4-(1H-2,3-Dihydronaphtho[1,8-de][1,3,2]-diazaborinin-2-yl)-1-ethylpyridin-1-ium iodide monohydrate

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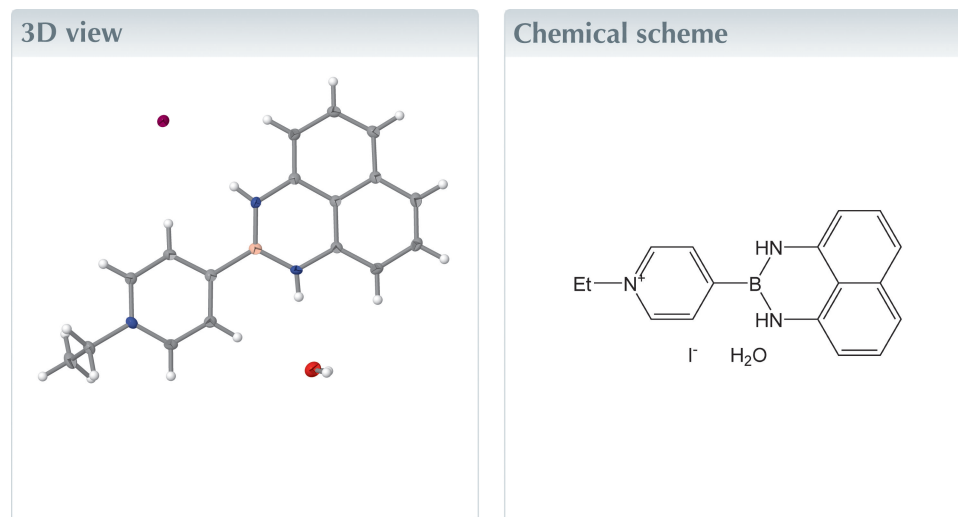
The cation of the title hydrated salt, $C_{17}H_{17}BN_3^+ \cdot I^- \cdot H_2O$, is a diazaborinane featuring substitution at the 1, 2, and 3 positions in the nitrogen–boron six-membered heterocycle. The cation is approximately planar with a dihedral angle between the pyridyl ring and the diazaborinane ring system of 5.40 (5)°. In the crystal, the cations stack along [100] in an alternating head-to-tail manner, while the iodide ion and water molecule form one-dimensional hydrogen-bonded chains beside the cation stack. The cation stacks and I^-–water chains are crosslinked by N—H···I and N—H···O hydrogen bonds.

**3D view**

Chemical scheme

Structure description

The title compound, $C_{17}H_{17}BN_3^+ \cdot I^- \cdot H_2O$, is a hydrated diazaborinane derivative featuring substitution at the 1, 2, and 3 positions in the nitrogen–boron six-membered heterocycle (Fig. 1). Diazaborinanes are found to stabilize organic radicals (LaPorte *et al.*, 2023). Recently we reported of the anhydrous polymorph of the title compound (Hashimoto & Okuno, 2024).

In the hydrated polymorph, the organic unit is almost planar with a dihedral angle between the N1/C1–C5 pyridyl ring and N2/N3/C6–C15/B1 ring system of 5.40 (5)°. The structure is similar to those of the anhydrous polymorph and other diazaborinanes (Akerman *et al.*, 2011; Hashimoto & Okuno, 2024; Slabber *et al.*, 2011).

In the crystal, the organic cations stack in an alternating head-to-tail manner along the *a* axis as shown in Fig. 2, where the B1···B1^{iv} and B1···B1^{iii} distances are 3.395 (6) and 3.436 (6) Å, respectively [symmetry codes: (iv) −x + 1, −y + 2, −z + 1; (iii) −x + 2, −y + 2, −z + 1]. The iodide ion accepts three C—H···I contacts from adjacent cations and two O—H···I links from the water molecules. The iodide anions and water molecules form a one-dimensional hydrogen-bonded chain beside the alternating cation stack and the stacks and hydrogen-bond chains are crosslinked by N—H···O and N—H···I links.
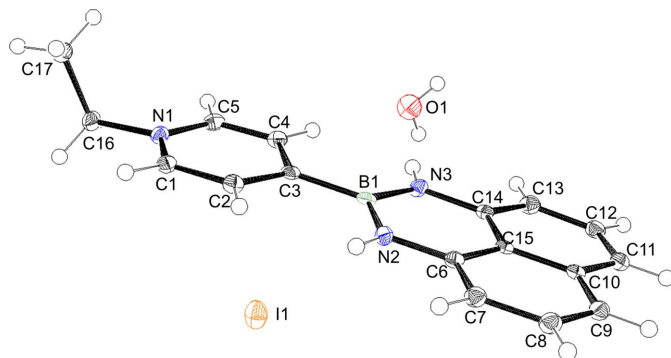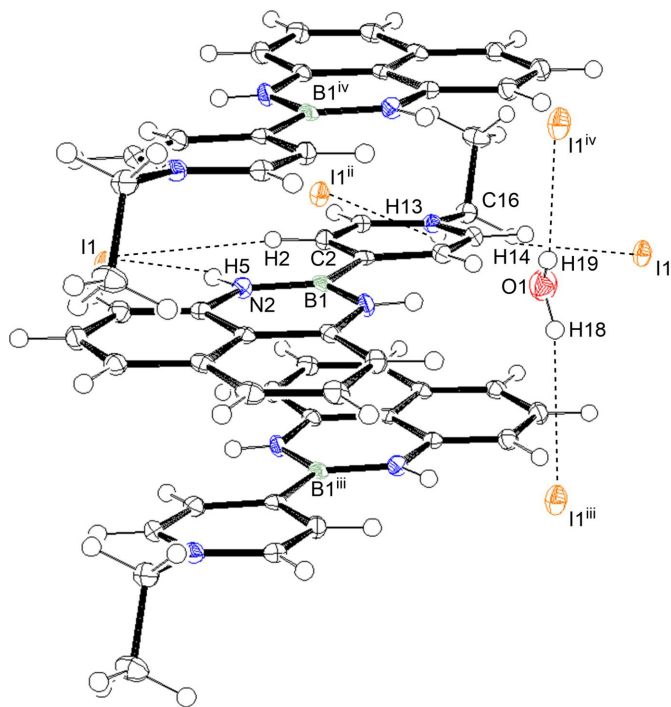
Figure 1
The asymmetric unit of the title compound with displacement ellipsoids drawn at the 50% probability level.

The geometry of the hydrogen bonds is summarized in Table 1. The contamination of water in acetonitrile is thought to give the hydrated polymorph. Selective formation of the hydrated polymorph has not yet been achieved.

Synthesis and crystallization

Single crystals in the form of pale-yellow blocks of sufficient quality were obtained by recrystallization of 1-ethyl-4-(1H-naphtho[1,8-de] [1,3,2]diazaborinin-2(3H)-yl)pyridin-1-ium iodide (Hashimoto & Okuno, 2024) from acetonitrile solution, which was apparently contaminated with water.

Figure 2
Intermolecular interactions of the title compound. [symmetry codes: (i) x, $y - 1$, z; (ii) x, $-y + \frac{3}{2}$, $z - \frac{1}{2}$; (iii) $-x + 2$, $-y + 2$, $-z + 1$; (iv) $-x + 1$, $-y + 2$, $-z + 1$].

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{17}BN_3{}^+ \cdot I^- \cdot H_2O$
M_r	419.06
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	93
a, b, c (Å)	6.746 (2), 23.041 (7), 10.939 (3)
β (°)	97.616 (5)
V (Å^3)	1685.4 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.91
Crystal size (mm)	$0.18 \times 0.18 \times 0.10$
Data collection	
Diffractometer	Saturn724+
Absorption correction	Numerical (NUMABS; Rigaku, 1999)
T_{min}, T_{max}	0.879, 0.900
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13511, 3846, 3463
R_{int}	0.030
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.056, 1.04
No. of reflections	3846
No. of parameters	224
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.92, −0.40

Computer programs: CrystalClear (Rigaku, 2008), SHELXT2014/4 (Sheldrick, 2015a), SHELXL2014/7 (Sheldrick, 2015b) and OLEX2 (Dolomanov et al., 2009).

Refinement

Experimental details and crystal data are summarized in Table 2.

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full crystallographic data

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Crystal data

$C_{17}H_{17}BN_3{}^+ \cdot I^- \cdot H_2O$	$F(000) = 832$
$M_r = 419.06$	$D_x = 1.652$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
$a = 6.746$ (2) Å	Cell parameters from 6255 reflections
$b = 23.041$ (7) Å	$\theta = 1.8–30.9°$
$c = 10.939$ (3) Å	$\mu = 1.91$ mm^{-1}
$\beta = 97.616$ (5)°	$T = 93$ K
$V = 1685.4$ (9) Å^3	Block, pale yellow
$Z = 4$	$0.18 \times 0.18 \times 0.10$ mm

Data collection

Saturn724+ diffractometer	3846 independent reflections
Detector resolution: 28.445 pixels mm^{-1}	3463 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.030$
Absorption correction: numerical (*NUMABS*; Rigaku, 1999)	$\theta_{max} = 27.5°$, $\theta_{min} = 3.2°$
$T_{min} = 0.879$, $T_{max} = 0.900$	$h = -6\rightarrow8$
13511 measured reflections	$k = -22\rightarrow29$
	$l = -14\rightarrow14$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.026$	
$wR(F^2) = 0.056$	$w = 1/[\sigma^2(F_o^2) + (0.0201P)^2 + 1.9341P]$
$S = 1.04$	where $P = (F_o^2 + 2F_c^2)/3$
3846 reflections	$(\Delta/\sigma)_{max} = 0.002$
224 parameters	$\Delta\rho_{max} = 0.92$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.40$ e Å^{-3}

Special details

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

Refinement. The positions of the N-bound and O-bound H atoms were obtained from difference Fourier maps and were refined isotropically. The C-bound H atoms were placed at ideal positions and were refined as riding on their parent C atoms. U_{iso}(H) values of the H atoms were set at $1.2U_{eq}$(carrier) or $1.5U_{eq}$(methyl carrier).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.89530 (2)	0.83028 (2)	0.76189 (2)	0.01877 (6)
O1	0.6094 (4)	1.10388 (9)	0.20283 (18)	0.0265 (4)
N1	0.7490 (3)	0.86217 (8)	0.19278 (17)	0.0134 (4)
N2	0.7739 (3)	0.97508 (8)	0.61095 (18)	0.0129 (4)
N3	0.7269 (3)	1.05026 (8)	0.45657 (18)	0.0134 (4)
C9	0.7933 (3)	1.09991 (10)	0.8927 (2)	0.0151 (5)
H8	0.8004	1.1279	0.9569	0.018*
C3	0.7379 (3)	0.94374 (10)	0.3791 (2)	0.0126 (4)
C14	0.7397 (3)	1.09351 (10)	0.5472 (2)	0.0125 (4)
C12	0.7480 (3)	1.19358 (10)	0.6120 (2)	0.0164 (5)
H10	0.7463	1.2336	0.5911	0.020*
C5	0.7167 (3)	0.91855 (10)	0.1633 (2)	0.0150 (5)
H4	0.6979	0.9300	0.0791	0.018*
C7	0.7968 (3)	0.99955 (10)	0.8283 (2)	0.0152 (5)
H6	0.8050	0.9596	0.8500	0.018*
C11	0.7647 (3)	1.17771 (10)	0.7336 (2)	0.0165 (5)
H9	0.7718	1.2068	0.7956	0.020*
C1	0.7676 (3)	0.84457 (10)	0.3109 (2)	0.0139 (4)
H1	0.7844	0.8045	0.3298	0.017*
C13	0.7334 (3)	1.15171 (10)	0.5175 (2)	0.0159 (5)
H11	0.7192	1.1635	0.4336	0.019*
C4	0.7108 (3)	0.95958 (10)	0.2540 (2)	0.0148 (5)
H3	0.6880	0.9991	0.2318	0.018*
C8	0.8044 (3)	1.04216 (10)	0.9213 (2)	0.0163 (5)
H7	0.8174	1.0305	1.0053	0.020*
C17	0.5808 (4)	0.78797 (11)	0.0480 (2)	0.0214 (5)
H16	0.6051	0.7605	−0.0168	0.026*
H15	0.5339	0.7668	0.1165	0.026*
H17	0.4789	0.8161	0.0145	0.026*
C15	0.7622 (3)	1.07573 (9)	0.6732 (2)	0.0117 (4)
C6	0.7776 (3)	1.01577 (10)	0.7059 (2)	0.0126 (4)
C10	0.7714 (3)	1.11839 (10)	0.7680 (2)	0.0133 (4)
C2	0.7624 (3)	0.88432 (10)	0.4052 (2)	0.0144 (4)
H2	0.7756	0.8713	0.4883	0.017*
C16	0.7726 (3)	0.81952 (10)	0.0940 (2)	0.0161 (5)
H13	0.8756	0.7907	0.1259	0.019*
H14	0.8206	0.8400	0.0240	0.019*
B1	0.7452 (4)	0.99074 (11)	0.4849 (2)	0.0127 (5)
H12	0.704 (4)	1.0625 (12)	0.386 (3)	0.024 (8)*
H5	0.787 (4)	0.9418 (13)	0.639 (3)	0.022 (8)*
H18	0.704 (6)	1.1246 (18)	0.201 (4)	0.058 (13)*
H19	0.517 (6)	1.1225 (17)	0.212 (3)	0.049 (12)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.02772 (10)	0.01391 (8)	0.01487 (8)	0.00169 (6)	0.00351 (6)	0.00146 (6)
O1	0.0302 (12)	0.0232 (10)	0.0257 (10)	−0.0001 (9)	0.0025 (9)	0.0040 (8)
N1	0.0122 (10)	0.0158 (10)	0.0123 (9)	−0.0011 (7)	0.0020 (7)	−0.0026 (7)
N2	0.0141 (10)	0.0104 (9)	0.0141 (9)	0.0002 (7)	0.0011 (7)	0.0004 (7)
N3	0.0157 (10)	0.0151 (10)	0.0089 (9)	0.0000 (7)	−0.0007 (7)	0.0008 (7)
C9	0.0120 (11)	0.0190 (12)	0.0146 (11)	−0.0001 (9)	0.0022 (8)	−0.0020 (9)
C3	0.0063 (10)	0.0146 (11)	0.0167 (11)	−0.0008 (8)	0.0008 (8)	−0.0002 (8)
C14	0.0087 (11)	0.0153 (11)	0.0132 (10)	0.0012 (8)	−0.0001 (8)	−0.0010 (8)
C12	0.0140 (12)	0.0128 (11)	0.0215 (12)	0.0020 (9)	−0.0010 (9)	0.0015 (9)
C5	0.0138 (11)	0.0187 (12)	0.0120 (10)	−0.0018 (9)	−0.0006 (8)	0.0016 (9)
C7	0.0152 (12)	0.0143 (11)	0.0157 (11)	−0.0001 (9)	0.0002 (8)	0.0011 (8)
C11	0.0122 (11)	0.0154 (11)	0.0216 (12)	0.0012 (9)	0.0006 (9)	−0.0033 (9)
C1	0.0117 (11)	0.0144 (11)	0.0157 (11)	−0.0014 (8)	0.0017 (8)	−0.0002 (8)
C13	0.0161 (12)	0.0156 (11)	0.0157 (11)	0.0006 (9)	0.0002 (9)	0.0028 (9)
C4	0.0131 (12)	0.0154 (11)	0.0153 (11)	−0.0007 (9)	0.0000 (8)	0.0013 (8)
C8	0.0157 (12)	0.0197 (12)	0.0133 (11)	0.0010 (9)	0.0010 (9)	0.0005 (9)
C17	0.0164 (13)	0.0222 (13)	0.0250 (13)	−0.0001 (10)	0.0008 (10)	−0.0090 (10)
C15	0.0061 (10)	0.0141 (11)	0.0146 (10)	0.0015 (8)	0.0007 (8)	−0.0004 (8)
C6	0.0091 (11)	0.0144 (11)	0.0143 (10)	−0.0007 (8)	0.0016 (8)	0.0001 (8)
C10	0.0082 (11)	0.0151 (11)	0.0163 (11)	0.0019 (8)	−0.0002 (8)	−0.0013 (9)
C2	0.0140 (11)	0.0171 (11)	0.0122 (10)	0.0003 (9)	0.0019 (8)	0.0012 (8)
C16	0.0161 (12)	0.0172 (12)	0.0155 (11)	−0.0001 (9)	0.0038 (9)	−0.0045 (9)
B1	0.0062 (11)	0.0173 (12)	0.0142 (12)	0.0012 (9)	−0.0006 (9)	0.0004 (10)

Geometric parameters (Å, º)

O1—H18	0.80 (4)	C5—H4	0.9500
O1—H19	0.77 (4)	C5—C4	1.375 (3)
N1—C5	1.349 (3)	C7—H6	0.9500
N1—C1	1.344 (3)	C7—C8	1.410 (3)
N1—C16	1.485 (3)	C7—C6	1.380 (3)
N2—C6	1.397 (3)	C11—H9	0.9500
N2—B1	1.413 (3)	C11—C10	1.417 (3)
N2—H5	0.83 (3)	C1—H1	0.9500
N3—C14	1.400 (3)	C1—C2	1.383 (3)
N3—B1	1.408 (3)	C13—H11	0.9500
N3—H12	0.81 (3)	C4—H3	0.9500
C9—H8	0.9500	C8—H7	0.9500
C9—C8	1.367 (3)	C17—H16	0.9800
C9—C10	1.418 (3)	C17—H15	0.9800
C3—C4	1.404 (3)	C17—H17	0.9800
C3—C2	1.404 (3)	C17—C16	1.511 (3)
C3—B1	1.581 (3)	C15—C6	1.427 (3)
C14—C13	1.379 (3)	C15—C10	1.424 (3)
C14—C15	1.426 (3)	C2—H2	0.9500

C12—H10	0.9500	C16—H13	0.9900
C12—C11	1.370 (3)	C16—H14	0.9900
C12—C13	1.408 (3)		
H18—O1—H19	109 (4)	C14—C13—H11	120.1
C5—N1—C16	119.52 (19)	C12—C13—H11	120.1
C1—N1—C5	120.79 (19)	C3—C4—H3	119.6
C1—N1—C16	119.64 (19)	C5—C4—C3	120.8 (2)
C6—N2—B1	122.7 (2)	C5—C4—H3	119.6
C6—N2—H5	111 (2)	C9—C8—C7	121.1 (2)
B1—N2—H5	127 (2)	C9—C8—H7	119.4
C14—N3—B1	122.82 (19)	C7—C8—H7	119.4
C14—N3—H12	114 (2)	H16—C17—H15	109.5
B1—N3—H12	123 (2)	H16—C17—H17	109.5
C8—C9—H8	119.7	H15—C17—H17	109.5
C8—C9—C10	120.5 (2)	C16—C17—H16	109.5
C10—C9—H8	119.7	C16—C17—H15	109.5
C4—C3—B1	121.5 (2)	C16—C17—H17	109.5
C2—C3—C4	116.6 (2)	C14—C15—C6	121.0 (2)
C2—C3—B1	121.8 (2)	C10—C15—C14	119.6 (2)
N3—C14—C15	117.9 (2)	C10—C15—C6	119.4 (2)
C13—C14—N3	121.9 (2)	N2—C6—C15	117.99 (19)
C13—C14—C15	120.2 (2)	C7—C6—N2	122.0 (2)
C11—C12—H10	119.4	C7—C6—C15	120.0 (2)
C11—C12—C13	121.3 (2)	C9—C10—C15	118.8 (2)
C13—C12—H10	119.4	C11—C10—C9	122.7 (2)
N1—C5—H4	119.7	C11—C10—C15	118.4 (2)
N1—C5—C4	120.6 (2)	C3—C2—H2	119.7
C4—C5—H4	119.7	C1—C2—C3	120.5 (2)
C8—C7—H6	120.0	C1—C2—H2	119.7
C6—C7—H6	120.0	N1—C16—C17	113.04 (19)
C6—C7—C8	120.1 (2)	N1—C16—H13	109.0
C12—C11—H9	119.6	N1—C16—H14	109.0
C12—C11—C10	120.7 (2)	C17—C16—H13	109.0
C10—C11—H9	119.6	C17—C16—H14	109.0
N1—C1—H1	119.7	H13—C16—H14	107.8
N1—C1—C2	120.6 (2)	N2—B1—C3	121.8 (2)
C2—C1—H1	119.7	N3—B1—N2	117.4 (2)
C14—C13—C12	119.7 (2)	N3—B1—C3	120.8 (2)
N1—C5—C4—C3	0.0 (3)	C8—C9—C10—C11	−178.3 (2)
N1—C1—C2—C3	−0.1 (3)	C8—C9—C10—C15	−0.3 (3)
N3—C14—C13—C12	−179.6 (2)	C8—C7—C6—N2	178.6 (2)
N3—C14—C15—C6	2.0 (3)	C8—C7—C6—C15	−1.0 (3)
N3—C14—C15—C10	−178.65 (19)	C15—C14—C13—C12	−0.4 (3)
C14—N3—B1—N2	1.2 (3)	C6—N2—B1—N3	2.3 (3)
C14—N3—B1—C3	−177.6 (2)	C6—N2—B1—C3	−178.9 (2)
C14—C15—C6—N2	1.2 (3)	C6—C7—C8—C9	−0.1 (3)

C14—C15—C6—C7	−179.2 (2)	C6—C15—C10—C9	−0.7 (3)
C14—C15—C10—C9	179.9 (2)	C6—C15—C10—C11	177.3 (2)
C14—C15—C10—C11	−2.1 (3)	C10—C9—C8—C7	0.8 (4)
C12—C11—C10—C9	178.5 (2)	C10—C15—C6—N2	−178.15 (19)
C12—C11—C10—C15	0.5 (3)	C10—C15—C6—C7	1.4 (3)
C5—N1—C1—C2	−2.8 (3)	C2—C3—C4—C5	−2.6 (3)
C5—N1—C16—C17	−96.2 (2)	C2—C3—B1—N2	−0.9 (3)
C11—C12—C13—C14	−1.3 (4)	C2—C3—B1—N3	177.9 (2)
C1—N1—C5—C4	2.8 (3)	C16—N1—C5—C4	−174.6 (2)
C1—N1—C16—C17	86.3 (3)	C16—N1—C1—C2	174.7 (2)
C13—C14—C15—C6	−177.3 (2)	B1—N2—C6—C7	177.0 (2)
C13—C14—C15—C10	2.1 (3)	B1—N2—C6—C15	−3.4 (3)
C13—C12—C11—C10	1.2 (4)	B1—N3—C14—C13	176.0 (2)
C4—C3—C2—C1	2.7 (3)	B1—N3—C14—C15	−3.2 (3)
C4—C3—B1—N2	−179.5 (2)	B1—C3—C4—C5	176.1 (2)
C4—C3—B1—N3	−0.8 (3)	B1—C3—C2—C1	−176.0 (2)

Hydrogen-bond geometry (Å, °)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H18$\cdots$I1[i]	0.80 (4)	2.87 (4)	3.643 (3)	162 (4)
O1—H19$\cdots$I1[ii]	0.77 (4)	3.04 (4)	3.793 (3)	167 (4)
N2—H5$\cdots$I1	0.83 (3)	2.95 (3)	3.764 (2)	171 (2)
N3—H12$\cdots$O1	0.82 (3)	2.23 (3)	3.046 (3)	172 (3)
C2—H2$\cdots$I1	0.95	3.14	4.081 (2)	171
C16—H14$\cdots$I1[iii]	0.99	2.98	3.840 (3)	145
C16—H13$\cdots$I1[iv]	0.99	3.15	3.946 (3)	138

Symmetry codes: (i) −x+2, −y+2, −z+1; (ii) −x+1, −y+2, −z+1; (iii) x, y, z−1; (iv) x, −y+3/2, z−1/2.