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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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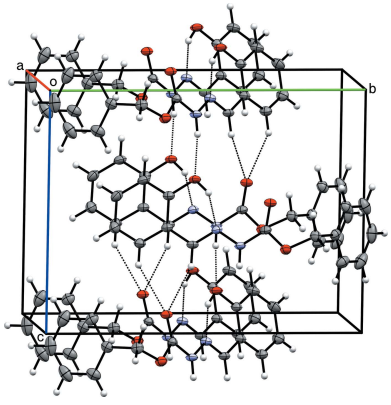
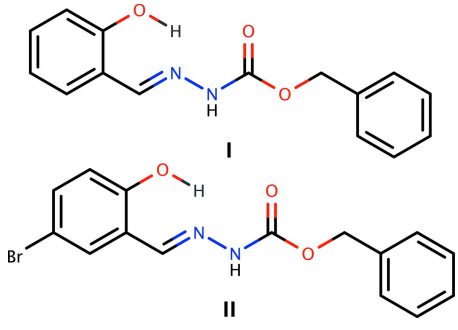
Benzyl *N*′-[(*E*)-2-hydroxybenzylidene]hydrazinecarboxylate, $C_{15}H_{14}N_2O_3$ (**I**) and benzyl *N*′-[(*E*)-5-bromo-2-hydroxybenzylidene]hydrazinecarboxylate (**II**), $C_{15}H_{13}BrN_2O_3$, have been synthesized by the reaction of either 2-hydroxybenzaldehyde or 5-bromo-2-hydroxybenzaldehyde 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

Hydroxybenzylidene 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 benzylidene hydrazines and benzaldehydehydrazone derivatives in general, this paper reports the crystal structures of the title compounds, $C_{15}H_{14}N_2O_3$ (**I**), and $C_{15}H_{13}BrN_2O_3$ (**II**).





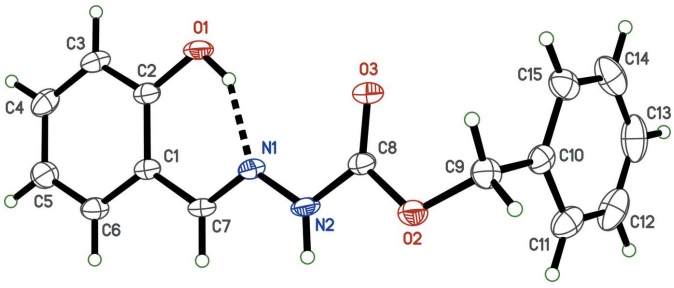


Figure 1
An ellipsoid plot (50% probability) of **I**, showing the intramolecular hydrogen bond (O1—H1*O*···N1) as a dashed line.

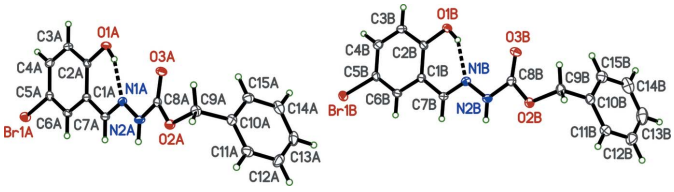


Figure 2
An ellipsoid plot of the asymmetric unit of **II**, showing the intramolecular hydrogen bonds (O1*A*—H1*AO*···N1*A* and O1*B*—H1*BO*···N1*B*) as dashed lines.

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*′-methylidenemethoxycarboxyl 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]carbohydrazide moieties are essentially planar [r.m.s. deviations 0.0429 Å (**I**), 0.0905 Å (**IIA**), 0.0692 (**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).

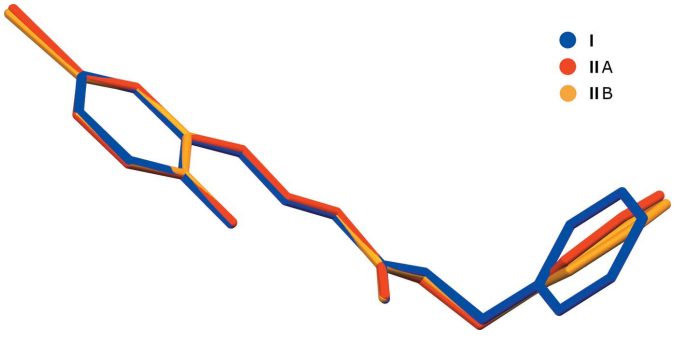


Figure 3
A least-squares fit overlay of **I**, **IIA**, and **IIB** showing the similarity of their conformations. That of **I** (blue) differs primarily in the orientation of the benzyl group (right). Diagram generated using *Mercury* (Macrae *et al.*, 2020).

Table 1
Hydrogen-bond geometry (Å, °) for **I**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···N1	0.90 (3)	1.73 (3)	2.546 (2)	148 (2)
N2—H2*N*···O1^{i}	0.87 (2)	1.97 (2)	2.8225 (19)	168 (2)
C7—H7···O3^{ii}	0.95	2.43	3.271 (2)	147

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

Table 2
Hydrogen-bond geometry (Å, °) for **II**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*AO*···N1*A*	0.82 (2)	1.81 (2)	2.565 (2)	151 (2)
N2*A*—H2*AN*···O1*A*^{i}	0.87 (2)	2.04 (2)	2.902 (2)	171 (2)
C3*A*—H3*A*···O2*A*^{ii}	0.95	2.50	3.392 (2)	156
C6*A*—H6*A*···O3*A*^{i}	0.95	2.38	3.296 (2)	161
O1*B*—H1*BO*···N1*B*	0.80 (2)	1.84 (2)	2.558 (2)	148 (2)
N2*B*—H2*BN*···O1*B*^{iii}	0.88 (2)	2.04 (2)	2.915 (2)	171 (2)
C3*B*—H3*B*···O2*B*^{iv}	0.95	2.44	3.360 (2)	164
C6*B*—H6*B*···O3*B*^{iii}	0.95	2.39	3.297 (2)	159

Symmetry codes: (i) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$.

Table 3
Selected torsion angles (°) for **I**, **IIA** and **IIB**.

I			
C8—O2—C9—C10	−78.01 (18)	O2—C9—C10—C11	−59.9 (2)
II			
C8*A*—O2*A*—C9*A*—C10*A*	−98.12 (19)	O2*A*—C9*A*—C10*A*—C11*A*	−88.3 (2)
C8*B*—O2*B*—C9*B*—C10*B*	−98.0 (2)	O2*B*—C9*B*—C10*B*—C11*B*	−84.5 (2)

The above torsion angles quantify the most substantive differences between the conformations of **I**, **IIA** and **IIB**.

3. Supramolecular features

In addition to the strong O—H···N *intra*molecular hydrogen bonds in **I** and **II**, the structures both feature strong N—H···O and weaker C—H···O *inter*molecular 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—H2*N*···O1^{i} (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^{ii} and C7—H7···O3^{ii} (Table 1) hydrogen bonds. In combination, these interactions produce layers that extend in the *ac* plane (Fig. 5), which in turn stack along [010].

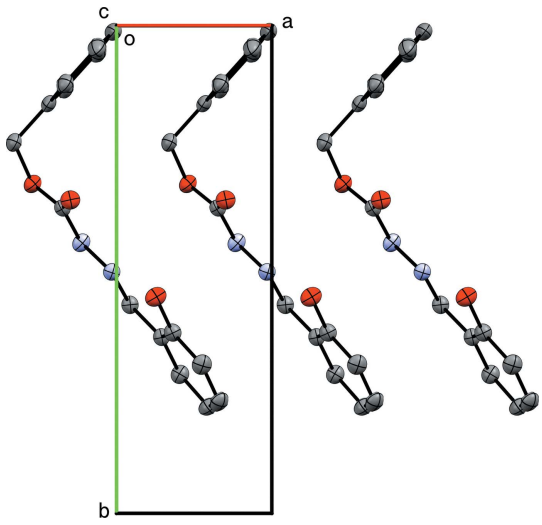


Figure 4
V-shaped molecules of **I** stack into columns parallel to the *a*-axis direction.

In **II**, the independent molecules (*A* and *B*) make hydrogen bonds to 2_1-screw-related copies of themselves *via* strong (N2—H2*N*···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 Br1*A* atoms and the centroid of the inversion-related C10*A*–C15*A* ring. There is no corresponding close contact for the **II*B*** molecule (Fig. 7).

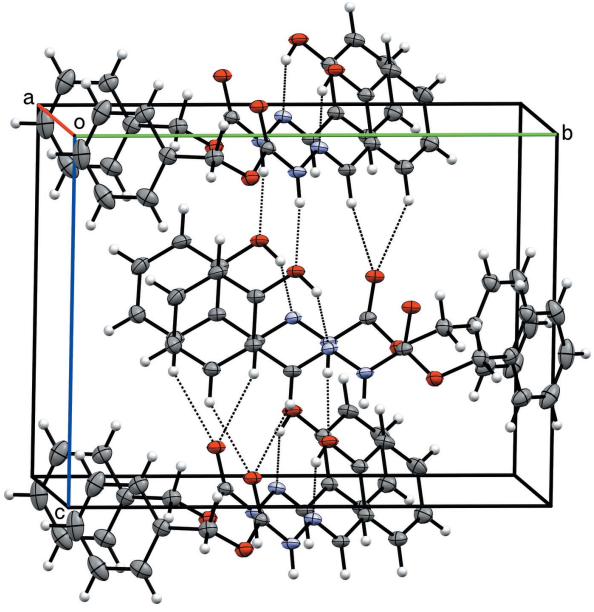


Figure 5
A partial packing plot of **I** showing hydrogen bonding as dashed lines. N—H···O and a pair of C—H···O (bifurcated) hydrogen bonds link *n*-glide-related molecules into layers parallel to *ac*.

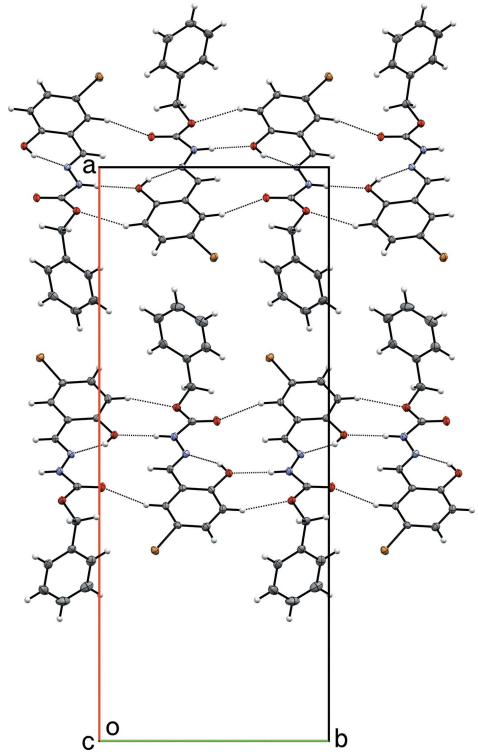


Figure 6
A partial packing plot of **II** showing N—H···O and C—H···O hydrogen-bonded ribbons along [010] of **II*A*** (upper) and **II*B*** (lower) molecules.

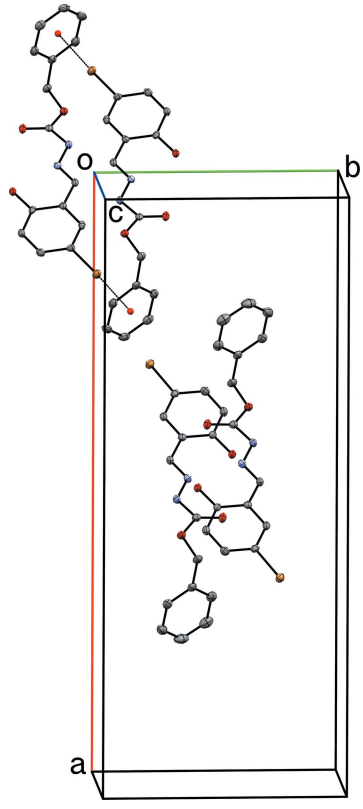


Figure 7
In spite of their similar conformations, inversion-related pairs of **II*A*** molecules (upper) are different from inversion-related pairs of **II*B*** molecules (lower). For **II*A*** there are close contacts between bromine and the inversion-related benzene ring, as shown by the dotted line. No such interaction exists for **II*B***.

Table 4
A sample of structures similar to **I** and **II** in the CSD.

R and *R*′ represent groups attached at the equivalent of C4 and *R*″ represents the group attached at the equivalent of O3.

CSD refcode	*R*	*R*′	*R*″	Reference
HODLOC	2-hydroxyphenyl	H	methyl	Sun & Cheng (2008)
QOFLAZ	2-hydroxyphenyl	H	ethyl	Gao (2008)
KODVUV	4-hydroxyphenyl	H	methyl	Cheng (2008*a*)
XOGVEV	phenyl	methyl	methyl	Cheng (2008*b*)
XOGXEX	4-hydroxyphenyl	H	ethyl	Cheng (2008*c*)
XOGXIB	3-methoxy-4-hydroxyphenyl	H	methyl	Cheng (2008*d*)
AZOTAL	3-hydroxyphenyl	H	methyl	Li *et al.* (2011)
AWUJAE	3-hydroxyphenyl	H	ethyl	Hu *et al.* (2011)
WEFRUX	4-diethylamino-2-hydroxyphenyl	H	methyl	Lv *et al.* (2017)

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**/**II** 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), QAVFAY (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-1*H*-inden-1-ylidene) group is attached to the hydrazine. QAVFAY 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.

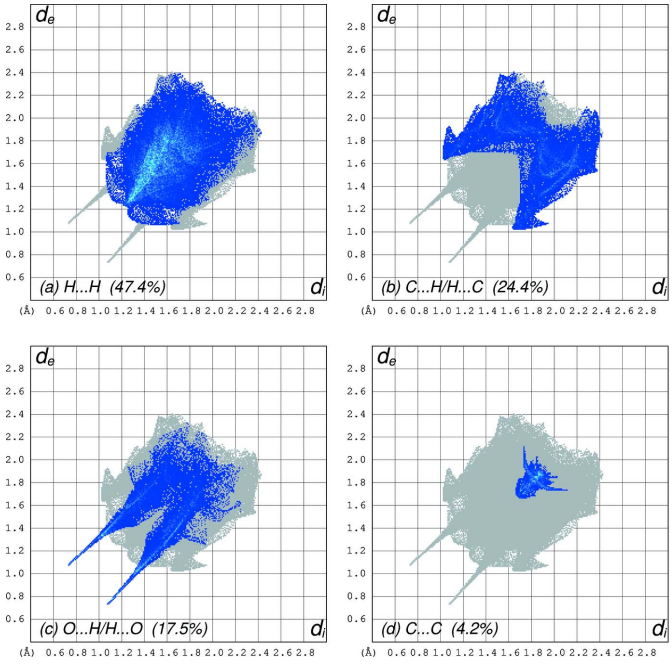


Figure 8
Fingerprint plots obtained from a Hirshfeld surface analysis for **I** using *CrystalExplorer*, separated into (*a*) H···H (47.4% coverage), (*b*) C···H/H···C (24.4%), (*c*) O···H/H···O (17.5%), (*d*) C···C (4.2%). All other contacts are negligible.

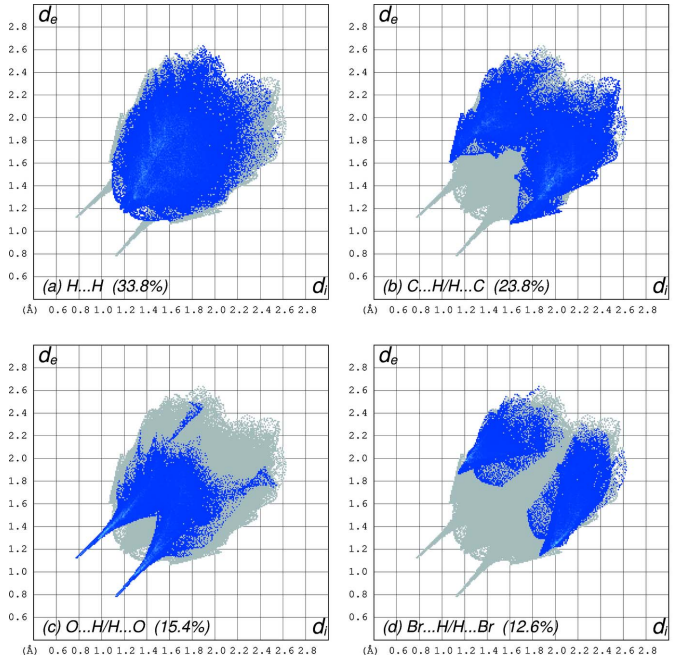


Figure 9
Fingerprint plots obtained from a Hirshfeld surface analysis for **II** using *CrystalExplorer*, separated into (*a*) H···H (33.8% coverage), (*b*) C···H/H···C (23.8%), (*c*) O···H/H···O (15.4%), (*d*) Br···H/H···Br (12.6%). All other contacts are negligible.

Table 5
Experimental details.

	I	II
Crystal data		
Chemical formula	$C_{15}H_{14}N_2O_3$	$C_{15}H_{13}BrN_2O_3$
M_r	270.28	349.18
Crystal system, space group	Monoclinic, *Pn*	Monoclinic, $P2_1/c$
Temperature (K)	90	90
a, *b*, *c* (Å)	4.5017 (12), 14.047 (4), 10.567 (3)	27.904 (2), 11.1207 (6), 9.0648 (7)
β (°)	96.300 (15)	94.485 (2)
V (Å^3)	664.2 (3)	2804.3 (3)
Z	2	8
Radiation type	Cu $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.79	2.94
Crystal size (mm)	0.41 × 0.23 × 0.02	0.24 × 0.22 × 0.05
Data collection		
Diffractometer	Bruker D8 Venture dual source	Bruker D8 Venture dual source
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.589, 0.958	0.598, 0.862
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7271, 2511, 2425	36145, 6401, 5004
R_{int}	0.028	0.047
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625	0.650
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.063, 1.04	0.028, 0.064, 1.03
No. of reflections	2511	6401
No. of parameters	187	391
No. of restraints	2	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.13, −0.13	0.36, −0.39
Absolute structure	Flack *x* determined using 1054 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)	–
Absolute structure parameter	0.04 (10)	–

Computer programs: *APEX3* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2019/2* (Sheldrick, 2015*b*), *XP* in *SHELXTL* (Sheldrick, 2008), *CIFFIX* (Parkin, 2013) and *publCIF* (Westrip, 2010).

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**).

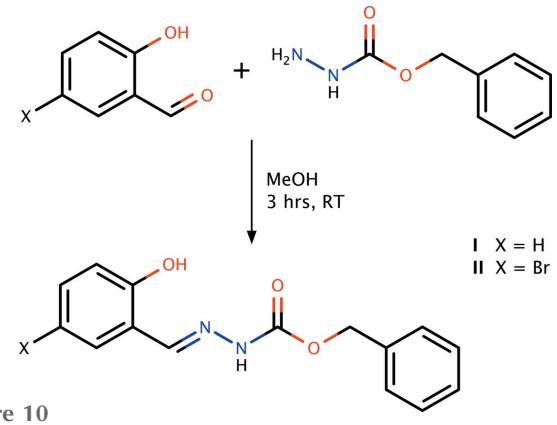


Figure 10
Reaction scheme for the synthesis of **I** and **II**.

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 from a shallow liquid-nitrogen dewar using tongs first developed for protein cryocrystallography (Parkin & Hope, 1998), while the crystal of **II** was mounted directly into a cold-nitrogen stream. Data for both samples (Cu $K\alpha$ for **I** and Mo $K\alpha$ 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 Csp^2H and 0.99 Å for R_2CH_2. 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.

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supporting information

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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 Parkin

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: *CIFFIX* (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) Å
b = 14.047 (4) Å
c = 10.567 (3) Å
β = 96.300 (15)°
V = 664.2 (3) Å^3
Z = 2
F(000) = 284
D_x = 1.351 Mg m^{-3}
Cu *Kα* radiation, *λ* = 1.54184 Å
Cell parameters from 6841 reflections
θ = 3.1–74.4°
μ = 0.79 mm^{-1}
T = 90 K
Plate, colourless
0.41 × 0.23 × 0.02 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)
T_{min} = 0.589, T_{max} = 0.958
7271 measured reflections
2511 independent reflections
2425 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 74.6°, θ_{min} = 3.2°
h = −5→5
k = −17→16
l = −13→12

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

$w = 1/[\sigma^2(F_o^2) + (0.0283P)^2 + 0.0531P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.13$ e Å^{-3}
$\Delta\rho_{min} = -0.13$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{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	0.863234	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*

C13	0.4787 (5)	0.98720 (14)	0.5483 (3)	0.0418 (6)
H13	0.619778	1.037661	0.558367	0.050*
C14	0.3742 (5)	0.95472 (15)	0.4275 (2)	0.0390 (5)
H14	0.444340	0.982844	0.354578	0.047*
C15	0.1674 (4)	0.88122 (13)	0.41314 (18)	0.0285 (4)
H15	0.096956	0.859121	0.330295	0.034*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
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, º)

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)

C4—C5	1.387 (3)	C14—H14	0.9500
C4—H4	0.9500	C15—H15	0.9500
C5—C6	1.381 (3)		

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)	H9A—C9—H9B	108.0
O1—C2—C3	118.50 (16)	C15—C10—C11	119.09 (18)
O1—C2—C1	121.20 (16)	C15—C10—C9	121.48 (16)
C3—C2—C1	120.30 (16)	C11—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

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, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···N1	0.90 (3)	1.73 (3)	2.546 (2)	148 (2)
N2—H2*N*···O1^{i}	0.87 (2)	1.97 (2)	2.8225 (19)	168 (2)
C7—H7···O3^{ii}	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

$C_{15}H_{13}BrN_2O_3$
M_r = 349.18
Monoclinic, $P2_1/c$
a = 27.904 (2) Å
b = 11.1207 (6) Å
c = 9.0648 (7) Å
β = 94.485 (2)°
V = 2804.3 (3) Å^3
Z = 8
$F(000)$ = 1408
D_x = 1.654 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9936 reflections
θ = 2.3–27.5°
μ = 2.94 mm^{-1}
T = 90 K
Plate, colourless
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)
T_{min} = 0.598, T_{max} = 0.862
36145 measured reflections
6401 independent reflections
5004 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 27.5°, θ_{min} = 2.0°
h = −36→36
k = −13→14
l = −11→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 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
$w = 1/[\sigma^2(F_o^2) + (0.024P)^2 + 0.4336P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −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 (Å²)

	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*

C1B	0.44047 (7)	0.36259 (17)	0.0590 (2)	0.0144 (4)
C2B	0.43755 (7)	0.48817 (17)	0.0413 (2)	0.0155 (4)
C3B	0.40395 (7)	0.53794 (18)	−0.0621 (2)	0.0187 (5)
H3B	0.402207	0.622759	−0.073766	0.022*
C4B	0.37308 (7)	0.46506 (18)	−0.1480 (2)	0.0186 (5)
H4B	0.349893	0.499454	−0.217909	0.022*
C5B	0.37609 (7)	0.34063 (18)	−0.1317 (2)	0.0157 (4)
C6B	0.40953 (7)	0.28942 (18)	−0.0301 (2)	0.0153 (4)
H6B	0.411493	0.204431	−0.020934	0.018*
C7B	0.47346 (7)	0.30758 (17)	0.1725 (2)	0.0159 (5)
H7B	0.475081	0.222686	0.183473	0.019*
C8B	0.55672 (7)	0.40391 (18)	0.4573 (2)	0.0164 (4)
C9B	0.61708 (7)	0.40024 (19)	0.6607 (3)	0.0199 (5)
H9B1	0.616291	0.369612	0.762983	0.024*
H9B2	0.609811	0.487367	0.661257	0.024*
C10B	0.66606 (7)	0.38057 (18)	0.6078 (2)	0.0177 (5)
C11B	0.69188 (7)	0.27764 (19)	0.6499 (3)	0.0243 (5)
H11B	0.678700	0.220613	0.713444	0.029*
C12B	0.73692 (8)	0.2581 (2)	0.5992 (3)	0.0314 (6)
H12B	0.754349	0.187171	0.627110	0.038*
C13B	0.75634 (8)	0.3413 (2)	0.5085 (3)	0.0339 (6)
H13B	0.787039	0.327312	0.473303	0.041*
C14B	0.73134 (8)	0.4452 (2)	0.4685 (3)	0.0302 (6)
H14B	0.745077	0.503149	0.407352	0.036*
C15B	0.68621 (7)	0.4646 (2)	0.5178 (2)	0.0216 (5)
H15B	0.668973	0.535692	0.489816	0.026*

Atomic displacement parameters (Å²)

	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)

C13A	0.0137 (10)	0.0311 (13)	0.0257 (15)	−0.0020 (9)	0.0000 (9)	−0.0118 (10)
C14A	0.0211 (11)	0.0254 (12)	0.0237 (14)	−0.0073 (9)	0.0026 (10)	−0.0037 (10)
C15A	0.0214 (10)	0.0154 (10)	0.0176 (13)	−0.0007 (8)	−0.0029 (9)	−0.0026 (9)
Br1B	0.0178 (1)	0.01828 (11)	0.01947 (13)	−0.00271 (8)	−0.00094 (8)	−0.00299 (9)
O1B	0.0174 (7)	0.0116 (7)	0.0227 (10)	−0.0013 (6)	−0.0037 (6)	−0.0002 (6)
O2B	0.0174 (7)	0.0154 (7)	0.0259 (10)	−0.0012 (6)	−0.0070 (6)	−0.0003 (6)
O3B	0.0230 (7)	0.0118 (7)	0.0284 (10)	−0.0024 (6)	−0.0017 (7)	−0.0006 (6)
N1B	0.0153 (9)	0.0139 (9)	0.0193 (12)	0.0015 (6)	−0.0009 (8)	0.0029 (7)
N2B	0.0183 (9)	0.0115 (8)	0.0221 (12)	0.0006 (7)	−0.0058 (8)	0.0015 (8)
C1B	0.0126 (9)	0.0146 (10)	0.0162 (12)	0.0002 (8)	0.0031 (8)	0.0001 (8)
C2B	0.0137 (9)	0.0133 (10)	0.0200 (13)	−0.0021 (8)	0.0034 (8)	−0.0029 (9)
C3B	0.0197 (10)	0.0124 (10)	0.0243 (14)	0.0013 (8)	0.0028 (9)	0.0013 (9)
C4B	0.0189 (10)	0.0177 (10)	0.0189 (13)	0.0015 (8)	−0.0004 (9)	0.0017 (9)
C5B	0.0125 (9)	0.0172 (10)	0.0176 (13)	−0.0023 (8)	0.0037 (8)	−0.0034 (9)
C6B	0.0167 (10)	0.0111 (10)	0.0186 (13)	−0.0006 (8)	0.0039 (9)	−0.0004 (8)
C7B	0.0152 (10)	0.0102 (9)	0.0222 (13)	0.0003 (8)	0.0009 (9)	0.0003 (8)
C8B	0.0132 (10)	0.0165 (10)	0.0197 (13)	0.0002 (8)	0.0024 (8)	0.0011 (9)
C9B	0.018 (1)	0.0211 (11)	0.0195 (13)	−0.0016 (8)	−0.0056 (9)	−0.0039 (9)
C10B	0.0174 (10)	0.0190 (11)	0.0160 (13)	−0.0011 (8)	−0.0033 (9)	−0.0051 (9)
C11B	0.0229 (11)	0.0182 (11)	0.0307 (15)	−0.0014 (9)	−0.0041 (10)	−0.002 (1)
C12B	0.0240 (12)	0.0267 (13)	0.0419 (17)	0.0059 (10)	−0.0069 (11)	−0.0121 (12)
C13B	0.0198 (12)	0.0505 (16)	0.0320 (17)	−0.0009 (11)	0.0052 (11)	−0.0142 (13)
C14B	0.0285 (12)	0.0410 (15)	0.0213 (15)	−0.0098 (11)	0.0042 (10)	−0.0048 (11)
C15B	0.0255 (11)	0.0225 (11)	0.0160 (13)	−0.0015 (9)	−0.0032 (9)	−0.0018 (9)

Geometric parameters (Å, º)

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)
C10A—C15A	1.392 (3)	C10B—C11B	1.390 (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)
C7A—N1A—N2A	119.20 (16)	C7B—N1B—N2B	119.03 (17)
C8A—N2A—N1A	117.02 (16)	N1B—N2B—C8B	117.14 (17)
C8A—N2A—H2AN	121.5 (15)	N1B—N2B—H2BN	122.0 (15)
N1A—N2A—H2AN	121.3 (15)	C8B—N2B—H2BN	120.8 (15)
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	118.04 (17)	O1B—C2B—C3B	117.61 (18)
O1A—C2A—C1A	121.65 (18)	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

O2A—C9A—H9A2	109.7	O2B—C9B—H9B2	109.7
C10A—C9A—H9A2	109.7	C10B—C9B—H9B2	109.7
H9A1—C9A—H9A2	108.2	H9B1—C9B—H9B2	108.2
C11A—C10A—C15A	119.15 (19)	C15B—C10B—C11B	119.4 (2)
C11A—C10A—C9A	120.30 (19)	C15B—C10B—C9B	120.74 (19)
C15A—C10A—C9A	120.48 (18)	C11B—C10B—C9B	119.9 (2)
C12A—C11A—C10A	120.6 (2)	C12B—C11B—C10B	120.1 (2)
C12A—C11A—H11A	119.7	C12B—C11B—H11B	119.9
C10A—C11A—H11A	119.7	C10B—C11B—H11B	119.9
C13A—C12A—C11A	119.9 (2)	C13B—C12B—C11B	120.0 (2)
C13A—C12A—H12A	120.1	C13B—C12B—H12B	120.0
C11A—C12A—H12A	120.1	C11B—C12B—H12B	120.0
C12A—C13A—C14A	120.4 (2)	C12B—C13B—C14B	120.3 (2)
C12A—C13A—H13A	119.8	C12B—C13B—H13B	119.9
C14A—C13A—H13A	119.8	C14B—C13B—H13B	119.9
C13A—C14A—C15A	119.6 (2)	C13B—C14B—C15B	119.8 (2)
C13A—C14A—H14A	120.2	C13B—C14B—H14B	120.1
C15A—C14A—H14A	120.2	C15B—C14B—H14B	120.1
C14A—C15A—C10A	120.4 (2)	C14B—C15B—C10B	120.4 (2)
C14A—C15A—H15A	119.8	C14B—C15B—H15B	119.8
C10A—C15A—H15A	119.8	C10B—C15B—H15B	119.8

C7A—N1A—N2A—C8A	−177.37 (18)	C7B—N1B—N2B—C8B	−177.79 (18)
C6A—C1A—C2A—O1A	−178.68 (17)	C6B—C1B—C2B—O1B	−179.66 (18)
C7A—C1A—C2A—O1A	3.0 (3)	C7B—C1B—C2B—O1B	3.1 (3)
C6A—C1A—C2A—C3A	1.6 (3)	C6B—C1B—C2B—C3B	0.8 (3)
C7A—C1A—C2A—C3A	−176.79 (18)	C7B—C1B—C2B—C3B	−176.38 (19)
O1A—C2A—C3A—C4A	179.10 (18)	O1B—C2B—C3B—C4B	−179.38 (19)
C1A—C2A—C3A—C4A	−1.2 (3)	C1B—C2B—C3B—C4B	0.2 (3)
C2A—C3A—C4A—C5A	0.0 (3)	C2B—C3B—C4B—C5B	−0.7 (3)
C3A—C4A—C5A—C6A	0.6 (3)	C3B—C4B—C5B—C6B	0.2 (3)
C3A—C4A—C5A—Br1A	−179.20 (15)	C3B—C4B—C5B—Br1B	178.02 (16)
C4A—C5A—C6A—C1A	−0.2 (3)	C4B—C5B—C6B—C1B	0.8 (3)
Br1A—C5A—C6A—C1A	179.65 (14)	Br1B—C5B—C6B—C1B	−176.99 (15)
C2A—C1A—C6A—C5A	−0.9 (3)	C2B—C1B—C6B—C5B	−1.3 (3)
C7A—C1A—C6A—C5A	177.49 (18)	C7B—C1B—C6B—C5B	175.98 (19)
N2A—N1A—C7A—C1A	177.06 (16)	N2B—N1B—C7B—C1B	178.03 (17)
C6A—C1A—C7A—N1A	−176.88 (18)	C6B—C1B—C7B—N1B	−177.23 (19)
C2A—C1A—C7A—N1A	1.5 (3)	C2B—C1B—C7B—N1B	0.0 (3)
C9A—O2A—C8A—O3A	−11.2 (3)	C9B—O2B—C8B—O3B	−8.9 (3)
C9A—O2A—C8A—N2A	169.09 (15)	C9B—O2B—C8B—N2B	171.53 (16)
N1A—N2A—C8A—O3A	−7.7 (3)	N1B—N2B—C8B—O3B	−4.0 (3)
N1A—N2A—C8A—O2A	171.98 (15)	N1B—N2B—C8B—O2B	175.60 (16)
C8A—O2A—C9A—C10A	−98.12 (19)	C8B—O2B—C9B—C10B	−98.0 (2)
O2A—C9A—C10A—C11A	−88.3 (2)	O2B—C9B—C10B—C15B	95.9 (2)
O2A—C9A—C10A—C15A	88.5 (2)	O2B—C9B—C10B—C11B	−84.5 (2)
C15A—C10A—C11A—C12A	−1.6 (3)	C15B—C10B—C11B—C12B	−1.5 (3)
C9A—C10A—C11A—C12A	175.19 (19)	C9B—C10B—C11B—C12B	178.9 (2)

C10A—C11A—C12A—C13A	0.0 (3)	C10B—C11B—C12B—C13B	0.8 (4)
C11A—C12A—C13A—C14A	1.7 (3)	C11B—C12B—C13B—C14B	0.6 (4)
C12A—C13A—C14A—C15A	−1.8 (3)	C12B—C13B—C14B—C15B	−1.1 (4)
C13A—C14A—C15A—C10A	0.1 (3)	C13B—C14B—C15B—C10B	0.4 (3)
C11A—C10A—C15A—C14A	1.6 (3)	C11B—C10B—C15B—C14B	1.0 (3)
C9A—C10A—C15A—C14A	−175.24 (19)	C9B—C10B—C15B—C14B	−179.5 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*AO*···N1*A*	0.82 (2)	1.81 (2)	2.565 (2)	151 (2)
N2*A*—H2*AN*···O1*A*^{i}	0.87 (2)	2.04 (2)	2.902 (2)	171 (2)
C3*A*—H3*A*···O2*A*^{ii}	0.95	2.50	3.392 (2)	156
C6*A*—H6*A*···O3*A*^{i}	0.95	2.38	3.296 (2)	161
O1*B*—H1*BO*···N1*B*	0.80 (2)	1.84 (2)	2.558 (2)	148 (2)
N2*B*—H2*BN*···O1*B*^{iii}	0.88 (2)	2.04 (2)	2.915 (2)	171 (2)
C3*B*—H3*B*···O2*B*^{iv}	0.95	2.44	3.360 (2)	164
C6*B*—H6*B*···O3*B*^{iii}	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.