Crystal structures of the dioxane hemisolvates of N-(7-bromomethyl-1,8-naphthyridin-2-yl)acetamide and bis[N-(7-dibromomethyl-1,8-naphthyridin-2-yl)acetamide]

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The syntheses and crystal structures of N-(7-bromomethyl-1,8-naphthyridin-2-yl)acetamide dioxane hemisolvate, $C_{11}H_{10}BrN_3O\cdot0.5C_4H_8O_2$, (I), and bis[N-(7-dibromomethyl-1,8-naphthyridin-2-yl)acetamide] dioxane hemisolvate, $2C_{11}H_9Br_2N_3O\cdot0.5C_4H_8O_2$, (II), are described. The molecules adopt a conformation with the N—H hydrogen pointing towards the lone electron pair of the adjacent naphthyridine N atom. The crystals of (I) are stabilized by a three-dimensional supramolecular network comprising N—H···N, C—H···N and C—H···O hydrogen bonds, as well as C—Br···π halogen bonds. The crystals of compound (II) are stabilized by a three-dimensional supramolecular network comprising N—H···N, C—H···N and C—H···O hydrogen bonds, as well as C—H···π contacts and C—Br···π halogen bonds. The structure of the substituent attached in the 7-position of the naphthyridine skeleton has a fundamental influence on the pattern of intermolecular noncovalent bonding. While the Br atom of (I) participates in weak C—Br···O_{guest} and C—Br···π contacts, the Br atoms of compound (II) are involved in host–host interactions via C—Br···O═C, C—Br···N and C—Br···π bonding.

1. Chemical context

In recent decades, 1,8-naphthyridines have attracted increasing interest because of their biological and medicinal activities (Ferrarini et al., 1998; Roma et al., 2010; Badaweh et al., 2001; Litvinov, 2004), as ligands in the synthesis of metal complexes (Tang et al., 2015; Matveeva et al., 2013; Kolotuchin & Zimmerman, 1998) and as building blocks for various supramolecular systems (Kolotuchin & Zimmerman, 1998; Park et al., 2005; Liang et al., 2012). Compound (I) represents a useful precursor for the synthesis of artificial receptor molecules, for example, for carbohydrate receptors bearing naphthyridine units (Mazik & Cavga, 2007; Mazik & Sicking, 2001; Cuntze et al., 1995).

2. Structural commentary

The molecular structures of the title compounds, (I) and (II), are illustrated in Figs. 1 and 2, respectively. The asymmetric unit of compound (I) consists of one molecule of the naphthyridine derivative and one half of a 1,4-dioxane solvent molecule, with the whole molecule being generated by inversion symmetry. The naphthyridine ring of the host molecule is essentially planar [maximum deviations from the mean plane being 0.034 (3) Å for N1 and −0.034 (3) Å for C6]. The plane defined by the acetamido group is inclined at an angle of 18.9 (2)° with respect to the mean plane of the 1,8-naphthyr-
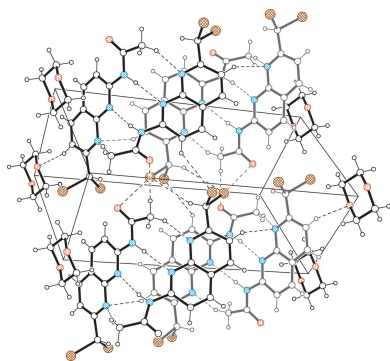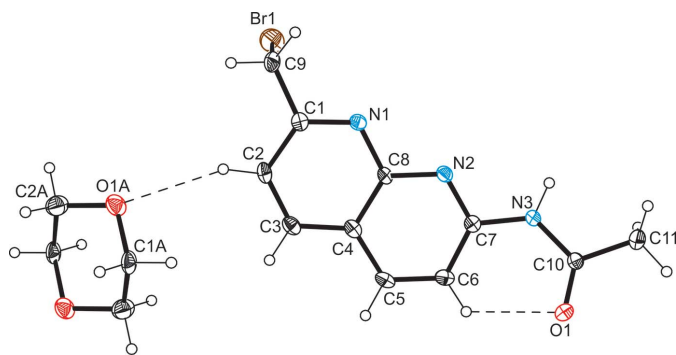
Figure 1
A view of the molecular structure of compound (I), showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines represent halogen bonds (Table 1).

idine moiety. The torsion angle along the atomic sequence N2—C1—C9—Br1 is 83.6 (4)°. The dioxane molecule is connected to the host molecule *via* C—H⋯O hydrogen bonding (Table 1 and Fig. 1).

(I)

(II)
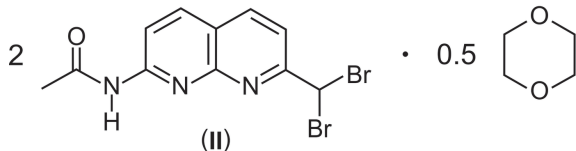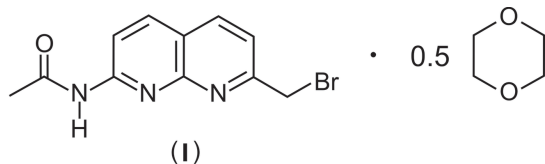
The asymmetric unit of the inclusion compound (II) contains two crystallographically independent, but conformationally similar molecules of the 1,8-naphthyridine derivative and one half molecule of a positionally disordered 1,4-dioxane, the whole molecule of the latter is generated by inversion symmetry and is disordered over two positions [occupancy ratio = 0.890 (5):0110 (5)]. The structural features of the host molecule in (II) resemble those found in the

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

*Cg*1 and *Cg*2 are the centroids of rings N1/C1–C4/C8, and N2/C4–C8, respectively.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C6—H6⋯O1	0.95	2.29	2.836 (6)	116
N3—H3A⋯N2[i]	0.88 (1)	2.18 (1)	3.053 (5)	173 (5)
C1A—H1A1⋯O1[ii]	0.99	2.55	3.462 (6)	153
C2—H2⋯O1A[iii]	0.95	2.54	3.438 (5)	157
C5—H5⋯O1[ii]	0.95	2.48	3.376 (6)	157
C9—H9A⋯N1[iv]	0.99	2.47	3.418 (6)	161
C9—Br1⋯*Cg*1[v]	1.94 (1)	3.70 (1)	5.563 (5)	161 (1)
C9—Br1⋯*Cg*2[vi]	1.94 (1)	3.70 (1)	5.436 (5)	148 (1)

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

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

*Cg*1, *Cg*2 and *Cg*4 are the centroids of rings N1/C1–C4/C8, N2/C4–C8 and N2A/C4A–C8A, respectively.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C6—H6⋯O1	0.95	2.37	2.886 (4)	113
C6A—H6A⋯O1A	0.95	2.32	2.871 (5)	116
N3—H3⋯N2A[i]	0.89 (3)	2.10 (3)	2.985 (4)	171 (4)
N3A—H3A⋯N2[i]	0.89 (3)	2.09 (3)	2.950 (4)	163 (3)
C2—H2⋯N1A	0.95	2.56	3.397 (4)	147
C2A—H2A⋯O1B[ii]	0.95	2.42	3.344 (5)	163
C11—H11B⋯N1A[i]	0.98	2.44	3.411 (5)	169
C11A—H11D⋯O1[iii]	0.98	2.46	3.437 (5)	179
C11A—H11E⋯N1[i]	0.98	2.54	3.459 (4)	156
C3—H3AA⋯*Cg*4	0.95	2.82	3.548 (3)	134
C2BA—H2B3⋯*Cg*4[iv]	0.99	2.96	3.82 (9)	145
C9—Br1⋯*Cg*1[ii]	1.94 (1)	3.62 (1)	5.270 (4)	141 (1)
C9—Br1⋯*Cg*2[ii]	1.94 (1)	3.32 (1)	5.247 (4)	173 (1)

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

reported structure of *N*-(7-dibromomethyl-5-methyl-1,8-naphthyridin-2-yl)acetamide (Gou *et al.*, 2013). The dihedral angles between the mean planes of the naphthyridine moiety and the acetylamido group are 27.6 (1) and 20.4 (1)°, respectively. The dibromomethyl group is oriented in such a way that the two Br atoms are tilted away from the plane of the respective naphthyridine moiety. The dioxane molecule is connected to the host molecule *via* C—H⋯O hydrogen bonding (Table 2 and Fig. 2).

3. Supramolecular features

In the crystal of compound (I), 1:1 host–guest units related by the 2_1 screw axis are linked *via* hydrogen bonding to form infinite supramolecular strands (Fig. 3 and Table 1). In this molecular arrangement, the amino H atom and atom N2 participate in intermolecular N—H⋯N hydrogen bonding, whereas atom N1 is involved in the formation of a weaker C—H⋯N interaction with one of the methylene H atoms of a symmetry-related molecule acting as a donor. These hydrogen
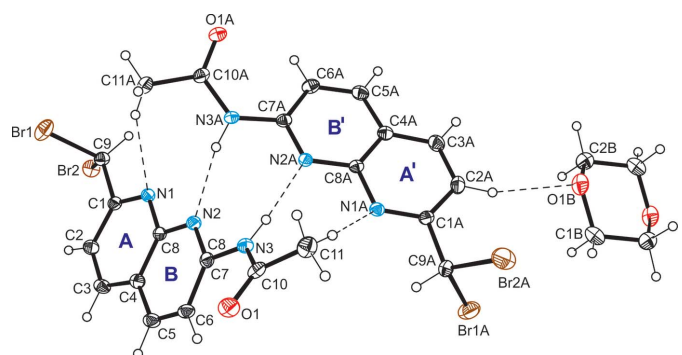

Figure 2
A view of the two independent molecules of compound (II), showing the atom labelling and ring specification. Displacement ellipsoids are drawn at the 50% probability level. For the sake of clarity, the minor-disordered component of the dioxane molecule has been omitted. Dashed lines represent hydrogen bonds (Table 2).
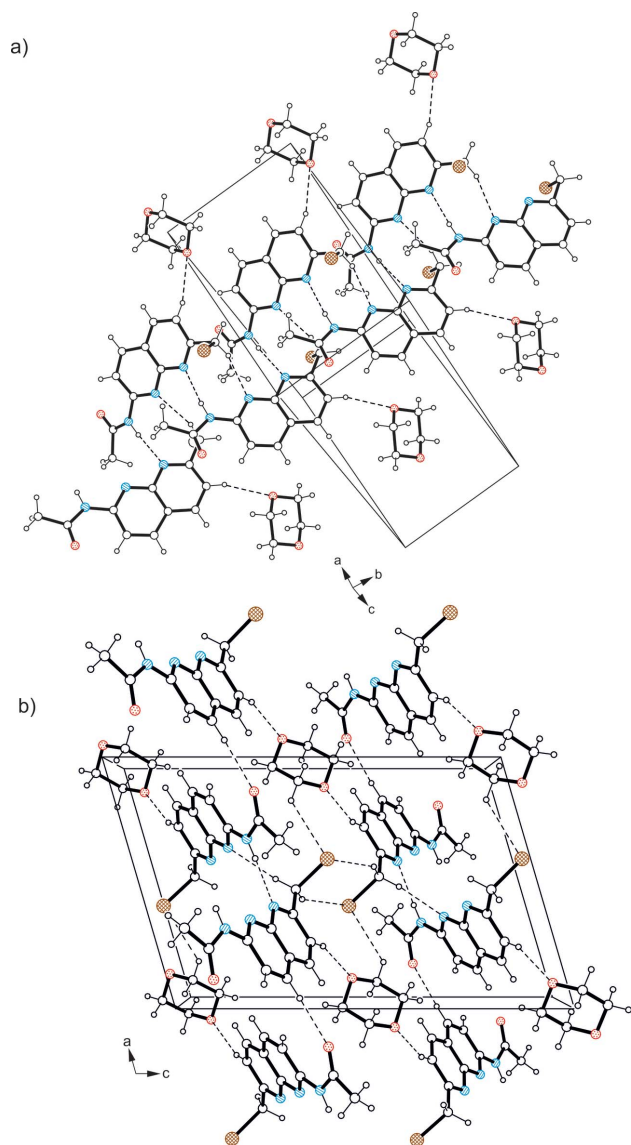
Atom Br1 is involved in the formation of a weak C—H···Br contact. Moreover, the Br1···Cg(B) distance of 3.317 (2) Å and the well-defined bonding geometry [C9—Br1···Cg(B) = 173.0 (1)°] indicate the presence of an intermolecular Br···π halogen bond (Mazik *et al.*, 2010*a,b*; Koch *et al.*, 2017; Legon, 1999; Megrangolo & Resnati, 2008). The distance of 3.213 (2) Å between atom Br2 and amide atom O1*A* of an adjacent molecule [symmetry code: (A) $x + 1$, $y - 1$, z], which is considerably less than the sum of the van der Waals radii of the respective atoms (3.37 Å), suggests the existence of an attractive Br···O halogen bond (Politzer *et al.*, 2007; Koch *et al.*, 2014, 2015). One of the host molecules participates in offset π–π stacking [Cg···Cg = 3.709 (2) Å; symmetry code: $-x$, $-y$, $-z + 1$]. The combination of these interactions results in the formation of a three-dimensional supramolecular network.

4. Database survey

The search of the Cambridge Structural Database (Groom *et al.*, 2016; Version 5.38, last update February 2017) for compounds representing 7-substituted 2-(*N*-acylamino)-1,8-naph-thyridines including solvates/hydrates resulted in 14 hits. Of particular interest are the unsolvated crystal structures of *N*-(7-methyl-1,8-naphthyridin-2-yl)acetamide (Goswami *et al.*, 2007), and *N*-(7-chloro-1,8-naphthyridin-2-yl)acetamide and *N*-(7-chloro-1,8-naphthyridin-2-yl)butanoylamide (Ghosh *et al.*, 2010). These two compounds (space group $P2_1/c$) reveal molecular assemblies similar to that observed for compound (I), *viz*. forming infinite chains of hydrogen-bonded molecules, whereas the enhanced steric demand of the butanoyl group of the latter compound favours dimer formation.

Figure 3
A view of the crystal packing of compound (I) (*a*) normal to the 101 plane and (*b*) along the *b* axis. Dashed lines represent hydrogen bonds.

bonds create a loop with graph-set motif $R_2^2(8)$. An interstrand interaction is accomplished by C$_{arene}$—H···O and C—H···Br hydrogen bonds, as well as weak C—Br···π [C—Br···C$_{naph}$ = 3.527 (2) Å and 170.1 (1)°] contacts, thus creating a three-dimensional supramolecular architecture.

According to the observed stoichiometric ratio of the crystal components in (II), the host molecules contribute in a different way in noncovalent intermolecular bonding. The crystal structure is constructed of 2:1 host–guest complexes (Fig. 2 and Table 2), in which the independent host molecules form a strongly distorted dimer held together by two N—H···N hydrogen bonds and two weak C$_{methyl}$—H···N contacts. One of the arene H atoms of this dimeric unit acts as a donor for C—H···O hydrogen bonding to the guest molecule. As is shown in Fig. 4 and Table 2, the Br atoms of only one host molecule participate in intermolecular interactions.
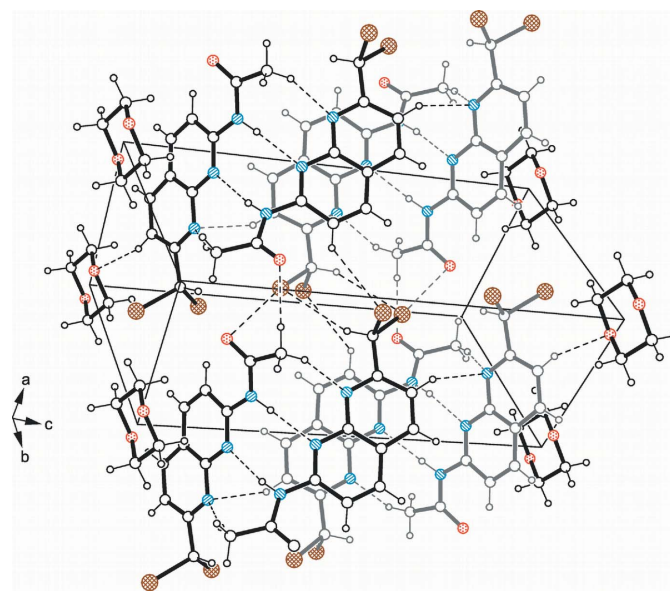

Figure 4
A view of the crystal packing of compound (II). For the sake of clarity, the minor component of the disordered dioxane molecule has been omitted. Dashed lines represent hydrogen and halogen bonds.

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_{11}H_{10}BrN_3O \cdot 0.5C_4H_8O_2$	$2C_{11}H_9Br_2N_3O \cdot 0.5C_4H_8O_2$
M_r	324.19	762.11
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
Temperature (K)	100	100
a, b, c (Å)	10.8863 (10), 7.6256 (7), 16.5300 (15)	9.4065 (5), 9.5271 (5), 16.6464 (10)
α, β, γ (°)	90, 106.310 (4), 90	88.777 (3), 81.057 (2), 64.928 (2)
V (Å³)	1317.0 (2)	1333.15 (13)
Z	4	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm⁻¹)	3.12	6.08
Crystal size (mm)	$0.34 \times 0.06 \times 0.06$	$0.40 \times 0.18 \times 0.09$
Data collection		
Diffractometer	Bruker APEXII CCD area detector	Bruker APEXII CCD area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.417, 0.835	0.195, 0.611
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	9345, 2493, 1965	32569, 5659, 5247
R_{int}	0.043	0.025
$(\sin \theta/\lambda)_{max}$ (Å⁻¹)	0.610	0.636
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.144, 1.03	0.029, 0.074, 1.12
No. of reflections	2493	5659
No. of parameters	177	354
No. of restraints	1	6
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)	0.93, −0.85	0.92, −0.80

Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *SHELXTL* (Sheldrick, 2008).

5. Synthesis and crystallization

N-(7-Methyl-1,8-naphthyridin-2-yl)acetamide (9.67 g, 48.1 mmol), N-bromosuccinimide (9.07 g, 55.6 mmol) and 2,2′-azobisiso-butyronitrile (AIBN; 0.10 g, 0.6 mmol), dissolved in 300 ml of dry chloroform, were refluxed for 8 h with vigorous stirring in the presence of light from a 500 W lamp. The succinimide precipitate was filtered off and the organic filtrate washed several times with water. After drying of the filtrate over anhydrous Na_2SO_4 and removing the solvent, the crude product [a mixture containing N-(7-bromomethyl-1,8-naphthyridin-2-yl)acetamide and N-(7-dibromomethyl-1,8-naphthyridin-2-yl)acetamide] was purified by column chromatography (SiO_2, eluent: ethyl acetate).

N-(7-Bromomethyl-1,8-naphthyridin-2-yl)acetamide: white solid (2.56 g). ¹H NMR (500 MHz, CDCl₃): δ 2.29 (s, 3H, CH₃), 4.70 (s, 2H, CH₂), 7.59 (d, J = 8.3 Hz, 1H, CH$_{Ar}$), 8.16 (d, J = 8.3 Hz, 1H, CH$_{Ar}$), 8.19 (d, J = 8.8 Hz, 1H, Ar), 8.54 (d, J = 8.8 Hz, 1H, CH$_{Ar}$), 8.93 (s, 1H, NH). ¹³C NMR (125 MHz, CDCl₃): δ 25.1, 33.8, 115.6, 119.7, 120.9, 137.7, 139.3, 153.8, 154.0, 160.8, 169.7.

N-(7-Dibromomethyl-1,8-naphthyridin-2-yl)acetamide: white solid (3.20 g). ¹H NMR (500 MHz, CDCl₃): δ 2.31 (s, 3H, CH₃), 6.87 (s, 1H, CH), 7.98 (d, J = 8.4 Hz, 1H, CH$_{Ar}$), 8.21 (d, J = 8.8 Hz, 1H, CH$_{Ar}$), 8.26 (d, J = 8.4 Hz, 1H, CH$_{Ar}$), 8.59 (d, J = 8.8 Hz, 1H, CH$_{Ar}$), 8.97 (s, NH). ¹³C NMR (125 MHz, CDCl₃): δ 25.0, 41.6, 116.2, 119.4, 120.3, 138.6, 139.1, 152.4, 154.6, 161.8, 169.6.

Crystals of (I) and (II) suitable for X-ray analysis were obtained by slow evaporation of the solvent (1,4-dioxane) from solutions of the respective compounds.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. In both compounds, the N—H H atoms were located from difference Fourier maps and refined freely. C-bound H atoms were placed geometrically and allowed to ride on their attached C atoms, with C—H distances of 0.95–1.00 Å and $U_{iso}(H) = 1.5U_{eq}$(C-methyl), or $1.2U_{eq}$(C) for other H atoms.

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supporting information

Crystal structures of the dioxane hemisolvates of *N*-(7-bromomethyl-1,8-naphthyridin-2-yl)acetamide and bis[*N*-(7-dibromomethyl-1,8-naphthyridin-2-yl)acetamide]

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Computing details

For both structures, data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

N-(7-Bromomethyl-1,8-naphthyridin-2-yl)acetamide dioxane hemisolvate (I)

Crystal data

$C_{11}H_{10}BrN_3O \cdot 0.5C_4H_8O_2$	$F(000) = 656$
$M_r = 324.19$	$D_x = 1.635$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.8863$ (10) Å	Cell parameters from 1901 reflections
$b = 7.6256$ (7) Å	$\theta = 3.3–25.6°$
$c = 16.5300$ (15) Å	$\mu = 3.12$ mm^{-1}
$\beta = 106.310$ (4)°	$T = 100$ K
$V = 1317.0$ (2) Å^3	Needle, colourless
$Z = 4$	$0.34 \times 0.06 \times 0.06$ mm

Data collection

CCD area detector diffractometer	2493 independent reflections
phi and ω scans	1965 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2014)	$R_{int} = 0.043$
	$\theta_{max} = 25.7°$, $\theta_{min} = 2.0°$
$T_{min} = 0.417$, $T_{max} = 0.835$	$h = -13 \rightarrow 9$
9345 measured reflections	$k = -8 \rightarrow 9$
	$l = -14 \rightarrow 20$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.051$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.144$	
$S = 1.03$	Hydrogen site location: mixed
2493 reflections	H atoms treated by a mixture of independent and constrained refinement
177 parameters	
1 restraint	

$w = 1/[\sigma^2(F_o^2) + (0.074P)^2 + 4.7912P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.93$ e Å^{-3}
$\Delta\rho_{min} = -0.85$ 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.

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

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Br1	0.40285 (5)	0.22955 (7)	0.01016 (3)	0.0276 (2)
O1	0.8581 (3)	1.1345 (5)	0.3581 (2)	0.0284 (9)
N1	0.6444 (3)	0.7095 (5)	0.2424 (2)	0.0102 (8)
N2	0.5954 (3)	0.4391 (5)	0.1799 (2)	0.0102 (8)
N3	0.6749 (3)	0.9809 (5)	0.3027 (2)	0.0112 (8)
H3A	0.598 (2)	0.977 (7)	0.310 (3)	0.019 (14)*
C1	0.6261 (4)	0.3046 (6)	0.1387 (3)	0.0109 (9)
C2	0.7405 (4)	0.2935 (6)	0.1146 (3)	0.0135 (9)
H2	0.7594	0.1920	0.0870	0.016*
C3	0.8233 (4)	0.4320 (6)	0.1320 (3)	0.0139 (10)
H3	0.8999	0.4294	0.1152	0.017*
C4	0.7944 (4)	0.5784 (6)	0.1749 (3)	0.0106 (9)
C5	0.8705 (4)	0.7317 (6)	0.1931 (3)	0.0134 (9)
H5	0.9469	0.7402	0.1763	0.016*
C6	0.8334 (4)	0.8676 (6)	0.2351 (3)	0.0133 (10)
H6	0.8830	0.9719	0.2474	0.016*
C7	0.7196 (4)	0.8491 (6)	0.2596 (3)	0.0102 (9)
C8	0.6797 (4)	0.5770 (6)	0.1993 (3)	0.0083 (9)
C9	0.5270 (4)	0.1624 (6)	0.1145 (3)	0.0150 (10)
H9A	0.4841	0.1468	0.1595	0.018*
H9B	0.5680	0.0501	0.1069	0.018*
C10	0.7442 (4)	1.1158 (6)	0.3487 (3)	0.0143 (10)
C11	0.6664 (5)	1.2360 (6)	0.3869 (3)	0.0176 (10)
H11A	0.7232	1.3202	0.4242	0.026*
H11B	0.6211	1.1668	0.4195	0.026*
H11C	0.6041	1.2992	0.3420	0.026*
O1A	0.8985 (3)	0.9736 (4)	0.0366 (2)	0.0184 (7)
C1A	1.0174 (4)	1.0481 (6)	0.0834 (3)	0.0166 (10)
H1A1	1.0749	0.9539	0.1135	0.020*
H1A2	1.0025	1.1303	0.1260	0.020*
C2A	0.9197 (5)	0.8555 (7)	−0.0259 (3)	0.0206 (11)
H2A1	0.8369	0.8059	−0.0594	0.025*
H2A2	0.9751	0.7574	0.0020	0.025*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0237 (3)	0.0352 (4)	0.0229 (3)	−0.0019 (2)	0.0047 (2)	−0.0049 (2)
O1	0.0186 (19)	0.033 (2)	0.037 (2)	−0.0123 (16)	0.0134 (17)	−0.0229 (18)
N1	0.0104 (18)	0.0098 (18)	0.0115 (19)	0.0001 (14)	0.0051 (15)	0.0003 (15)
N2	0.0113 (18)	0.0105 (19)	0.0100 (19)	−0.0009 (15)	0.0051 (15)	0.0007 (15)
N3	0.0088 (18)	0.0130 (19)	0.0137 (19)	−0.0012 (15)	0.0064 (15)	−0.0031 (15)
C1	0.013 (2)	0.012 (2)	0.007 (2)	0.0023 (18)	0.0016 (17)	0.0027 (17)
C2	0.016 (2)	0.015 (2)	0.010 (2)	0.0055 (18)	0.0037 (18)	−0.0025 (18)
C3	0.012 (2)	0.021 (3)	0.010 (2)	0.0032 (19)	0.0047 (18)	0.0000 (19)
C4	0.011 (2)	0.015 (2)	0.006 (2)	0.0039 (17)	0.0027 (17)	0.0032 (17)
C5	0.009 (2)	0.019 (2)	0.013 (2)	0.0012 (18)	0.0040 (18)	0.0026 (18)
C6	0.010 (2)	0.017 (2)	0.013 (2)	−0.0019 (18)	0.0033 (18)	0.0009 (18)
C7	0.011 (2)	0.012 (2)	0.007 (2)	0.0015 (17)	0.0012 (17)	0.0021 (17)
C8	0.010 (2)	0.013 (2)	0.002 (2)	0.0011 (17)	0.0022 (16)	0.0006 (17)
C9	0.019 (2)	0.015 (2)	0.012 (2)	0.0000 (19)	0.0050 (19)	−0.0037 (18)
C10	0.015 (2)	0.017 (2)	0.013 (2)	−0.0035 (18)	0.0070 (19)	−0.0039 (18)
C11	0.020 (3)	0.017 (3)	0.017 (2)	−0.0029 (19)	0.007 (2)	−0.006 (2)
O1A	0.0185 (17)	0.0224 (18)	0.0162 (17)	0.0009 (14)	0.0082 (14)	−0.0020 (14)
C1A	0.020 (2)	0.017 (2)	0.013 (2)	0.0031 (19)	0.004 (2)	−0.0062 (19)
C2A	0.021 (3)	0.021 (3)	0.020 (3)	−0.005 (2)	0.007 (2)	−0.002 (2)

Geometric parameters (Å, º)

Br1—C9	1.938 (5)	C5—C6	1.370 (6)
O1—C10	1.214 (5)	C6—H6	0.9500
N1—C7	1.324 (6)	C6—C7	1.414 (6)
N1—C8	1.352 (5)	C9—H9A	0.9900
N2—C1	1.325 (6)	C9—H9B	0.9900
N2—C8	1.373 (6)	C10—C11	1.503 (6)
N3—C10	1.372 (6)	C11—H11A	0.9800
N3—C7	1.398 (6)	C11—H11B	0.9800
N3—H3A	0.883 (10)	C11—H11C	0.9800
C1—C9	1.502 (6)	O1A—C1A	1.426 (6)
C1—C2	1.412 (6)	O1A—C2A	1.438 (6)
C2—H2	0.9500	C1A—C2A^i	1.510 (7)
C2—C3	1.366 (6)	C1A—H1A1	0.9900
C3—H3	0.9500	C1A—H1A2	0.9900
C3—C4	1.405 (6)	C2A—C1A^i	1.510 (7)
C4—C8	1.416 (6)	C2A—H2A1	0.9900
C4—C5	1.415 (6)	C2A—H2A2	0.9900
C5—H5	0.9500		
C7—N1—C8	117.6 (4)	N2—C1—C9	115.4 (4)
C1—N2—C8	117.7 (4)	N1—C8—N2	115.1 (4)
C10—N3—C7	127.3 (4)	N1—C8—C4	123.2 (4)
C10—N3—H3A	110 (3)	N2—C8—C4	121.6 (4)

C7—N3—H3A	122 (3)	Br1—C9—H9A	110.0
N1—C7—N3	113.9 (4)	Br1—C9—H9B	110.0
N1—C7—C6	123.9 (4)	O1—C10—N3	122.8 (4)
N3—C7—C6	122.2 (4)	O1—C10—C11	123.4 (4)
C1—C2—H2	120.8	N3—C10—C11	113.7 (4)
C1—C9—H9A	110.0	C10—C11—H11A	109.5
C1—C9—H9B	110.0	C10—C11—H11B	109.5
C1—C9—Br1	108.4 (3)	H11A—C11—H11B	109.5
C2—C1—C9	120.4 (4)	C10—C11—H11C	109.5
C2—C3—C4	119.5 (4)	H11A—C11—H11C	109.5
C2—C3—H3	120.2	H11B—C11—H11C	109.5
C3—C2—C1	118.4 (4)	C1A—O1A—C2A	109.6 (3)
C3—C2—H2	120.8	O1A—C1A—C2A^i	110.8 (4)
C3—C4—C5	124.3 (4)	O1A—C1A—H1A1	109.5
C3—C4—C8	118.5 (4)	C2A^i—C1A—H1A1	109.5
C4—C3—H3	120.2	O1A—C1A—H1A2	109.5
C4—C5—H5	120.2	C2A^i—C1A—H1A2	109.5
C5—C4—C8	117.1 (4)	H1A1—C1A—H1A2	108.1
C5—C6—C7	118.4 (4)	O1A—C2A—C1A^i	109.9 (4)
C5—C6—H6	120.8	O1A—C2A—H2A1	109.7
C6—C5—C4	119.7 (4)	C1A^i—C2A—H2A1	109.7
C6—C5—H5	120.2	O1A—C2A—H2A2	109.7
C7—C6—H6	120.8	C1A^i—C2A—H2A2	109.7
H9A—C9—H9B	108.4	H2A1—C2A—H2A2	108.2
N2—C1—C2	124.1 (4)		

C8—N1—C7—N3	178.8 (4)	C5—C4—C8—N1	−3.6 (6)
C8—N1—C7—C6	0.4 (6)	C5—C4—C8—N2	175.9 (4)
C10—N3—C7—N1	160.8 (4)	C6—C5—C4—C3	179.7 (4)
C10—N3—C7—C6	−20.8 (7)	C6—C5—C4—C8	2.0 (6)
N1—C7—C6—C5	−1.9 (7)	C7—C6—C5—C4	0.5 (6)
N3—C7—C6—C5	179.9 (4)	C7—N1—C8—N2	−177.2 (4)
C1—N2—C8—C4	1.3 (6)	C7—N1—C8—C4	2.4 (6)
C1—N2—C8—N1	−179.1 (4)	C7—N3—C10—O1	−1.0 (8)
C2—C1—C9—Br1	−93.8 (4)	C7—N3—C10—C11	179.7 (4)
C3—C2—C1—N2	−2.4 (7)	C8—C4—C3—C2	0.3 (6)
C3—C2—C1—C9	174.8 (4)	C8—N2—C1—C2	0.9 (6)
C3—C4—C8—N1	178.5 (4)	C8—N2—C1—C9	−176.4 (4)
C3—C4—C8—N2	−1.9 (6)	N2—C1—C9—Br1	83.6 (4)
C4—C3—C2—C1	1.7 (7)	C2A—O1A—C1A—C2A^i	58.6 (5)
C5—C4—C3—C2	−177.3 (4)	C1A—O1A—C2A—C1A^i	−58.0 (5)

Symmetry code: (i) −*x*+2, −*y*+2, −*z*.

Hydrogen-bond geometry (Å, º)

Cg1 and Cg2 are the centroids of rings N1/C1-C4/C8, and N2/C4-C8, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···O1	0.95	2.29	2.836 (6)	116

N3—H3A···N2^{ii}	0.88 (1)	2.18 (1)	3.053 (5)	173 (5)
C1A—H1A1···O1^{iii}	0.99	2.55	3.462 (6)	153
C2—H2···O1A^{iv}	0.95	2.54	3.438 (5)	157
C5—H5···O1^{iii}	0.95	2.48	3.376 (6)	157
C9—H9A···N1^{v}	0.99	2.47	3.418 (6)	161
C9—Br1···Cg1^{vi}	1.94 (1)	3.70 (1)	5.563 (5)	161 (1)
C9—Br1···Cg2^{vii}	1.94 (1)	3.70 (1)	5.436 (5)	148 (1)

Symmetry codes: (ii) $-x+1, y+1/2, -z+1/2$; (iii) $-x+2, y-1/2, -z+1/2$; (iv) $x, y-1, z$; (v) $-x+1, y-1/2, -z+1/2$; (vi) $-x+1, -y+1, -z$; (vii) $-x+1, -y, -z$.

Bis[N-(7-dibromomethyl-1,8-naphthyridin-2-yl)acetamide] dioxane hemisolvate (II)

Crystal data

2C$_{11}$H$_9$Br$_2$N$_3$O·0.5C$_4$H$_8$O$_2$	$Z = 2$
$M_r = 762.11$	$F(000) = 744$
Triclinic, $P\bar{1}$	$D_x = 1.899$ Mg m^{-3}
$a = 9.4065 (5)$ Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 9.5271 (5)$ Å	Cell parameters from 9921 reflections
$c = 16.6464 (10)$ Å	$\theta = 2.4$–$29.1°$
$\alpha = 88.777 (3)°$	$\mu = 6.08$ mm^{-1}
$\beta = 81.057 (2)°$	$T = 100$ K
$\gamma = 64.928 (2)°$	Plate, colourless
$V = 1333.15 (13)$ Å^3	$0.40 \times 0.18 \times 0.09$ mm

Data collection

CCD area detector diffractometer	5659 independent reflections
φ and ω scans	5247 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2014)	$R_{int} = 0.025$
	$\theta_{max} = 26.9°$, $\theta_{min} = 2.4°$
$T_{min} = 0.195$, $T_{max} = 0.611$	$h = -11 \rightarrow 11$
32569 measured reflections	$k = -12 \rightarrow 12$
	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.029$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.074$	
$S = 1.12$	$w = 1/[\sigma^2(F_o^2) + (0.0205P)^2 + 4.6947P]$ where $P = (F_o^2 + 2F_c^2)/3$
5659 reflections	
354 parameters	$(\Delta/\sigma)_{max} = 0.001$
6 restraints	$\Delta\rho_{max} = 0.92$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.80$ 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Br1	0.65226 (4)	−0.27545 (4)	0.46303 (2)	0.02418 (9)	
Br2	0.50091 (4)	−0.43628 (4)	0.36111 (2)	0.01949 (8)	
O1	−0.1936 (3)	0.5684 (2)	0.70075 (14)	0.0193 (5)	
N1	0.2448 (3)	−0.0854 (3)	0.52469 (15)	0.0117 (5)	
N2	0.0579 (3)	0.1182 (3)	0.60845 (15)	0.0122 (5)	
N3	−0.1214 (3)	0.3074 (3)	0.70039 (16)	0.0136 (5)	
H3	−0.125 (5)	0.230 (3)	0.730 (2)	0.032 (12)*	
C1	0.3284 (3)	−0.1392 (3)	0.45189 (18)	0.0125 (6)	
C2	0.3087 (4)	−0.0548 (4)	0.38070 (18)	0.0149 (6)	
H2	0.3725	−0.1004	0.3299	0.018*	
C3	0.1948 (4)	0.0948 (4)	0.38720 (19)	0.0155 (6)	
H3AA	0.1775	0.1550	0.3404	0.019*	
C4	0.1032 (4)	0.1593 (3)	0.46373 (18)	0.0133 (6)	
C5	−0.0132 (4)	0.3143 (3)	0.4786 (2)	0.0157 (6)	
H5	−0.0388	0.3810	0.4346	0.019*	
C6	−0.0883 (4)	0.3676 (3)	0.55553 (19)	0.0142 (6)	
H6	−0.1660	0.4717	0.5662	0.017*	
C7	−0.0479 (3)	0.2642 (3)	0.61988 (18)	0.0127 (6)	
C8	0.1333 (3)	0.0649 (3)	0.53149 (18)	0.0113 (5)	
C9	0.4604 (4)	−0.2989 (3)	0.45387 (18)	0.0139 (6)	
H9	0.4325	−0.3480	0.5039	0.017*	
C10	−0.1954 (4)	0.4554 (3)	0.73566 (19)	0.0146 (6)	
C11	−0.2752 (4)	0.4634 (4)	0.8217 (2)	0.0192 (6)	
H11A	−0.1986	0.4466	0.8588	0.029*	
H11B	−0.3147	0.3831	0.8283	0.029*	
H11C	−0.3644	0.5658	0.8345	0.029*	
Br1A	0.80621 (4)	−0.30529 (4)	0.21420 (2)	0.02498 (9)	
Br2A	0.76639 (5)	−0.42214 (4)	0.04563 (2)	0.03087 (10)	
O1A	−0.3475 (3)	0.3086 (3)	0.21196 (14)	0.0213 (5)	
N1A	0.3820 (3)	−0.1632 (3)	0.17991 (15)	0.0114 (5)	
N2A	0.1123 (3)	−0.0240 (3)	0.21618 (14)	0.0108 (5)	
N3A	−0.1546 (3)	0.1001 (3)	0.26087 (16)	0.0131 (5)	
H3A	−0.139 (4)	0.027 (3)	0.2972 (17)	0.018 (9)*	
C1A	0.5218 (3)	−0.1707 (3)	0.14603 (17)	0.0121 (6)	
C2A	0.5460 (4)	−0.0467 (4)	0.10905 (19)	0.0168 (6)	
H2A	0.6490	−0.0594	0.0843	0.020*	
C3A	0.4166 (4)	0.0928 (4)	0.10975 (19)	0.0163 (6)	
H3AB	0.4288	0.1791	0.0856	0.020*	
C4A	0.2652 (4)	0.1076 (3)	0.14659 (18)	0.0123 (6)	
C5A	0.1237 (4)	0.2459 (3)	0.15230 (19)	0.0152 (6)	
H5A	0.1267	0.3378	0.1306	0.018*	
C6A	−0.0172 (4)	0.2474 (3)	0.18892 (19)	0.0142 (6)	
H6A	−0.1130	0.3399	0.1933	0.017*	
C7A	−0.0175 (3)	0.1079 (3)	0.22022 (17)	0.0121 (6)	
C8A	0.2525 (3)	−0.0247 (3)	0.18011 (17)	0.0100 (5)	

C9A	0.6575 (4)	−0.3261 (3)	0.15233 (18)	0.0149 (6)	
H9A	0.6132	−0.3952	0.1817	0.018*	
C10A	−0.3099 (4)	0.1975 (3)	0.25486 (18)	0.0137 (6)	
C11A	−0.4289 (4)	0.1510 (4)	0.30498 (19)	0.0166 (6)	
H11D	−0.5366	0.2314	0.3038	0.025*	
H11E	−0.4088	0.1389	0.3613	0.025*	
H11F	−0.4190	0.0524	0.2825	0.025*	
O1B	0.1348 (3)	0.0280 (3)	1.00203 (17)	0.0237 (7)	0.890 (5)
C1B	0.0015 (15)	0.1333 (9)	0.9682 (7)	0.0242 (16)	0.890 (5)
H1B1	0.0192	0.1083	0.9090	0.029*	0.890 (5)
H1B2	−0.0083	0.2401	0.9755	0.029*	0.890 (5)
C2B	0.150 (2)	−0.1267 (10)	0.9930 (6)	0.0223 (10)	0.890 (5)
H2B1	0.2389	−0.1990	1.0191	0.027*	0.890 (5)
H2B2	0.1721	−0.1587	0.9345	0.027*	0.890 (5)
O1BA	0.099 (3)	−0.003 (3)	0.9249 (13)	0.0237 (7)	0.110 (5)
C1BA	−0.008 (13)	0.147 (8)	0.960 (7)	0.0242 (16)	0.110 (5)
H1B3	−0.0491	0.2215	0.9175	0.029*	0.110 (5)
H1B4	0.0424	0.1879	0.9953	0.029*	0.110 (5)
C2BA	0.146 (18)	−0.107 (10)	0.988 (5)	0.0223 (10)	0.110 (5)
H2B3	0.1887	−0.0616	1.0262	0.027*	0.110 (5)
H2B4	0.2343	−0.2048	0.9640	0.027*	0.110 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01616 (16)	0.02553 (18)	0.03175 (19)	−0.00758 (13)	−0.01019 (13)	0.00084 (14)
Br2	0.02109 (16)	0.01804 (16)	0.01863 (16)	−0.00768 (12)	−0.00289 (12)	−0.00092 (12)
O1	0.0206 (12)	0.0118 (10)	0.0266 (12)	−0.0073 (9)	−0.0054 (9)	0.0013 (9)
N1	0.0120 (12)	0.0130 (12)	0.0119 (12)	−0.0066 (10)	−0.0036 (9)	0.0025 (9)
N2	0.0119 (12)	0.0109 (12)	0.0149 (12)	−0.0055 (10)	−0.0034 (10)	0.0026 (9)
N3	0.0124 (12)	0.0104 (12)	0.0162 (13)	−0.0033 (10)	−0.0022 (10)	0.0022 (10)
C1	0.0118 (14)	0.0133 (14)	0.0137 (14)	−0.0062 (11)	−0.0040 (11)	0.0020 (11)
C2	0.0164 (15)	0.0185 (15)	0.0107 (14)	−0.0078 (12)	−0.0037 (11)	0.0013 (11)
C3	0.0195 (15)	0.0183 (15)	0.0139 (14)	−0.0111 (13)	−0.0083 (12)	0.0051 (12)
C4	0.0149 (14)	0.0133 (14)	0.0157 (15)	−0.0088 (12)	−0.0059 (11)	0.0026 (11)
C5	0.0167 (15)	0.0129 (14)	0.0205 (16)	−0.0079 (12)	−0.0073 (12)	0.0054 (12)
C6	0.0137 (14)	0.0102 (13)	0.0195 (15)	−0.0050 (11)	−0.0059 (12)	0.0035 (11)
C7	0.0115 (14)	0.0119 (14)	0.0168 (15)	−0.0069 (11)	−0.0026 (11)	0.0019 (11)
C8	0.0109 (13)	0.0115 (13)	0.0138 (14)	−0.0065 (11)	−0.0038 (11)	0.0028 (11)
C9	0.0139 (14)	0.0137 (14)	0.0127 (14)	−0.0043 (12)	−0.0030 (11)	0.0003 (11)
C10	0.0102 (14)	0.0121 (14)	0.0207 (16)	−0.0032 (11)	−0.0049 (11)	−0.0011 (12)
C11	0.0179 (16)	0.0149 (15)	0.0231 (17)	−0.0059 (12)	−0.0014 (13)	−0.0025 (12)
Br1A	0.01866 (17)	0.02336 (17)	0.03252 (19)	−0.00674 (13)	−0.01008 (14)	0.00544 (14)
Br2A	0.0356 (2)	0.02085 (17)	0.01875 (17)	0.00176 (15)	0.00427 (14)	−0.00107 (13)
O1A	0.0134 (11)	0.0211 (12)	0.0242 (12)	−0.0023 (9)	−0.0046 (9)	0.0091 (10)
N1A	0.0120 (12)	0.0110 (11)	0.0096 (11)	−0.0032 (10)	−0.0016 (9)	0.0005 (9)
N2A	0.0104 (12)	0.0127 (12)	0.0089 (11)	−0.0043 (10)	−0.0022 (9)	0.0010 (9)
N3A	0.0105 (12)	0.0112 (12)	0.0149 (13)	−0.0019 (10)	−0.0028 (10)	0.0043 (9)

C1A	0.0115 (14)	0.0122 (14)	0.0101 (13)	−0.0024 (11)	−0.0022 (11)	−0.0005 (10)
C2A	0.0136 (15)	0.0181 (15)	0.0175 (15)	−0.0068 (12)	0.0010 (12)	0.0014 (12)
C3A	0.0182 (15)	0.0141 (14)	0.0176 (15)	−0.0082 (12)	−0.0021 (12)	0.0032 (12)
C4A	0.0142 (14)	0.0123 (14)	0.0109 (13)	−0.0055 (11)	−0.0035 (11)	0.0000 (11)
C5A	0.0177 (15)	0.0122 (14)	0.0162 (15)	−0.0064 (12)	−0.0041 (12)	0.0034 (11)
C6A	0.0142 (14)	0.0087 (13)	0.0178 (15)	−0.0026 (11)	−0.0044 (12)	−0.0003 (11)
C7A	0.0126 (14)	0.0125 (14)	0.0104 (13)	−0.0041 (11)	−0.0036 (11)	0.0002 (11)
C8A	0.0111 (13)	0.0102 (13)	0.0079 (13)	−0.0033 (11)	−0.0027 (10)	−0.0011 (10)
C9A	0.0124 (14)	0.0149 (14)	0.0142 (14)	−0.0036 (12)	0.0006 (11)	−0.0001 (11)
C10A	0.0114 (14)	0.0149 (14)	0.0112 (14)	−0.0019 (11)	−0.0019 (11)	−0.0023 (11)
C11A	0.0116 (14)	0.0181 (15)	0.0182 (15)	−0.0048 (12)	−0.0018 (12)	0.0008 (12)
O1B	0.0220 (14)	0.0322 (15)	0.0239 (15)	−0.0181 (12)	−0.0031 (11)	−0.0030 (11)
C1B	0.034 (3)	0.025 (2)	0.019 (4)	−0.0170 (18)	−0.007 (2)	0.004 (2)
C2B	0.0226 (19)	0.023 (4)	0.021 (2)	−0.008 (3)	−0.0051 (17)	−0.0025 (18)
O1BA	0.0220 (14)	0.0322 (15)	0.0239 (15)	−0.0181 (12)	−0.0031 (11)	−0.0030 (11)
C1BA	0.034 (3)	0.025 (2)	0.019 (4)	−0.0170 (18)	−0.007 (2)	0.004 (2)
C2BA	0.0226 (19)	0.023 (4)	0.021 (2)	−0.008 (3)	−0.0051 (17)	−0.0025 (18)

Geometric parameters (Å, º)

Br1—C9	1.939 (3)	N3A—C7A	1.391 (4)
Br2—C9	1.929 (3)	N3A—H3A	0.892 (10)
O1—C10	1.218 (4)	C1A—C2A	1.407 (4)
N1—C1	1.318 (4)	C1A—C9A	1.505 (4)
N1—C8	1.364 (4)	C2A—C3A	1.368 (4)
N2—C7	1.320 (4)	C2A—H2A	0.9500
N2—C8	1.357 (4)	C3A—C4A	1.410 (4)
N3—C10	1.376 (4)	C3A—H3AB	0.9500
N3—C7	1.392 (4)	C4A—C8A	1.411 (4)
N3—H3	0.890 (10)	C4A—C5A	1.413 (4)
C1—C2	1.410 (4)	C5A—C6A	1.364 (4)
C1—C9	1.506 (4)	C5A—H5A	0.9500
C2—C3	1.366 (4)	C6A—C7A	1.418 (4)
C2—H2	0.9500	C6A—H6A	0.9500
C3—C4	1.409 (4)	C9A—H9A	1.0000
C3—H3AA	0.9500	C10A—C11A	1.504 (4)
C4—C5	1.415 (4)	C11A—H11D	0.9800
C4—C8	1.415 (4)	C11A—H11E	0.9800
C5—C6	1.357 (5)	C11A—H11F	0.9800
C5—H5	0.9500	O1B—C1B	1.423 (8)
C6—C7	1.423 (4)	O1B—C2B	1.430 (8)
C6—H6	0.9500	C1B—C2B[i]	1.49 (2)
C9—H9	1.0000	C1B—H1B1	0.9900
C10—C11	1.498 (5)	C1B—H1B2	0.9900
C11—H11A	0.9800	C2B—C1B[i]	1.49 (2)
C11—H11B	0.9800	C2B—H2B1	0.9900
C11—H11C	0.9800	C2B—H2B2	0.9900
Br1A—C9A	1.936 (3)	O1BA—C1BA	1.419 (10)

Br2A—C9A	1.937 (3)	O1BA—C2BA	1.420 (10)
O1A—C10A	1.218 (4)	C1BA—C2BA[i]	1.6 (2)
N1A—C1A	1.321 (4)	C1BA—H1B3	0.9900
N1A—C8A	1.364 (4)	C1BA—H1B4	0.9900
N2A—C7A	1.324 (4)	C2BA—C1BA[i]	1.6 (2)
N2A—C8A	1.359 (4)	C2BA—H2B3	0.9900
N3A—C10A	1.377 (4)	C2BA—H2B4	0.9900
C1—N1—C8	117.0 (3)	C4A—C3A—H3AB	120.2
C7—N2—C8	118.1 (3)	C3A—C4A—C8A	118.1 (3)
C10—N3—C7	126.9 (3)	C3A—C4A—C5A	124.7 (3)
C10—N3—H3	118 (3)	C8A—C4A—C5A	117.1 (3)
C7—N3—H3	115 (3)	C6A—C5A—C4A	120.0 (3)
N1—C1—C2	125.1 (3)	C6A—C5A—H5A	120.0
N1—C1—C9	112.1 (3)	C4A—C5A—H5A	120.0
C2—C1—C9	122.5 (3)	C5A—C6A—C7A	118.5 (3)
C3—C2—C1	117.9 (3)	C5A—C6A—H6A	120.7
C3—C2—H2	121.1	C7A—C6A—H6A	120.7
C1—C2—H2	121.1	N2A—C7A—N3A	114.2 (3)
C2—C3—C4	119.6 (3)	N2A—C7A—C6A	123.4 (3)
C2—C3—H3AA	120.2	N3A—C7A—C6A	122.4 (3)
C4—C3—H3AA	120.2	N2A—C8A—N1A	114.9 (3)
C3—C4—C5	124.7 (3)	N2A—C8A—C4A	123.1 (3)
C3—C4—C8	118.0 (3)	N1A—C8A—C4A	122.0 (3)
C5—C4—C8	117.2 (3)	C1A—C9A—Br1A	110.6 (2)
C6—C5—C4	120.0 (3)	C1A—C9A—Br2A	111.2 (2)
C6—C5—H5	120.0	Br1A—C9A—Br2A	110.01 (15)
C4—C5—H5	120.0	C1A—C9A—H9A	108.3
C5—C6—C7	118.5 (3)	Br1A—C9A—H9A	108.3
C5—C6—H6	120.7	Br2A—C9A—H9A	108.3
C7—C6—H6	120.7	O1A—C10A—N3A	123.5 (3)
N2—C7—N3	114.0 (3)	O1A—C10A—C11A	123.1 (3)
N2—C7—C6	123.3 (3)	N3A—C10A—C11A	113.4 (3)
N3—C7—C6	122.6 (3)	C10A—C11A—H11D	109.5
N2—C8—N1	114.9 (3)	C10A—C11A—H11E	109.5
N2—C8—C4	122.7 (3)	H11D—C11A—H11E	109.5
N1—C8—C4	122.3 (3)	C10A—C11A—H11F	109.5
C1—C9—Br2	115.1 (2)	H11D—C11A—H11F	109.5
C1—C9—Br1	107.8 (2)	H11E—C11A—H11F	109.5
Br2—C9—Br1	109.38 (15)	C1B—O1B—C2B	110.0 (8)
C1—C9—H9	108.1	O1B—C1B—C2B[i]	112.0 (10)
Br2—C9—H9	108.1	O1B—C1B—H1B1	109.2
Br1—C9—H9	108.1	C2B[i]—C1B—H1B1	109.2
O1—C10—N3	123.2 (3)	O1B—C1B—H1B2	109.2
O1—C10—C11	123.3 (3)	C2B[i]—C1B—H1B2	109.2
N3—C10—C11	113.5 (3)	H1B1—C1B—H1B2	107.9
C10—C11—H11A	109.5	O1B—C2B—C1B[i]	109.4 (10)
C10—C11—H11B	109.5	O1B—C2B—H2B1	109.8

H11A—C11—H11B	109.5	C1Bⁱ—C2B—H2B1	109.8
C10—C11—H11C	109.5	O1B—C2B—H2B2	109.8
H11A—C11—H11C	109.5	C1Bⁱ—C2B—H2B2	109.8
H11B—C11—H11C	109.5	H2B1—C2B—H2B2	108.2
C1A—N1A—C8A	117.6 (3)	C1BA—O1BA—C2BA	109 (8)
C7A—N2A—C8A	117.9 (3)	O1BA—C1BA—C2BAⁱ	100 (9)
C10A—N3A—C7A	127.5 (3)	O1BA—C1BA—H1B3	111.8
C10A—N3A—H3A	117 (2)	C2BAⁱ—C1BA—H1B3	111.8
C7A—N3A—H3A	115 (2)	O1BA—C1BA—H1B4	111.8
N1A—C1A—C2A	124.6 (3)	C2BAⁱ—C1BA—H1B4	111.8
N1A—C1A—C9A	113.4 (3)	H1B3—C1BA—H1B4	109.5
C2A—C1A—C9A	122.1 (3)	O1BA—C2BA—C1BAⁱ	116 (9)
C3A—C2A—C1A	118.0 (3)	O1BA—C2BA—H2B3	108.4
C3A—C2A—H2A	121.0	C1BAⁱ—C2BA—H2B3	108.4
C1A—C2A—H2A	121.0	O1BA—C2BA—H2B4	108.3
C2A—C3A—C4A	119.6 (3)	C1BAⁱ—C2BA—H2B4	108.3
C2A—C3A—H3AB	120.2	H2B3—C2BA—H2B4	107.4
C8—N1—C1—C2	−1.6 (4)	N1A—C1A—C2A—C3A	1.6 (5)
C8—N1—C1—C9	173.1 (2)	C9A—C1A—C2A—C3A	−176.7 (3)
N1—C1—C2—C3	0.4 (5)	C1A—C2A—C3A—C4A	−0.3 (5)
C9—C1—C2—C3	−173.8 (3)	C2A—C3A—C4A—C8A	−1.4 (4)
C1—C2—C3—C4	0.5 (4)	C2A—C3A—C4A—C5A	178.9 (3)
C2—C3—C4—C5	177.3 (3)	C3A—C4A—C5A—C6A	179.6 (3)
C2—C3—C4—C8	−0.1 (4)	C8A—C4A—C5A—C6A	−0.1 (4)
C3—C4—C5—C6	−176.0 (3)	C4A—C5A—C6A—C7A	−0.3 (4)
C8—C4—C5—C6	1.4 (4)	C8A—N2A—C7A—N3A	−177.6 (2)
C4—C5—C6—C7	−0.5 (4)	C8A—N2A—C7A—C6A	0.0 (4)
C8—N2—C7—N3	178.7 (3)	C10A—N3A—C7A—N2A	−159.0 (3)
C8—N2—C7—C6	0.9 (4)	C10A—N3A—C7A—C6A	23.4 (5)
C10—N3—C7—N2	157.9 (3)	C5A—C6A—C7A—N2A	0.4 (5)
C10—N3—C7—C6	−24.3 (5)	C5A—C6A—C7A—N3A	177.8 (3)
C5—C6—C7—N2	−0.8 (5)	C7A—N2A—C8A—N1A	178.3 (2)
C5—C6—C7—N3	−178.3 (3)	C7A—N2A—C8A—C4A	−0.5 (4)
C7—N2—C8—N1	177.8 (3)	C1A—N1A—C8A—N2A	−179.7 (3)
C7—N2—C8—C4	0.1 (4)	C1A—N1A—C8A—C4A	−0.8 (4)
C1—N1—C8—N2	−175.7 (3)	C3A—C4A—C8A—N2A	−179.2 (3)
C1—N1—C8—C4	2.0 (4)	C5A—C4A—C8A—N2A	0.5 (4)
C3—C4—C8—N2	176.4 (3)	C3A—C4A—C8A—N1A	2.0 (4)
C5—C4—C8—N2	−1.2 (4)	C5A—C4A—C8A—N1A	−178.2 (3)
C3—C4—C8—N1	−1.2 (4)	N1A—C1A—C9A—Br1A	−118.3 (2)
C5—C4—C8—N1	−178.8 (3)	C2A—C1A—C9A—Br1A	60.3 (3)
N1—C1—C9—Br2	143.1 (2)	N1A—C1A—C9A—Br2A	119.2 (2)
C2—C1—C9—Br2	−42.1 (4)	C2A—C1A—C9A—Br2A	−62.3 (3)
N1—C1—C9—Br1	−94.6 (3)	C7A—N3A—C10A—O1A	−1.1 (5)
C2—C1—C9—Br1	80.3 (3)	C7A—N3A—C10A—C11A	177.5 (3)
C7—N3—C10—O1	−6.4 (5)	C2B—O1B—C1B—C2Bⁱ	58.1 (11)
C7—N3—C10—C11	174.9 (3)	C1B—O1B—C2B—C1Bⁱ	−56.6 (11)

C8A—N1A—C1A—C2A	−1.1 (4)		C2BA—O1BA—C1BA—C2BA^i	−58 (10)
C8A—N1A—C1A—C9A	177.4 (2)		C1BA—O1BA—C2BA—C1BA^i	68 (11)

Symmetry code: (i) −*x*, −*y*, −*z*+2.

Hydrogen-bond geometry (Å, º)

Cg1, Cg2 and Cg4 are the centroids of rings N1/C1-C4/C8, N2/C4-C8 and N2A/C4A-C8A, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···O1	0.95	2.37	2.886 (4)	113
C6*A*—H6*A*···O1*A*	0.95	2.32	2.871 (5)	116
N3—H3···N2*A*^{ii}	0.89 (3)	2.10 (3)	2.985 (4)	171 (4)
N3*A*—H3*A*···N2^{ii}	0.89 (3)	2.09 (3)	2.950 (4)	163 (3)
C2—H2···N1*A*	0.95	2.56	3.397 (4)	147
C2*A*—H2*A*···O1*B*^{iii}	0.95	2.42	3.344 (5)	163
C11—H11*B*···N1*A*^{ii}	0.98	2.44	3.411 (5)	169
C11*A*—H11*D*···O1^{iv}	0.98	2.46	3.437 (5)	179
C11*A*—H11*E*···N1^{ii}	0.98	2.54	3.459 (4)	156
C3—H3*AA*···Cg4	0.95	2.82	3.548 (3)	134
C2*BA*—H2*B*3···Cg4^v	0.99	2.96	3.82 (9)	145
C9—Br1···Cg1^{iii}	1.94 (1)	3.62 (1)	5.270 (4)	141 (1)
C9—Br1···Cg2^{iii}	1.94 (1)	3.32 (1)	5.247 (4)	173 (1)

Symmetry codes: (ii) −*x*, −*y*, −*z*+1; (iii) −*x*+1, −*y*, −*z*+1; (iv) −*x*−1, −*y*+1, −*z*+1; (v) *x*, *y*, *z*+1.