O3—C8 | 1.204 (2) | C9—H9A | 0.9900 |
| N1—C7 | 1.283 (2) | C9—H9B | 0.9900 |
| N1—N2 | 1.365 (2) | C10—C15 | 1.384 (3) |
| N2—C8 | 1.355 (2) | C10—C11 | 1.393 (3) |
| N2—H2N | 0.87 (2) | C11—C12 | 1.383 (3) |
| C1—C6 | 1.399 (2) | C11—H11 | 0.9500 |
| C1—C2 | 1.405 (2) | C12—C13 | 1.376 (4) |
| C1—C7 | 1.459 (2) | C12—H12 | 0.9500 |
| C2—C3 | 1.390 (3) | C13—C14 | 1.388 (4) |
| C3—C4 | 1.386 (3) | C13—H13 | 0.9500 |
| C3—H3 | 0.9500 | C14—C15 | 1.387 (3) |
| Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|
| C4—C5         | 1.387 (3)    | C14—H14       | 0.9500       |
| C4—H4         | 0.9500       | C15—H15       | 0.9500       |
| C5—C6         | 1.381 (3)    |               |              |

| Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|
| C2—O1—H1O    | 107.5 (17)   | O3—C8—O2     | 125.21 (16)  |
| C8—O2—C9     | 114.27 (13)  | O3—C8—N2     | 126.12 (17)  |
| C7—N1—N2     | 118.33 (14)  | O2—C8—N2     | 108.67 (14)  |
| C8—N2—N1     | 117.65 (14)  | O2—C9—C10    | 110.94 (13)  |
| C8—N2—H2N    | 121.3 (14)   | O2—C9—H9A    | 109.5        |
| N1—N2—H2N    | 120.8 (15)   | C10—C9—H9A   | 109.5        |
| C6—C1—C2     | 118.71 (16)  | O2—C9—H9B    | 109.5        |
| C6—C1—C7     | 119.42 (15)  | C10—C9—H9B   | 109.5        |
| C2—C1—C7     | 121.85 (15)  | C10—C9—H11   | 119.9        |
| O1—C2—C3     | 118.50 (16)  | C10—C11—H11  | 119.9        |
| O1—C2—C1     | 121.20 (16)  | C15—C10—C11  | 120.7 (2)    |
| C3—C2—C1     | 120.30 (16)  | C15—C10—C9   | 119.43 (17)  |
| C4—C3—C2     | 119.79 (17)  | C12—C11—C10  | 120.1 (2)    |
| C4—C3—H3     | 120.1        | C12—C11—H11  | 119.9        |
| C2—C3—H3     | 120.1        | C10—C11—H11  | 119.9        |
| C3—C4—C5     | 120.55 (17)  | C13—C12—C11  | 120.7 (2)    |
| C3—C4—H4     | 119.7        | C13—C12—H12  | 119.7        |
| C5—C4—H4     | 119.7        | C11—C12—H12  | 119.7        |
| C6—C5—C4     | 119.83 (17)  | C12—C13—C14  | 119.5 (2)    |
| C6—C5—H5     | 120.1        | C12—C13—H13  | 120.2        |
| C4—C5—H5     | 120.1        | C14—C13—H13  | 120.2        |
| C5—C6—C1     | 120.81 (16)  | C15—C14—C13  | 120.0 (2)    |
| C5—C6—H6     | 119.6        | C15—C14—H14  | 120.0        |
| C1—C6—H6     | 119.6        | C13—C14—H14  | 120.0        |
| N1—C7—C1     | 118.70 (14)  | C10—C15—C14  | 120.53 (19)  |
| N1—C7—H7     | 120.7        | C10—C15—H15  | 119.7        |
| C1—C7—H7     | 120.7        | C14—C15—H15  | 119.7        |

| Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|
| C7—N1—N2—C8  | 179.79 (15)  | C9—O2—C8—O3  | −7.2 (2)     |
| C6—C1—C2—O1  | −179.68 (16) | C9—O2—C8—N2  | 173.15 (13)  |
| C7—C1—C2—O1  | 2.1 (2)      | N1—N2—C8—O3  | −1.1 (3)     |
| C6—C1—C2—C3  | −0.3 (2)     | N1—N2—C8—O2  | 178.58 (13)  |
| C7—C1—C2—C3  | −178.51 (16) | C8—O2—C9—C10 | −78.01 (18)  |
| O1—C2—C3—C4  | −179.13 (17) | O2—C9—C10—C15 | 119.80 (18) |
| C1—C2—C3—C4  | 1.4 (3)      | O2—C9—C10—C11 | −59.9 (2)   |
| C2—C3—C4—C5  | −1.5 (3)     | C15—C10—C11—C12 | 0.3 (3)   |
| C3—C4—C5—C6  | 0.3 (3)      | C9—C10—C11—C12 | −179.98 (17) |
| C4—C5—C6—C1  | 0.9 (3)      | C10—C11—C12—C13 | 0.1 (3)   |
| C2—C1—C6—C5  | −0.9 (3)     | C11—C12—C13—C14 | −0.3 (3)   |
| C7—C1—C6—C5  | 177.40 (16)  | C12—C13—C14—C15 | 0.2 (3)   |
| N2—N1—C7—C1  | 178.01 (14)  | C11—C10—C15—C14 | −0.4 (3)   |
| C6—C1—C7—N1  | −177.06 (15) | C9—C10—C15—C14 | 179.89 (17) |
| C2—C1—C7—N1  | 1.2 (2)      | C13—C14—C15—C10 | 0.2 (3)   |
Hydrogen-bond geometry (Å, °)

| D—H···A   | D—H  | H···A | D···A  | D—H···A |
|-----------|------|------|--------|---------|
| O1···H10···N1 | 0.90 (3) | 1.73 (3) | 2.546 (2) | 148 (2) |
| N2···H2N···O1i | 0.87 (2) | 1.97 (2) | 2.8225 (19) | 168 (2) |
| C7···H7···O3ii | 0.95 | 2.43 | 3.271 (2) | 147 |

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

Benzyl N’-[(E)-5-bromo-2-hydroxybenzylidene]hydrazinecarboxylate (II)

Crystal data

C15H13BrN2O3

Mr = 349.18

Monoclinic, P21/c

a = 27.904 (2) Å

b = 11.1207 (6) Å

c = 9.0648 (7) Å

β = 94.485 (2)°

V = 2804.3 (3) Å³

Z = 8

F(000) = 1408

Dx = 1.654 Mg m⁻³

Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 9936 reflections

θ = 2.3–27.5°

µ = 2.94 mm⁻¹

T = 90 K

0.24 × 0.22 × 0.05 mm

Data collection

Bruker D8 Venture dual source diffractometer

Radiation source: microsource

Detector resolution: 7.41 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan

(SADABS; Krause et al., 2015)

36145 measured reflections

6401 independent reflections

5004 reflections with I > 2σ(I)

Rint = 0.047

θmax = 27.5°, θmin = 2.0°

Refinement

Refinement on F²

Least-squares matrix: full

R[F² > 2σ(F²)] = 0.028

wR(F²) = 0.064

S = 1.03

6401 reflections

391 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(Fo²) + (0.024P)² + 0.4336P]

where P = (Fo² + 2Fc²)/3

(Δρ)max = 0.001

Δρmax = 0.36 e Å⁻³

Δρmin = −0.39 e Å⁻³

Special details

Experimental. The crystal was mounted using polyisobutene oil on the tip of a fine glass fibre, which was fastened in a copper mounting pin with electrical solder. It was placed directly into the cold gas stream of a liquid-nitrogen based cryostat (Parkin & Hope, 1998).

Diffraction data were collected with the crystal at 90K, which is standard practice in this laboratory for the majority of flash-cooled crystals.

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 progress was checked using *Platon* (Spek, 2020) and by an $R$-tensor (Parkin, 2000). The final model was further checked with the IUCr utility *checkCIF*.

**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\AA^2$)**

|     | $x$    | $y$    | $z$     | $U_{iso}/U_{eq}$ |
|-----|--------|--------|---------|------------------|
| Br1A| -0.15724 (2) | 0.00040 (2) | -0.27291 (2) | 0.01837 (6) |
| O1A | -0.03689 (5)  | 0.32791 (12)  | 0.13515 (17)  | 0.0155 (3)  |
| H1AO| -0.0212 (8)    | 0.285 (2)    | 0.195 (3)    | 0.023*      |
| O2A | 0.07623 (4)    | 0.09899 (12)  | 0.57652 (16)  | 0.0147 (3)  |
| O3A | 0.05320 (5)    | 0.27304 (12)  | 0.45841 (16)  | 0.0164 (3)  |
| N1A | 0.00001 (5)    | 0.13879 (14)  | 0.25999 (19)  | 0.0131 (4)  |
| N2A | 0.03016 (6)    | 0.08825 (15)  | 0.3687 (2)    | 0.0144 (4)  |
| H2AN| 0.0326 (8)     | 0.011 (2)     | 0.378 (3)     | 0.022*      |
| C1A | -0.05776 (6)   | 0.12521 (17)  | 0.0571 (2)    | 0.0123 (4)  |
| C2A | -0.06384 (6)   | 0.25104 (17)  | 0.0464 (2)    | 0.0128 (4)  |
| C3A | -0.09807 (7)   | 0.29968 (17)  | -0.0559 (2)   | 0.0151 (4)  |
| H3A | -0.102322      | 0.384378      | -0.061072     | 0.018*      |
| C4A | -0.12600 (7)   | 0.22594 (18)  | -0.1503 (2)   | 0.0161 (4)  |
| H4A | -0.149393      | 0.259472      | -0.220254     | 0.019*      |
| C5A | -0.11949 (6)   | 0.10144 (17)  | -0.1417 (2)   | 0.0135 (4)  |
| C6A | -0.08603 (7)   | 0.05145 (17)  | -0.0399 (2)   | 0.0133 (4)  |
| H6A | -0.082137      | -0.033375     | -0.035397     | 0.016*      |
| C7A | -0.02400 (7)   | 0.07044 (17)  | 0.1679 (2)    | 0.0135 (4)  |
| H7A | -0.019897      | -0.014331     | 0.171790      | 0.016*      |
| C8A | 0.05341 (7)    | 0.16443 (17)  | 0.4676 (2)    | 0.0134 (4)  |
| C9A | 0.11033 (7)    | 0.16320 (18)  | 0.6787 (2)    | 0.0159 (4)  |
| H9A1| 0.108034       | 0.132746      | 0.780527      | 0.019*      |
| H9A2| 0.102462       | 0.250018      | 0.677625      | 0.019*      |
| C10A| 0.16046 (7)    | 0.14533 (18)  | 0.6338 (2)    | 0.0152 (4)  |
| C11A| 0.18757 (7)    | 0.04758 (18)  | 0.6867 (3)    | 0.0199 (5)  |
| H11A| 0.175224       | -0.004677     | 0.757468      | 0.024*      |
| C12A| 0.23246 (7)    | 0.0256 (2)    | 0.6372 (3)    | 0.0244 (5)  |
| H12A| 0.250802       | -0.041479     | 0.673897      | 0.029*      |
| C13A| 0.25050 (7)    | 0.1014 (2)    | 0.5344 (3)    | 0.0236 (5)  |
| H13A| 0.280911       | 0.084987      | 0.498459      | 0.028*      |
| C14A| 0.22449 (7)    | 0.2012 (2)    | 0.4832 (3)    | 0.0234 (5)  |
| H14A| 0.237391       | 0.254413      | 0.414556      | 0.028*      |
| C15A| 0.17947 (7)    | 0.22296 (18)  | 0.5330 (2)    | 0.0184 (5)  |
| H15A| 0.161541       | 0.291233      | 0.498007      | 0.022*      |
| Br1B| 0.33187 (2)    | 0.24274 (2)   | -0.24668 (2)  | 0.01864 (6) |
| O1B | 0.46666 (5)    | 0.56485 (12)  | 0.12357 (18)  | 0.0175 (3)  |
| H1BO| 0.4824 (8)     | 0.526 (2)     | 0.183 (3)     | 0.026*      |
| O2B | 0.58093 (5)    | 0.33767 (12)  | 0.56327 (17)  | 0.0200 (3)  |
| O3B | 0.55787 (5)    | 0.51149 (12)  | 0.44468 (17)  | 0.0213 (3)  |
| N1B | 0.50017 (6)    | 0.37664 (15)  | 0.2571 (2)    | 0.0163 (4)  |
| N2B | 0.53006 (6)    | 0.32678 (15)  | 0.3664 (2)    | 0.0177 (4)  |
| H2BN| 0.5316 (8)     | 0.248 (2)     | 0.381 (3)     | 0.027*      |
|       | U_{11}    | U_{22}    | U_{33}    | U_{12}   | U_{13}   | U_{23}   |
|-------|-----------|-----------|-----------|----------|----------|----------|
| Br1A  | 0.02056 (10) | 0.01578 (11) | 0.01793 (13) | −0.00204 (8) | −0.00389 (8) | −0.00260 (9) |
| O1A   | 0.0167 (7) | 0.0096 (7) | 0.0194 (9) | −0.0001 (5) | −0.0033 (6) | 0.0007 (6) |
| O2A   | 0.0156 (7) | 0.0133 (7) | 0.0146 (9) | −0.0002 (5) | −0.0031 (6) | −0.0003 (6) |
| O3A   | 0.0195 (7) | 0.0107 (7) | 0.0193 (9) | −0.0015 (5) | 0.0025 (6) | −0.0002 (6) |
| N1A   | 0.0121 (8) | 0.0127 (8) | 0.0143 (11) | 0.0018 (6) | 0.0009 (7) | 0.0020 (7) |
| N2A   | 0.0173 (8) | 0.0093 (8) | 0.0159 (11) | 0.0011 (7) | −0.0025 (7) | 0.0005 (7) |
| C1A   | 0.0124 (9) | 0.0113 (9) | 0.0134 (12) | 0.0006 (7) | 0.0033 (8) | 0.0007 (8) |
| C2A   | 0.0120 (9) | 0.0116 (9) | 0.0153 (12) | −0.0028 (8) | 0.0051 (8) | −0.0014 (8) |
| C3A   | 0.0155 (10) | 0.0102 (9) | 0.0196 (13) | 0.0018 (8) | 0.0019 (9) | 0.0018 (8) |
| C4A   | 0.015 (1) | 0.0161 (10) | 0.0172 (13) | 0.0025 (8) | 0.0018 (8) | 0.0035 (9) |
| C5A   | 0.0113 (9) | 0.0159 (10) | 0.0132 (12) | −0.0019 (8) | −0.0002 (8) | −0.0021 (8) |
| C6A   | 0.0158 (10) | 0.0101 (9) | 0.0145 (12) | −0.0009 (8) | 0.0049 (8) | 0.0007 (8) |
| C7A   | 0.0145 (9) | 0.0100 (9) | 0.0164 (13) | 0.0005 (7) | 0.0042 (8) | 0.0005 (8) |
| C8A   | 0.0109 (9) | 0.0134 (10) | 0.0164 (12) | −0.0005 (7) | 0.0045 (8) | −0.0003 (8) |
| C9A   | 0.0176 (10) | 0.0171 (10) | 0.0125 (12) | −0.0022 (8) | −0.0018 (9) | −0.0042 (8) |
| C10A  | 0.0155 (10) | 0.0172 (10) | 0.0124 (12) | −0.0013 (8) | −0.0029 (8) | −0.0060 (8) |
| C11A  | 0.0235 (11) | 0.0167 (10) | 0.0185 (13) | −0.0030 (9) | −0.0049 (9) | 0.0007 (9) |
| C12A  | 0.0185 (11) | 0.0253 (12) | 0.0278 (15) | 0.0061 (9) | −0.0083 (9) | −0.0055 (10) |
Geometric parameters (Å, °)

| Bond          | Length (Å) | Bond          | Length (Å) |
|---------------|------------|---------------|------------|
| Br1A—C5A      | 1.8949 (19) | Br1B—C5B     | 1.896 (2)  |
| O1A—C2A       | 1.360 (2)  | O1B—C2B      | 1.360 (2)  |
| O1A—H1AO      | 0.82 (2)   | O1B—H1BO     | 0.80 (2)   |
| O2A—C8A       | 1.346 (2)  | O2B—C8B      | 1.349 (2)  |
| O2A—C9A       | 1.461 (2)  | O2B—C9B      | 1.464 (2)  |
| O3A—C8A       | 1.211 (2)  | O3B—C8B      | 1.203 (2)  |
| N1A—C7A       | 1.279 (2)  | N1B—C7B      | 1.282 (2)  |
| N1A—N2A       | 1.365 (2)  | N1B—N2B      | 1.362 (2)  |
| N2A—C8A       | 1.361 (3)  | N2B—C8B      | 1.369 (3)  |
| N2A—H2AN      | 0.87 (2)   | N2B—H2BN     | 0.88 (2)   |
| C1A—C6A       | 1.399 (3)  | C1B—C6B      | 1.397 (3)  |
| C1A—C2A       | 1.412 (3)  | C1B—C2B      | 1.407 (3)  |
| C1A—C7A       | 1.456 (3)  | C1B—C7B      | 1.460 (3)  |
| C2A—C3A       | 1.388 (3)  | C2B—C3B      | 1.388 (3)  |
| C3A—C4A       | 1.381 (3)  | C3B—C4B      | 1.378 (3)  |
| C3A—H3A       | 0.9500     | C3B—H3B      | 0.9500     |
| C4A—C5A       | 1.398 (3)  | C4B—C5B      | 1.394 (3)  |
| C4A—H4A       | 0.9500     | C4B—H4B      | 0.9500     |
| C5A—C6A       | 1.378 (3)  | C5B—C6B      | 1.381 (3)  |
| C6A—H6A       | 0.9500     | C6B—H6B      | 0.9500     |
| C7A—H7A       | 0.9500     | C7B—H7B      | 0.9500     |
C9A—C10A 1.500 (3)  C9B—C10B 1.499 (3)
C9A—H9A1 0.9900  C9B—H9B1 0.9900
C9A—H9A2 0.9900  C9B—H9B2 0.9900
C10A—C11A 1.388 (3)  C10B—C15B 1.388 (3)
C11A—C12A 1.385 (3)  C11B—C12B 1.389 (3)
C11A—H11A 0.9500  C11B—H11B 0.9500
C12A—C13A 1.380 (3)  C12B—C13B 1.377 (4)
C12A—H12A 0.9500  C12B—H12B 0.9500
C13A—C14A 1.386 (3)  C13B—C14B 1.384 (4)
C13A—H13A 0.9500  C13B—H13B 0.9500
C14A—C15A 1.389 (3)  C14B—C15B 1.385 (3)
C14A—H14A 0.9500  C14B—H14B 0.9500
C15A—H15A 0.9500  C15B—H15B 0.9500
C2A—O1A—H1AO 105.5 (16)  C2B—O1B—H1BO 107.9 (17)
C8A—O2A—C9A 116.62 (15)  C8B—O2B—C9B 116.93 (16)
C8A—N2A—N1A 119.20 (16)  C8B—N2B—N1B 119.03 (17)
C7A—N1A—N2A 119.04 (17)  C7B—N1B—N2B 117.14 (17)
C6A—C1A—C2A 118.64 (18)  C6B—C1B—C2B 118.97 (18)
C6A—C1A—C7A 119.38 (17)  C6B—C1B—C7B 119.38 (18)
C2A—C1A—C7A 121.97 (18)  C2B—C1B—C7B 121.59 (18)
O1A—C2A—C3A 121.5 (18)  O1B—C2B—C3B 122.20 (18)
O1A—C2A—C1A 118.04 (17)  O1B—C2B—C1B 122.20 (18)
C3A—C2A—C1A 120.30 (18)  C3B—C2B—C1B 120.18 (18)
C4A—C3A—C2A 120.53 (18)  C4B—C3B—C2B 120.41 (19)
C4A—C3A—H3A 119.7  C4B—C3B—H3B 119.8
C2A—C3A—H3A 119.7  C2B—C3B—H3B 119.8
C3A—C4A—C5A 119.28 (18)  C3B—C4B—C5B 119.61 (19)
C3A—C4A—H4A 120.4  C3B—C4B—H4B 120.2
C5A—C4A—H4A 120.4  C5B—C4B—H4B 120.2
C6A—C5A—C4A 121.02 (18)  C6B—C5B—C4B 120.81 (18)
C6A—C5A—Br1A 119.71 (14)  C6B—C5B—Br1B 120.43 (15)
C4A—C5A—Br1A 119.27 (15)  C4B—C5B—Br1B 118.72 (15)
C5A—C6A—C1A 120.22 (18)  C5B—C6B—C1B 120.00 (18)
C5A—C6A—H6A 119.9  C5B—C6B—H6B 120.0
C1A—C6A—H6A 119.9  C1B—C6B—H6B 120.0
N1A—C7A—C1A 118.65 (17)  N1B—C7B—C1B 118.39 (18)
N1A—C7A—H7A 120.7  N1B—C7B—H7B 120.8
C1A—C7A—H7A 120.7  C1B—C7B—H7B 120.8
O3A—C8A—O2A 126.12 (19)  O3B—C8B—O2B 126.55 (19)
O3A—C8A—N2A 125.18 (19)  O3B—C8B—N2B 125.7 (2)
O2A—C8A—N2A 108.70 (16)  O2B—C8B—N2B 107.76 (17)
O2A—C9A—C10A 109.76 (16)  O2B—C9B—C10B 109.90 (17)
O2A—C9A—H9A1 109.7  O2B—C9B—H9B1 109.7
C10A—C9A—H9A1 109.7  C10B—C9B—H9B1 109.7
| Bond/Angle/Distance | Value 1 | Value 2 | Value 3 |
|--------------------|---------|---------|---------|
| O2A—C9A—H9A2      | 109.7   |         |         |
| C10A—C9A—H9A2     | 109.7   |         |         |
| H9A1—C9A—H9A2     | 108.2   |         |         |
| C11A—C10A—C15A    | 119.15  | (19)    |         |
| C11A—C10A—C9A     | 120.30  | (19)    |         |
| C15A—C10A—C9A     | 120.48  | (18)    |         |
| C12A—C11A—C10A    | 120.6   | (2)     |         |
| C12A—C11A—H11A    | 119.7   |         |         |
| C10A—C11A—H11A    | 119.7   |         |         |
| C13A—C12A—C11A    | 119.9   | (2)     |         |
| C13A—C12A—H12A    | 120.1   |         |         |
| C11A—C12A—H12A    | 120.1   |         |         |
| C12A—C13A—C14A    | 120.4   | (2)     |         |
| C12A—C13A—H13A    | 119.8   |         |         |
| C14A—C13A—H13A    | 119.8   |         |         |
| C13A—C14A—C15A    | 119.6   | (2)     |         |
| C13A—C14A—H14A    | 120.2   |         |         |
| C15A—C14A—H14A    | 120.2   |         |         |
| C14A—C15A—C10A    | 120.4   | (2)     |         |
| C14A—C15A—H15A    | 119.8   |         |         |
| C10A—C15A—H15A    | 119.8   |         |         |
| C7A—N1A—N2A—C8A   | −177.37 | (18)    | −177.79 | (18) |
| C6A—C1A—C2A—O1A   | −178.68 | (17)    | −179.66 | (18) |
| C7A—C1A—C2A—O1A   | 3.0     | (3)     | 3.1     | (3)  |
| C6A—C1A—C2A—C3A   | 1.6     | (3)     | 0.8     | (3)  |
| C7A—C1A—C2A—C3A   | −176.79 | (18)    | −176.38 | (19) |
| O1A—C2A—C3A—C4A   | 179.10  | (18)    | −179.38 | (19) |
| C1A—C2A—C3A—C4A   | −1.2    | (3)     | 0.2     | (3)  |
| C2A—C3A—C4A—C5A   | 0.0     | (3)     | −0.7    | (3)  |
| C3A—C4A—C5A—C6A   | 0.6     | (3)     | 0.2     | (3)  |
| C3A—C4A—C5A—Br1A  | −179.20 | (15)    | 178.02  | (16) |
| C4A—C5A—C6A—C1A   | −0.2    | (3)     | 0.8     | (3)  |
| Br1A—C5A—C6A—C1A  | 179.65  | (14)    | −176.99 | (15) |
| C2A—C1A—C6A—C5A   | −0.9    | (3)     | −1.3    | (3)  |
| C7A—C1A—C6A—C5A   | 177.49  | (18)    | 175.98  | (19) |
| N2A—N1A—C7A—C1A   | 177.06  | (16)    | 178.03  | (17) |
| C6A—C1A—C7A—N1A   | −176.88 | (18)    | −177.23 | (19) |
| C2A—C1A—C7A—N1A   | 1.5     | (3)     | 0.0     | (3)  |
| C9A—O2A—C8A—O3A   | −11.2   | (3)     | −8.9    | (3)  |
| C9A—O2A—C8A—N2A   | 169.09  | (15)    | 171.53  | (16) |
| N1A—N2A—C8A—O3A   | −7.7    | (3)     | −4.0    | (3)  |
| N1A—N2A—C8A—O2A   | 171.98  | (15)    | 175.60  | (16) |
| C8A—O2A—C9A—C10A  | −98.12  | (19)    | −98.0   | (2)  |
| O2A—C9A—C10A—C11A | −88.3   | (2)     | 95.9    | (2)  |
| O2A—C9A—C10A—C15A | 88.5    | (2)     | −84.5   | (2)  |
| C15A—C10A—C11A—C12A | −1.6   | (3)   | −1.5    | (3)  |
| C9A—C10A—C11A—C12A | 175.19 | (19)   | 178.9   | (2)  |
**Hydrogen-bond geometry (Å, °)**

|        | D—H···A          | D—H  | H···A  | D···A  | D—H···A |
|--------|------------------|------|--------|--------|---------|
| O1A—H1AO···N1A | 0.82 (2) | 1.81 (2) | 2.565 (2) | 151 (2) |
| N2A—H2AN···O1A | 0.87 (2) | 2.04 (2) | 2.902 (2) | 171 (2) |
| C3A—H3A···O2A | 0.95   | 2.50   | 3.392 (2) | 156    |
| C6A—H6A···O3A | 0.95   | 2.38   | 3.296 (2) | 161    |
| O1B—H1BO···N1B | 0.80 (2) | 1.84 (2) | 2.558 (2) | 148 (2) |
| N2B—H2BN···O1B | 0.88 (2) | 2.04 (2) | 2.915 (2) | 171 (2) |
| C3B—H3B···O2B | 0.95   | 2.44   | 3.360 (2) | 164    |
| C6B—H6B···O3B | 0.95   | 2.39   | 3.297 (2) | 159    |

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