

# Crystal structure of (1*S*,4*S*)-2,5-diazabicyclo[2.2.1]heptane dibromide

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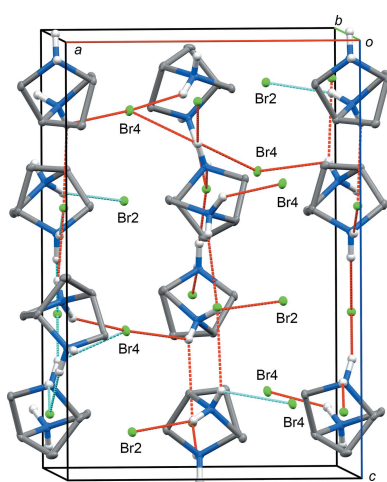
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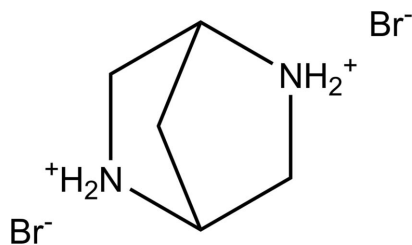
The cage of 2,5-diazabicyclo[2.2.1]heptane is frequently employed in synthetic chemistry as a rigid bicyclic counterpart of the piperazine ring. The 2,5-diazabicyclo[2.2.1]heptane scaffold is incorporated into a variety of compounds having pharmacological and catalytic applications. The unsubstituted parent ring of the system, 2,5-diazabicyclo[2.2.1]heptane itself, has not been structurally characterized. We herein report on the molecular structure of the parent ring in (1*S*,4*S*)-2,5-diazabicyclo[2.2.1]heptane dibromide, C<sub>5</sub>H<sub>12</sub>N<sub>2</sub><sup>2+</sup>·2Br<sup>-</sup>. The asymmetric unit contains two crystallographically independent cages of 2,5-diazabicyclo[2.2.1]heptane. Each cage is protonated at the two nitrogen sites. The overall charge balance is maintained by four crystallographically independent bromide ions. In the crystal, the components of the structure are linked *via* a complex three-dimensional network of N—H···Br hydrogen bonds.

## 1. Chemical context

Derivatives of the bicyclic nucleus of 2,5-diazabicyclo[2.2.1]heptane comprise a wide family of biochemically active compounds (Murineddu *et al.*, 2012), including antibiotics (McGuirk *et al.*, 1992; Remuzon *et al.*, 1993), vasodilating (López-Ortiz *et al.*, 2014) and antitumor agents (Hamblett *et al.*, 2007; Shchekotikhin *et al.*, 2014; Gerstenberger *et al.*, 2016; Laskar *et al.*, 2017). A broad range of these compounds have been found to exhibit potency as nicotinic acetylcholine receptor ligands (Toma *et al.*, 2002; Artali *et al.*, 2005; Bunnelle *et al.*, 2007; Anderson *et al.*, 2008; Li *et al.*, 2010; Beinat *et al.*, 2015; Bertrand *et al.*, 2015). As a result of the occurrence of two chiral centers, 2,5-diazabicyclo[2.2.1]heptanes are utilized as chiral scaffolds in asymmetric catalysis (Jordis *et al.*, 1999; González-Olvera *et al.*, 2008; Castillo *et al.*, 2013; Díaz-de-Villegas *et al.*, 2014; Avila-Ortiz *et al.*, 2015). The diamine system of 2,5-diazabicyclo[2.2.1]heptane is traditionally included in screening libraries as a rigid counterpart of the flexible piperazine ring (Siebeneicher *et al.*, 2016; Dam *et al.*, 2016; Cernak *et al.*, 2017; Llona-Minguez *et al.*, 2017; Wei *et al.*, 2017). As a consequence, numerous synthetic routes for the preparation of 2,5-diazabicyclo[2.2.1]heptane derivatives have been introduced (see: Portoghese & Mikhail, 1966; Jordis *et al.*, 1990; Yakovlev *et al.*, 2000; Fiorelli *et al.*, 2005; Beinat *et al.*, 2013; Cui *et al.*, 2015; Choi *et al.*, 2016 and the references cited therein). At the same time, the reported structural data on 2,5-diazabicyclo[2.2.1]heptane derivatives are surprisingly scarce (see the *Database survey*). Moreover, the parent ring of unsubstituted 2,5-diazabicyclo[2.2.1]heptane has not been structurally characterized. In the framework of current research on caged heterocyclic systems (Britvin & Lotnyk,

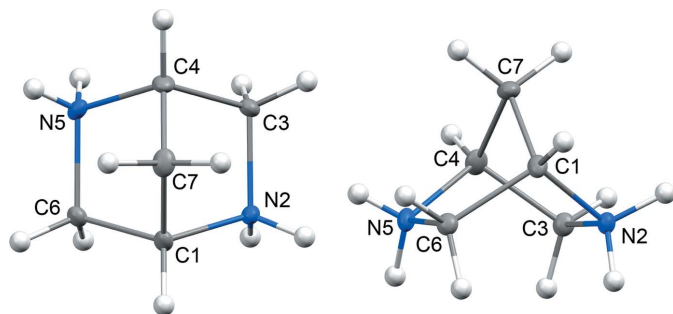


2015; Britvin *et al.*, 2016; 2017*a,b*; Britvin & Rumyantsev, 2017*b*), we herein describe the molecular structure of 2,5-diazabicyclo[2.2.1]heptane (Fig. 1) in its dihydrobromide salt, (1*S*,4*S*)-2,5-diazoniabicyclo[2.2.1]heptane dibromide (**1**).



## 2. Structural commentary

The asymmetric unit of **1** contains two structurally independent cages of 2,5-diazabicyclo[2.2.1]heptane (Fig. 2). The molecular geometries of the cages are statistically different: the biggest discrepancy, 0.044 Å, is observed for N2...N5 [2.868 (3) Å] and N2A...N5A [2.912 (3) Å], whereas the distances between the bridgehead C atoms C1...C4 [2.220 (4) Å] and C1A...C4A [2.226 (4) Å] are statistically the same (see the *Supporting information*). Therefore, in spite of bridge-imparted rigidity, the hexagonal ring of 2,5-diazabicyclo[2.2.1]heptane can be affected by some geometric distortions. The framework of 2,5-diazabicyclo[2.2.1]heptane is frequently considered to be the bicyclic counterpart of piperazine where the occurrence of the C1–C7–C4 bridge imparts rigidity to the hexagonal ring (Kiely *et al.*, 1991; Beinat *et al.*, 2013; 2015). It is worth noting that the bicyclic bridged structure of 2,5-diazabicyclo[2.2.1]heptane determines the boat conformation of its cage (Fig. 1). Contrary to that, the piperazine ring is flexible and can adopt four different conformations: chair, boat, twist-boat and half-boat, the former being the energetically most favourable (SenGupta *et al.*, 2014). A comparison of the hexagonal rings of 2,5-diazabicyclo[2.2.1]heptane and the chair conformer of piperazine (Fig. 2) shows that the interatomic distances between the opposing nitrogen atoms are remarkably close. The latter feature can be important because the nitrogen sites are known



**Figure 1**

Two views of the diprotonated 2,5-diazabicyclo[2.2.1]heptane parent ring in **1** (in one of the two independent molecules in the asymmetric unit). The atomic numbering scheme is according to IUPAC notation. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are depicted as fixed-size spheres of arbitrary radius. The bromide counter-ions have been omitted for clarity.

**Table 1**

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N2–H2A...Br3	0.93 (3)	2.49 (3)	3.358 (2)	156 (2)
N5–H5A...Br4	0.92 (3)	2.44 (3)	3.261 (2)	148 (3)
N5–H5B...Br1 <sup>i</sup>	0.78 (3)	2.50 (3)	3.242 (2)	161 (3)
N2A–H2AA...Br3	0.89 (3)	2.53 (4)	3.344 (2)	152 (3)
N2A–H2AB...Br1 <sup>ii</sup>	0.86 (3)	2.48 (3)	3.273 (2)	155 (2)
N5A–H5AA...Br2	0.91 (3)	2.42 (3)	3.292 (2)	160 (3)
N5A–H5AB...Br1	0.77 (3)	2.77 (3)	3.399 (2)	140 (3)

Symmetry codes: (i)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (ii)  $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$ .

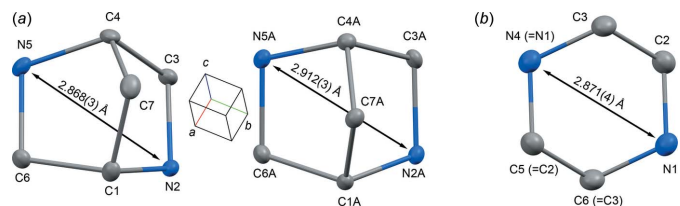
to be pharmacophores frequently determining the biochemical activity of piperazine derivatives (Patel & Park, 2013). Therefore, the implication of the 2,5-diazabicyclo[2.2.1]-heptane scaffold as a piperazine analogue in screening libraries looks quite reasonable from the structural point of view.

## 3. Supramolecular features

In the crystal structure of **1**, the protonated nitrogen sites in the two symmetrically non-equivalent 2,5-diazabicyclo[2.2.1]-heptane cages are counter balanced by the four structurally independent bromide ions. This results in the emergence of a complicated network of hydrogen bonds (Fig. 3). Hydrogen-bonded amine molecules are arranged into infinite slabs parallel to (100). The slabs are linked by N–H...Br hydrogen bonds into a three-dimensional network. The full listing of N–H...Br bonds is given in Table 1. This three-dimensional net of hydrogen bonds is much more complex than the flat ‘zigzag’ hydrogen bonding occurring in the geometrically similar cage of 7-azabicyclo[2.2.1]heptane (7-azanorbornane) (Britvin & Rumyantsev, 2017*a*).

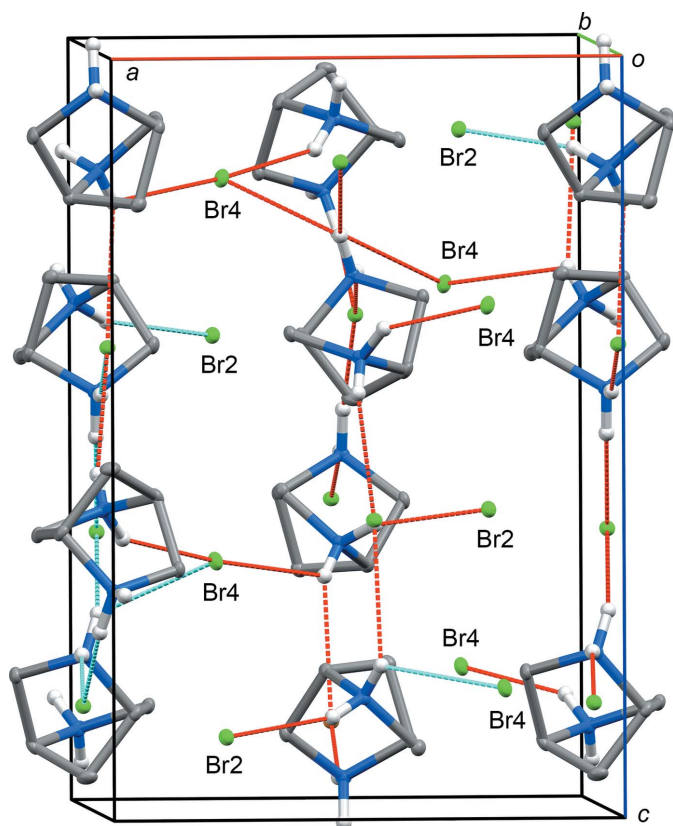
## 4. Database survey

In spite of extensive studies of 2,5-diazabicyclo[2.2.1]heptane derivatives (see the *Chemical context*), there are just 14 structures which comprise this bicyclic system in the Cambridge Structural Database (CSD version 5.38, May 2017;



**Figure 2**

(*a*) The two independent molecules of 2,5-diazabicyclo[2.2.1]heptane in the crystal structure of **1** (this work). (*b*) The chair conformer of piperazine in piperazine-1,4-dium dibromide monohydrate (Bujak, 2015). The atomic numbering schemes are given in IUPAC notation. Symmetrically equivalent atoms in the piperazine ring are noted in parentheses. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms, bromide counter-ions and water molecules have been omitted for clarity.


**Figure 3**

Hydrogen bonding in the crystal structure of **1**. Protonated molecules of 2,5-diazabicyclo[2.2.1]heptane are linked by N–H...Br hydrogen bonds, forming slabs parallel to (100). These slabs are linked by N–H...Br hydrogen bonds into a three-dimensional network. Displacement ellipsoids are drawn at the 30% probability level. H atoms not involved in hydrogen bonding have been omitted for clarity.

Groom *et al.*, 2016). Jordis *et al.* (1999) reported a series of substituted (1*S*,4*S*)-2,5-diazabicyclo[2.2.1]heptanes and provided the first structure determination of the 1,2,5-substituted derivative. Lauteslager *et al.* (2001) carried out a comparative study of chromophores containing piperazine and 2,5-diazabicyclo[2.2.1]heptane groups. Apart from the majority of the latest studies, which are devoted to different aspects of the organic chemistry of the title scaffold (Alvaro *et al.*, 2007; Mereiter *et al.*, 2007; Krasnov *et al.*, 2008; Melgar-Fernández *et al.*, 2008; Wu *et al.*, 2011), Pérez *et al.* (2011) and Castillo *et al.* (2013) have reported the first examples of coordination compounds between copper(II) and substituted 2,5-diazabicyclo[2.2.1]heptanes. To the best of our knowledge, no structural data on the unsubstituted parent ring of 2,5-diazabicyclo[2.2.1]heptane have been reported.

## 5. Synthesis and crystallization

(1*S*,4*S*)-Diazabicyclo[2.2.1]heptane dihydrobromide (**1**) was obtained from Sigma–Aldrich and found to be analytically pure [analysis calculated for C<sub>5</sub>H<sub>12</sub>Br<sub>2</sub>N<sub>2</sub> (259.97): C 23.10, H 4.65, N 10.78; found C 23.03, H 4.71, N 10.69]. NMR spectra (Bruker Avance 400 spectrometer, using SiMe<sub>4</sub> as an external

**Table 2**

Experimental details.

Crystal data	
Chemical formula	C <sub>5</sub> H <sub>12</sub> N <sub>2</sub> <sup>2+</sup> ·2Br <sup>−</sup>
<i>M</i> <sub>r</sub>	259.99
Crystal system, space group	Orthorhombic, <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.7298 (6), 11.8643 (5), 14.4933 (7)
<i>V</i> (Å <sup>3</sup> )	1673.07 (15)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
$\mu$ (mm <sup>−1</sup> )	9.61
Crystal size (mm)	0.2 × 0.08 × 0.05
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2015)
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	15838, 4031, 3959
<i>R</i> <sub>int</sub>	0.026
(sin θ/λ) <sub>max</sub> (Å <sup>−1</sup> )	0.661
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.014, 0.035, 1.02
No. of reflections	4031
No. of parameters	195
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>−3</sup> )	0.53, −0.34
Absolute structure	Flack <i>x</i> determined using 1676 quotients [( <i>I</i> <sup>+</sup> ) − ( <i>I</i> <sup>−</sup> )] / [( <i>I</i> <sup>+</sup> ) + ( <i>I</i> <sup>−</sup> )] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.009 (5)

Computer programs: *APEX2* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2008), *OLEX2* (Dolomanov *et al.*, 2009) and *pubCIF* (Westrip, 2010).

standard) are consistent with the previously published data (Melgar-Fernández *et al.*, 2008) and confirm the purity of the substance (atomic numbering according to Fig. 1): <sup>1</sup>H NMR (400.13 MHz, D<sub>2</sub>O): δ = 4.67 (*d*, 2H, CH at C1 and C4), 3.65–3.57 (*m*, 4H, CH<sub>2</sub> at C3 and C6), 2.29 (*s*, 2H, CH<sub>2</sub> at C7). <sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, D<sub>2</sub>O): δ = 56.36 (*s*, NCHCH<sub>2</sub>, C1 and C4), 47.09 (*s*, NCH<sub>2</sub>CH, C3 and C6), 34.73 (*s*, CHCH<sub>2</sub>CH, C7). Crystals of **1** suitable for structural study were obtained by slow evaporation of a saturated aqueous solution at room temperature.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms at nitrogen sites (*i.e.* those involved in hydrogen bonding) were freely refined whereas hydrogen atoms at all carbon centers were treated with fixed *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C) and riding coordinates (C–H = 0.97–0.98 Å).

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## supporting information

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Crystal structure of (1*S*,4*S*)-2,5-diazoniabicyclo[2.2.1]heptane dibromide

Sergey N. Britvin and Andrey M. Rumyantsev

## Computing details

Data collection: *APEX2* (Bruker, 2015); cell refinement: *SAINTE* (Bruker, 2015); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2008) and *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

(1*S*,4*S*)-2,5-Diazoniabicyclo[2.2.1]heptane dibromide

## Crystal data

$C_5H_{12}N_2^{2+} \cdot 2Br^-$

$M_r = 259.99$

Orthorhombic,  $P2_12_12_1$

$a = 9.7298$  (6) Å

$b = 11.8643$  (5) Å

$c = 14.4933$  (7) Å

$V = 1673.07$  (15) Å<sup>3</sup>

$Z = 8$

$F(000) = 1008$

$D_x = 2.064$  Mg m<sup>-3</sup>

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

Cell parameters from 9887 reflections

$\theta = 2.5\text{--}31.5^\circ$

$\mu = 9.61$  mm<sup>-1</sup>

$T = 100$  K

Block, colourless

$0.2 \times 0.08 \times 0.05$  mm

## Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(SADABS; Bruker, 2015)

15838 measured reflections

4031 independent reflections

3959 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\text{max}} = 28.0^\circ$ ,  $\theta_{\text{min}} = 2.2^\circ$

$h = -12 \rightarrow 12$

$k = -13 \rightarrow 15$

$l = -19 \rightarrow 17$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.014$

$wR(F^2) = 0.035$

$S = 1.02$

4031 reflections

195 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0162P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\text{max}} = 0.53$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.34$  e Å<sup>-3</sup>

Absolute structure: Flack  $x$  determined using

1676 quotients  $[(I^+) - (I^-)] / [(I^+) + (I^-)]$  (Parsons *et al.*, 2013)

Absolute structure parameter: 0.009 (5)

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.5925 (3)	0.3998 (2)	0.37609 (18)	0.0160 (5)
H1	0.6722	0.4501	0.3797	0.019*
N2	0.4926 (2)	0.4270 (2)	0.29906 (15)	0.0143 (4)
H2A	0.479 (3)	0.505 (3)	0.2960 (18)	0.011 (7)*
H2B	0.519 (4)	0.403 (3)	0.245 (3)	0.038 (11)*
C3	0.3610 (3)	0.3669 (2)	0.32592 (18)	0.0162 (5)
H3A	0.3377	0.3084	0.2818	0.019*
H3B	0.2848	0.4192	0.3310	0.019*
C4	0.3987 (3)	0.3168 (3)	0.41995 (18)	0.0183 (6)
H4	0.3203	0.2983	0.4596	0.022*
N5	0.4954 (2)	0.2198 (2)	0.40090 (17)	0.0167 (5)
H5A	0.454 (3)	0.170 (3)	0.361 (2)	0.024 (9)*
H5B	0.504 (3)	0.186 (3)	0.446 (2)	0.013 (8)*
C6	0.6277 (3)	0.2749 (2)	0.36993 (18)	0.0158 (5)
H6A	0.6511	0.2534	0.3073	0.019*
H6B	0.7033	0.2557	0.4106	0.019*
C7	0.4971 (3)	0.4045 (2)	0.45944 (18)	0.0205 (6)
H7A	0.4546	0.4778	0.4678	0.025*
H7B	0.5411	0.3802	0.5161	0.025*
C1A	0.6072 (3)	0.8241 (2)	0.59473 (17)	0.0139 (5)
H1A	0.6918	0.8624	0.5758	0.017*
N2A	0.4792 (2)	0.8628 (2)	0.54520 (15)	0.0141 (4)
H2AA	0.478 (4)	0.844 (3)	0.486 (2)	0.033 (10)*
H2AB	0.476 (3)	0.935 (3)	0.5432 (19)	0.010 (7)*
C3A	0.3626 (2)	0.8184 (2)	0.60478 (19)	0.0160 (5)
H3AA	0.3103	0.7610	0.5726	0.019*
H3AB	0.3011	0.8786	0.6233	0.019*
C4A	0.4384 (3)	0.7687 (2)	0.68803 (18)	0.0152 (5)
H4A	0.3835	0.7635	0.7446	0.018*
N5A	0.5014 (2)	0.6592 (2)	0.65645 (16)	0.0154 (4)
H5AA	0.437 (3)	0.612 (3)	0.631 (2)	0.019 (8)*
H5AB	0.534 (3)	0.629 (3)	0.698 (2)	0.021 (9)*
C6A	0.6121 (3)	0.6950 (2)	0.58809 (17)	0.0163 (5)
H6AA	0.5907	0.6694	0.5262	0.020*
H6AB	0.7015	0.6662	0.6059	0.020*
C7A	0.5656 (3)	0.8433 (2)	0.69531 (17)	0.0161 (5)
H7AA	0.6328	0.8149	0.7389	0.019*
H7AB	0.5439	0.9214	0.7087	0.019*
Br1	0.52194 (2)	0.62674 (2)	0.88905 (2)	0.01450 (6)

Br2	0.22116 (2)	0.51516 (2)	0.60873 (2)	0.01567 (6)
Br3	0.46504 (3)	0.70005 (2)	0.35710 (2)	0.01494 (6)
Br4	0.26144 (3)	0.04454 (2)	0.32745 (2)	0.01680 (6)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0142 (12)	0.0157 (14)	0.0181 (13)	-0.0018 (10)	-0.0058 (10)	0.0015 (10)
N2	0.0145 (10)	0.0138 (12)	0.0148 (10)	0.0003 (9)	0.0011 (8)	0.0031 (9)
C3	0.0109 (11)	0.0191 (14)	0.0185 (12)	-0.0006 (10)	0.0001 (10)	0.0020 (11)
C4	0.0136 (12)	0.0217 (15)	0.0195 (12)	0.0003 (10)	0.0063 (10)	0.0044 (11)
N5	0.0191 (11)	0.0135 (12)	0.0174 (11)	-0.0037 (9)	-0.0026 (9)	0.0043 (9)
C6	0.0125 (11)	0.0177 (14)	0.0173 (13)	0.0002 (10)	-0.0025 (9)	0.0005 (10)
C7	0.0285 (15)	0.0199 (15)	0.0130 (12)	0.0033 (11)	-0.0022 (10)	-0.0030 (10)
C1A	0.0107 (11)	0.0138 (14)	0.0173 (13)	-0.0008 (9)	-0.0006 (9)	0.0023 (10)
N2A	0.0172 (11)	0.0115 (12)	0.0135 (10)	0.0008 (9)	-0.0007 (8)	0.0004 (8)
C3A	0.0108 (11)	0.0168 (14)	0.0206 (13)	0.0024 (9)	-0.0019 (9)	0.0010 (11)
C4A	0.0143 (12)	0.0164 (14)	0.0150 (12)	-0.0014 (10)	0.0001 (9)	0.0016 (10)
N5A	0.0148 (10)	0.0141 (11)	0.0173 (11)	-0.0008 (9)	-0.0031 (8)	0.0034 (9)
C6A	0.0147 (12)	0.0163 (14)	0.0178 (12)	0.0029 (10)	0.0008 (9)	0.0006 (10)
C7A	0.0173 (12)	0.0147 (14)	0.0162 (12)	-0.0020 (10)	-0.0027 (10)	0.0012 (10)
Br1	0.01665 (12)	0.01277 (12)	0.01407 (12)	-0.00094 (9)	-0.00018 (9)	-0.00022 (9)
Br2	0.01471 (12)	0.01456 (13)	0.01775 (11)	-0.00228 (9)	-0.00073 (10)	0.00003 (10)
Br3	0.01588 (12)	0.01335 (13)	0.01560 (12)	0.00039 (9)	0.00032 (9)	0.00008 (9)
Br4	0.01390 (12)	0.01434 (13)	0.02214 (12)	-0.00278 (9)	0.00270 (9)	-0.00030 (10)

*Geometric parameters (Å, °)*

C1—H1	0.9800	C3A—H3AA	0.9700
C1—N2	1.516 (3)	C3A—H3AB	0.9700
C1—C6	1.523 (4)	C3A—C4A	1.532 (4)
C1—C7	1.525 (4)	C4A—H4A	0.9800
N2—H2A	0.93 (3)	C4A—N5A	1.508 (3)
N2—H2B	0.87 (4)	C4A—C7A	1.525 (4)
N2—C3	1.516 (3)	N5A—H5AA	0.91 (3)
C3—H3A	0.9700	N5A—H5AB	0.77 (3)
C3—H3B	0.9700	N5A—C6A	1.523 (3)
C3—C4	1.532 (4)	C6A—H6AA	0.9700
C4—H4	0.9800	C6A—H6AB	0.9700
C4—N5	1.512 (4)	C7A—H7AA	0.9700
C4—C7	1.525 (4)	C7A—H7AB	0.9700
N5—H5A	0.92 (3)	N2—N5	2.868 (3)
N5—H5B	0.78 (3)	N2A—N5A	2.912 (3)
N5—C6	1.512 (3)	C1—C4	2.220 (4)
C6—H6A	0.9700	C1A—C4A	2.226 (4)
C6—H6B	0.9700	C3—C6	2.887 (4)
C7—H7A	0.9700	C3A—C6A	2.845 (4)
C7—H7B	0.9700	N2—C7	2.340 (4)



C1A—H1A	0.9800	N2A—C7A	2.344 (3)
C1A—N2A	1.509 (3)	N5—C7	2.350 (4)
C1A—C6A	1.535 (4)	N5A—C7A	2.340 (4)
C1A—C7A	1.530 (3)	C3—C7	2.387 (4)
N2A—H2AA	0.89 (3)	C3A—C7A	2.390 (4)
N2A—H2AB	0.86 (3)	C6—C7	2.380 (4)
N2A—C3A	1.521 (3)	C6A—C7A	2.391 (4)
N2—C1—H1	114.7	N2A—C1A—H1A	114.8
N2—C1—C6	107.9 (2)	N2A—C1A—C6A	107.4 (2)
N2—C1—C7	100.66 (19)	N2A—C1A—C7A	101.0 (2)
C6—C1—H1	114.7	C6A—C1A—H1A	114.8
C6—C1—C7	102.7 (2)	C7A—C1A—H1A	114.8
C7—C1—H1	114.7	C7A—C1A—C6A	102.5 (2)
C1—N2—H2A	109.5 (17)	C1A—N2A—H2AA	113 (2)
C1—N2—H2B	114 (3)	C1A—N2A—H2AB	111 (2)
C1—N2—C3	104.64 (19)	C1A—N2A—C3A	103.90 (18)
H2A—N2—H2B	109 (3)	H2AA—N2A—H2AB	102 (3)
C3—N2—H2A	111.1 (18)	C3A—N2A—H2AA	117 (2)
C3—N2—H2B	109 (3)	C3A—N2A—H2AB	110 (2)
N2—C3—H3A	111.4	N2A—C3A—H3AA	111.2
N2—C3—H3B	111.4	N2A—C3A—H3AB	111.2
N2—C3—C4	102.0 (2)	N2A—C3A—C4A	102.76 (19)
H3A—C3—H3B	109.2	H3AA—C3A—H3AB	109.1
C4—C3—H3A	111.4	C4A—C3A—H3AA	111.2
C4—C3—H3B	111.4	C4A—C3A—H3AB	111.2
C3—C4—H4	114.9	C3A—C4A—H4A	114.9
N5—C4—C3	106.4 (2)	N5A—C4A—C3A	106.7 (2)
N5—C4—H4	114.9	N5A—C4A—H4A	114.9
N5—C4—C7	101.4 (2)	N5A—C4A—C7A	101.0 (2)
C7—C4—C3	102.7 (2)	C7A—C4A—C3A	102.9 (2)
C7—C4—H4	114.9	C7A—C4A—H4A	114.9
C4—N5—H5A	110 (2)	C4A—N5A—H5AA	112 (2)
C4—N5—H5B	108 (2)	C4A—N5A—H5AB	109 (3)
C4—N5—C6	104.7 (2)	C4A—N5A—C6A	104.2 (2)
H5A—N5—H5B	104 (3)	H5AA—N5A—H5AB	108 (3)
C6—N5—H5A	118 (2)	C6A—N5A—H5AA	113.2 (19)
C6—N5—H5B	113 (2)	C6A—N5A—H5AB	110 (2)
C1—C6—H6A	111.3	C1A—C6A—H6AA	111.3
C1—C6—H6B	111.3	C1A—C6A—H6AB	111.3
N5—C6—C1	102.2 (2)	N5A—C6A—C1A	102.4 (2)
N5—C6—H6A	111.3	N5A—C6A—H6AA	111.3
N5—C6—H6B	111.3	N5A—C6A—H6AB	111.3
H6A—C6—H6B	109.2	H6AA—C6A—H6AB	109.2
C1—C7—C4	93.4 (2)	C1A—C7A—H7AA	113.0
C1—C7—H7A	113.0	C1A—C7A—H7AB	113.0
C1—C7—H7B	113.0	C4A—C7A—C1A	93.6 (2)
C4—C7—H7A	113.0	C4A—C7A—H7AA	113.0

C4—C7—H7B	113.0	C4A—C7A—H7AB	113.0
H7A—C7—H7B	110.4	H7AA—C7A—H7AB	110.4
C1—N2—C3—C4	3.2 (3)	C1A—N2A—C3A—C4A	5.5 (3)
N2—C1—C6—N5	-71.1 (2)	N2A—C1A—C6A—N5A	-74.2 (2)
N2—C1—C7—C4	56.3 (2)	N2A—C1A—C7A—C4A	56.7 (2)
N2—C3—C4—N5	-73.1 (2)	N2A—C3A—C4A—N5A	-75.1 (2)
N2—C3—C4—C7	33.0 (3)	N2A—C3A—C4A—C7A	30.8 (3)
C3—C4—N5—C6	71.2 (2)	C3A—C4A—N5A—C6A	67.9 (2)
C3—C4—C7—C1	-55.1 (2)	C3A—C4A—C7A—C1A	-53.4 (2)
C4—N5—C6—C1	0.8 (3)	C4A—N5A—C6A—C1A	4.5 (2)
N5—C4—C7—C1	54.9 (2)	N5A—C4A—C7A—C1A	56.8 (2)
C6—C1—N2—C3	69.0 (2)	C6A—C1A—N2A—C3A	67.2 (2)
C6—C1—C7—C4	-55.1 (2)	C6A—C1A—C7A—C4A	-54.1 (2)
C7—C1—N2—C3	-38.2 (2)	C7A—C1A—N2A—C3A	-39.8 (2)
C7—C1—C6—N5	34.7 (2)	C7A—C1A—C6A—N5A	31.7 (2)
C7—C4—N5—C6	-35.9 (2)	C7A—C4A—N5A—C6A	-39.3 (2)

## Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2A...Br3	0.93 (3)	2.49 (3)	3.358 (2)	156 (2)
N5—H5A...Br4	0.92 (3)	2.44 (3)	3.261 (2)	148 (3)
N5—H5B...Br1 <sup>i</sup>	0.78 (3)	2.50 (3)	3.242 (2)	161 (3)
N2A—H2AA...Br3	0.89 (3)	2.53 (4)	3.344 (2)	152 (3)
N2A—H2AB...Br1 <sup>ii</sup>	0.86 (3)	2.48 (3)	3.273 (2)	155 (2)
N5A—H5AA...Br2	0.91 (3)	2.42 (3)	3.292 (2)	160 (3)
N5A—H5AB...Br1	0.77 (3)	2.77 (3)	3.399 (2)	140 (3)

Symmetry codes: (i)  $-x+1, y-1/2, -z+3/2$ ; (ii)  $-x+1, y+1/2, -z+3/2$ .