2-Bromo-6-hydrazinylpyridine

Valeri V. Mossine,[a]* Steven P. Kelley[b] and Thomas P. Mawhinney[a]

[a]Department of Biochemistry, University of Missouri, Columbia, MO 65211, USA, and [b]Department of Chemistry, University of Missouri, Columbia, MO 65211, USA. *Correspondence e-mail: MossineV@missouri.edu

The title compound, $C_5H_6BrN_3$, crystallizes in the orthorhombic space group $P2_12_12_1$ with two molecules with different conformations in the asymmetric unit. In the crystal, N—H···N and bifurcated N—H···(N,N) hydrogen bonds link the molecules into [100] chains; a short Br···Br halogen bond and π–π stacking interactions are also observed.

3D view

Chemical scheme
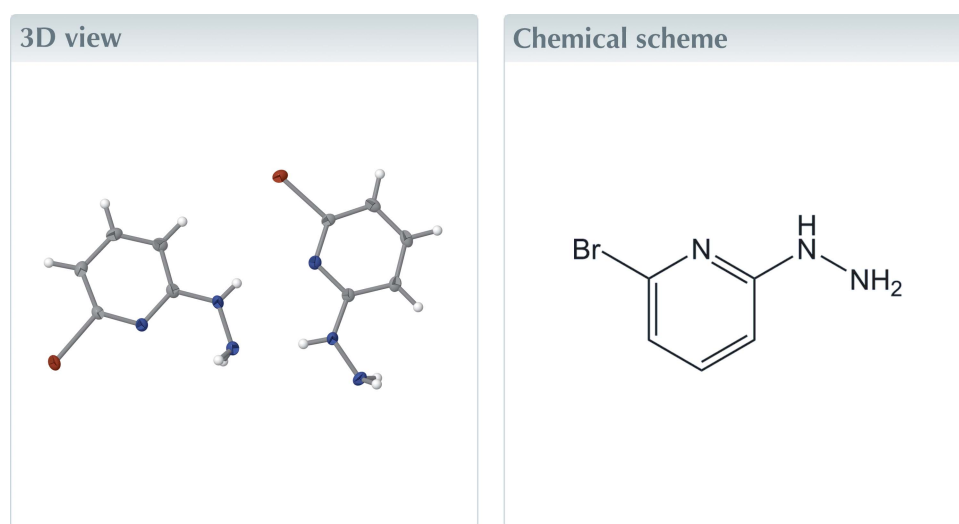
Structure description

Since Emil Fischer's discovery of phenylhydrazine nearly 150 years ago (Kauffman & Ciula, 1977), there has been a persistent interest in arylhydrazines because of their numerous applications in organic chemistry, for instance, as synthetic precursors to a number of antimicrobial (Rollas & Küçükgüzel, 2007), thrombopoietic (Kuter, 2010), anti-inflammatory (Fraga & Barreiro, 2006) or vasodilatory (Reece, 1981) drugs, but also due to their presence in wild and cultivated mushrooms, with a history of neurotoxic and carcinogenic effects (Toth, 2000). In the course of our search for inhibitors of bacterial virulence factors (Mossine *et al.*, 2016, 2020), we prepared the title compound, which was considered a potential precursor for pharmacologically active, metal-binding hydrazones. Here we report its crystal structure.

The title compound, (I), crystallizes in the orthorhombic space group $P2_12_12_1$, with eight molecules per unit cell. The asymmetric unit contains two conformationally non-equivalent molecules of 6-bromopyridin-2-ylhydrazine, (I1) and (I2), as shown in Fig. 1. All bond lengths and angles are within their expected ranges. The molecules are essentially flat, with the greatest deviations from the average molecular planes, among the non-hydrogen atoms, found for N2 at 0.081 (2) Å and N5 at 0.073 (2) Å in (I1) and (I2), respectively. The spatial arrangements of the hydrazino groups, as defined by the torsion angles H2A—N2—N3—H3A = 137 (3)° and H5—N5—N6—H6A = 121 (3)°, correspond to the low-energy conformation that has been calculated for acyl hydrazides (Centore *et al.*, 2010). There is a notable difference between the conformations of (I1)

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N2—H2A···N4	0.80 (3)	2.36 (3)	3.058 (3)	146 (3)
N3—H3A···N6[i]	0.85 (3)	2.43 (3)	3.212 (3)	154 (3)
N3—H3A···N5[ii]	0.85 (3)	2.67 (3)	3.149 (3)	117 (3)
N3—H3B···N2[iii]	0.84 (4)	2.74 (4)	3.543 (3)	161 (3)
N3—H3B···N6[ii]	0.84 (4)	2.69 (3)	3.183 (3)	119 (2)
N5—H5···N3	0.86 (3)	2.06 (3)	2.913 (3)	173 (3)
N6—H6B···N1[i]	0.82 (3)	2.46 (3)	3.257 (3)	164 (3)

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

Table 2
Halogen-bond geometry (Å, °).

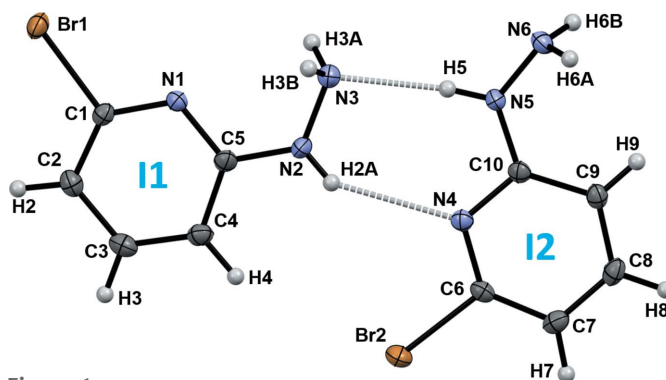| $C-D\cdots A-C$	$D\cdots A$	$C-D\cdots A$	$D\cdots A-C$	Symmetry code
C6—Br2···Br1—C1	3.6328 (7)	169.39 (6)	103.45 (7)	$-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$

Figure 1
Atomic numbering and displacement ellipsoids at the 50% probability level for molecules (**I1**) and (**I2**). Hydrogen bonds are shown as dashed lines.
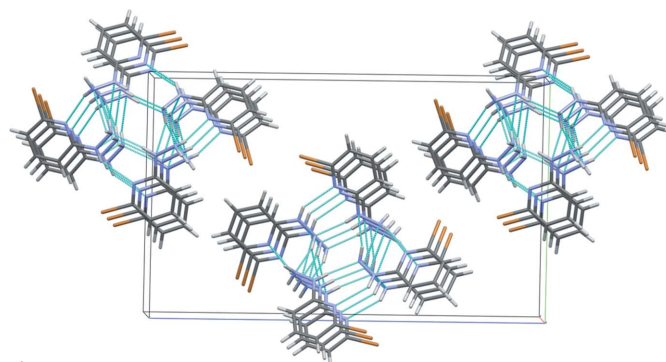

Figure 2
Molecular packing of (**I**). Hydrogen bonds are shown as cyan dotted lines. Crystallographic axes colour codes: *a* – red; *b* – green; *c* – blue.

and (**I2**), however. While in (**I1**) the hydrazine nitrogen atom N3 is in the *syn*-disposition with respect to the pyridine nitrogen atom N1, with N1—C5—N2—N3 = 5.4 (3)°, in (**I2**) the hydrazine group is in the *anti*-conformation, with the corresponding torsion angle N4—C10—N5—N6 = 171.0 (2)°. For comparison, in 3-chloropyrid-2-ylhydrazine (Wang *et al.*, 2010), the hydrazine group is in the *syn*-conformation, with the respective torsion angle being −9.6°. The only other structural analogue of (**I**) for which X-ray diffraction data are available is 2-hydrazinopyridine; however, no crystal structure of this molecule as a free base is known. In crystalline palladium(II) (Drożdżewski *et al.*, 2006) and copper(I) (Healy *et al.* 1988) complexes of 2-hydrazinopyridine, both the terminal hydrazine and pyridine nitrogen atoms are co-ordinated to the same metal ion, thus stabilizing the *syn*-conformation of this ligand. In the 2-hydrazinopyridine dihydrochloride salt (Zora *et al.*, 2006), both the terminal hydrazine and pyridine nitrogen atoms are protonated and thus forced into the *anti*-conformation.

The conventional hydrogen bonding in the crystal structure of (**I**) is extensive and involves all nitrogen atoms of both hydrazine groups and pyridine rings (Table 1) and is shown in Fig. 2. The hydrogen-bonding pattern is represented by a network of infinite chains, which propagate in the [100] direction. This network features $R_2^2(7)$ rings, which are formed by almost coplanar molecules (**I1**) and (**I2**), as shown in Fig. 1, and which represent the shortest intermolecular heteroatom contacts in the crystal. A centrepiece of the network is N3, which participates in five short heteroatom contacts, once as

an acceptor and four times as a donor of hydrogen bonds [two bifurcated N—H···(N,N) links]. Over half the hydrogen-bonding contacts are multicentered and include two bifurcated hydrogen bonds for donor atoms H3*A* and H3*B*, and N6 acts as a double acceptor (Fig. 2; Table 1).

In addition, there is one short intermolecular contact, Br1···Br2 [3.6328 (7) Å], which satisfies the distance and directionality conditions (Table 2) for a halogen bond (Desiraju *et al.*, 2013), with Br2 serving as a donor and Br1 as an acceptor of the bond, as shown in Fig. 3. Intermolecular non-polar interactions, which may contribute to the stability of molecular packing in the crystal, are represented by hydrogen–carbon contacts between the aromatic rings; the shortest of these contacts, C6—H6*A*···C9 [H6*A*···C9[i] = 2.72 (3) Å, symmetry code: (i) −1 + *x*, *y*, *z*] is about 0.18 Å shorter than the sum of the van der Waals radii. The aromatic

Table 3
π–π stacking geometry (Å, °).

(*a*) perpendicular distance of *Cg*(*I*) on ring *J*; (*b*) perpendicular distance of *Cg*(*J*) on ring *I*; (*c*) dihedral angle between Planes *I* and *J*; (*d*) angle between *Cg*(*I*)–>*Cg*(*J*) vector and normal to plane *I*; (*e*) angle between *Cg*(*I*)–>*Cg*(*J*) vector and normal to plane *J*.

$Cg(I)\cdots Cg(J)$	$Cgi\text{-}Cgj$	$Cg(I)\text{-perp}^a$	$Cg(J)\text{-perp}^b$	α^{ac}	β^{ad}	γ^e	Slippage
$Cg1\cdots Cg1^{iv}$	3.9607 (14)	3.4889 (10)	−3.4890 (10)	0.03 (11)	28.2	28.2	1.875
$Cg1\cdots Cg1^{v}$	3.9605 (14)	−3.4889 (10)	3.4888 (10)	0.03 (11)	28.2	28.2	1.875
$Cg2\cdots Cg2^{iv}$	3.9607 (14)	3.4345 (9)	−3.4346 (9)	0.00 (11)	29.9	29.9	1.972
$Cg2\cdots Cg2^{v}$	3.9605 (14)	−3.4345 (9)	3.4345 (9)	0.00 (11)	29.9	29.9	1.972

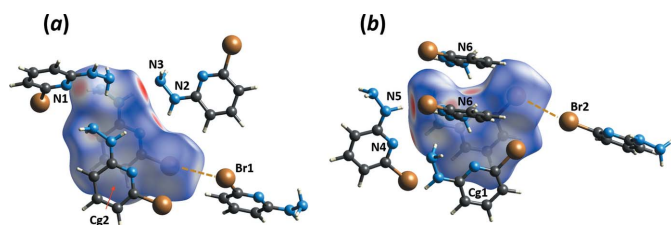Symmetry codes: (iv) $x - 1, y, z$; (v) $x + 1, y, z$.

Figure 3
Views of the Hirshfeld surface for (*a*) molecule (**I2**) and (*b*) molecule (**I1**), mapped over d_{norm} in the range −0.56 to 0.97 a.u. with the blue-to-red color palette reflecting distances from a point on the surface to the closest nuclei. The neighboring molecules involved in the shortest N—H···N hydrogen bonds, the Br···Br halogen bond, and the $Cg···Cg$ stacking interactions are shown.

rings of both (**I1**) and (**I2**) are involved in a well-defined system of staggered π–π stacking interactions (Table 3). These various interactions can be seen in the Hirshfeld surface of the title compound (Fig. 3).

Synthesis and crystallization

The title compound was prepared following an established synthetic route (Zoppellaro *et al.*, 2004). Specifically, 8.0 g (34 mmoles) of 2,6-dibromopyridine, 15 ml (310 mmoles) of hydrazine hydrate, and 2 ml of 1-propanol were heated at 80°C for 12 h. The reaction mixture slowly separated into two layers, with the lower layer taking about 5 ml, then the mixture homogenized back. After cooling overnight at 4°C, the solution deposited pale-yellow needles of the title compound suitable for further X-ray diffraction studies.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. Enantiopurity of the crystal chosen for data collection was established on the basis of the Flack absolute structure parameter determined [0.012 (5) for 999 quotients (Parsons *et al.*, 2013)].

Funding information

References

Bruker (2021). *AXScale*, *SAINT* and *APEX3*. Bruker AXS Inc., Madison, Wisconsin, USA.

Centore, R., Carella, A., Tuzi, A., Capobianco, A. & Peluso, A. (2010). *CrystEngComm*, **12**, 1186–1193.

Desiraju, G. R., Ho, P. S., Kloo, L., Legon, A. C., Marquardt, R., Metrangolo, P., Politzer, P., Resnati, G. & Rissanen, K. (2013). *Pure Appl. Chem.* **85**, 1711–1713.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Drożdżewski, P., Musiała, M. & Kubiak, M. (2006). *Aust. J. Chem.* **59**, 329–335.

Table 4
Experimental details.

Crystal data	
Chemical formula	$C_5H_6BrN_3$
M_r	188.04
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	150
a, b, c (Å)	3.9606 (3), 13.9649 (9), 23.0332 (14)
V (Å^3)	1273.95 (15)
Z	8
Radiation type	Cu $K\alpha$
μ (mm^{-1})	8.02
Crystal size (mm)	$0.24 \times 0.04 \times 0.03$
Data collection	
Diffractometer	Bruker APEXII area detector
Absorption correction	Multi-scan (*AXScale*; Bruker, 2021)
T_{min}, T_{max}	0.521, 0.754
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25559, 2564, 2546
R_{int}	0.027
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.624
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.013, 0.033, 1.07
No. of reflections	2564
No. of parameters	181
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.27, −0.36
Absolute structure	Flack x determined using 999 quotients [$(I^+)-(I^-)]/[(I^+)+(I^-)$] (Parsons *et al.*, 2013)
Absolute structure parameter	0.012 (5)

Computer programs: *APEX3* and *SAINT* (Bruker, 2021), *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015), *Crystal Explorer 17.5* (Mackenzie *et al.*, 2017), *Mercury* (Macrae *et al.*, 2020), *OLEX2* (Dolomanov *et al.*, 2009), and *publCIF* (Westrip, 2010).

Fraga, C. A. M. & Barreiro, E. J. (2006). *Curr. Med. Chem.* **13**, 167–198.

Healy, P. C., Kildea, J. D., Skelton, B. W. & White, A. H. (1988). *Aust. J. Chem.* **41**, 623–633.

Kauffman, G. B. & Ciula, R. P. (1977). *J. Chem. Educ.* **54**, 295.

Kuter, D. J. (2010). *Semin. Hematol.* **47**, 243–248.

Mackenzie, C. F., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *IUCrJ*, **4**, 575–587.

Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.

Mossine, V. V., Kelley, S. P. & Mawhinney, T. P. (2020). *Acta Cryst.* E**76**, 557–561.

Mossine, V. V., Waters, J. K., Chance, D. L. & Mawhinney, T. P. (2016). *Toxicol. Sci.* **154**, 403–415.

Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.

Reece, P. A. (1981). *Med. Res. Rev.* **1**, 73–96.

Rollas, S. & Küçükgüzel, Ş. G. (2007). *Molecules*, **12**, 1910–1939.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Toth, B. (2000). *In Vivo*, **14**, 299–319.

Wang, P., Wan, R., Yu, P., He, Q. & Zhang, J. (2010). *Acta Cryst.* E**66**, o2599.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Zoppellaro, G., Enkelmann, V., Geies, A. & Baumgarten, M. (2004). *Org. Lett.* **6**, 4929–4932.

Zora, M., Turgut, G., Odabaşoğlu, M. & Büyükgüngör, O. (2006). *Acta Cryst.* E**62**, o2677–o2679.

full crystallographic data

2-Bromo-6-hydrazinylpyridine

Valeri V. Mossine, Steven P. Kelley and Thomas P. Mawhinney

2-Bromo-6-hydrazinylpyridine

Crystal data

$C_5H_6BrN_3$	$D_x = 1.961$ Mg m^{-3}
$M_r = 188.04$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 9416 reflections
$a = 3.9606$ (3) Å	$\theta = 3.7$–73.7°
$b = 13.9649$ (9) Å	$\mu = 8.02$ mm^{-1}
$c = 23.0332$ (14) Å	$T = 150$ K
$V = 1273.95$ (15) Å^3	Needle, colourless
$Z = 8$	$0.24 \times 0.04 \times 0.03$ mm
$F(000) = 736$	

Data collection

Bruker APEXII area detector diffractometer	25559 measured reflections
Radiation source: Incoatec IMuS microfocus Cu tube	2564 independent reflections
	2546 reflections with $I > 2\sigma(I)$
Multi-layer optics monochromator	$R_{int} = 0.027$
φ and ω scans	$\theta_{max} = 74.3°$, $\theta_{min} = 3.7°$
Absorption correction: multi-scan (*AXScale*; Bruker, 2021)	$h = -4 \rightarrow 4$
	$k = -17 \rightarrow 17$
$T_{min} = 0.521$, $T_{max} = 0.754$	$l = -28 \rightarrow 28$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.013$	$w = 1/[\sigma^2(F_o^2) + (0.0151P)^2 + 0.5435P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.033$	
$S = 1.07$	$(\Delta/\sigma)_{max} = 0.001$
2564 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
181 parameters	$\Delta\rho_{min} = -0.36$ e Å^{-3}
0 restraints	Absolute structure: Flack x determined using 999 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Primary atom site location: structure-invariant direct methods	
Hydrogen site location: mixed	Absolute structure parameter: 0.012 (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.

Refinement. The hydrazine H atoms were treated by a mixture of independent and constrained refinement while the methine hydrogen atoms were initially placed in calculated positions. All hydrogen-atom coordinates were allowed to refine freely, while displacement parameters were constrained to ride on the carrier atoms [U_{iso}(methine H) = 1.2U_{eq}].

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Br2	0.82558 (6)	−0.11957 (2)	0.41033 (2)	0.02165 (7)
N5	0.2752 (6)	0.10488 (14)	0.55037 (8)	0.0196 (4)
N4	0.5314 (5)	−0.00629 (12)	0.49331 (8)	0.0161 (4)
Br1	−0.03786 (6)	0.36607 (2)	0.24286 (2)	0.02079 (7)
N2	0.2746 (6)	0.13007 (15)	0.39929 (8)	0.0252 (5)
N1	0.1329 (5)	0.22862 (13)	0.32263 (8)	0.0150 (4)
N6	0.1173 (5)	0.14093 (14)	0.60068 (8)	0.0185 (4)
C3	0.4274 (6)	0.10092 (16)	0.24479 (10)	0.0209 (5)
H3	0.526775	0.057251	0.218189	0.025*
C8	0.6904 (6)	−0.12096 (17)	0.58795 (10)	0.0198 (4)
H8	0.742112	−0.160750	0.620199	0.024*
N3	0.1114 (6)	0.19152 (15)	0.43885 (9)	0.0198 (4)
C9	0.5193 (6)	−0.03596 (15)	0.59669 (10)	0.0171 (4)
H9	0.455892	−0.016115	0.634609	0.021*
C5	0.2734 (6)	0.14643 (15)	0.34125 (9)	0.0171 (4)
C1	0.1477 (6)	0.24529 (14)	0.26623 (10)	0.0153 (4)
C4	0.4229 (6)	0.08000 (16)	0.30289 (10)	0.0194 (5)
H4	0.518306	0.022107	0.317038	0.023*
C2	0.2855 (7)	0.18666 (17)	0.22446 (10)	0.0198 (5)
H2	0.284680	0.203175	0.184451	0.024*
C6	0.6988 (6)	−0.08743 (15)	0.48825 (10)	0.0160 (4)
C10	0.4416 (6)	0.02050 (15)	0.54774 (9)	0.0154 (4)
C7	0.7876 (6)	−0.14892 (16)	0.53255 (10)	0.0194 (5)
H7	0.907529	−0.206701	0.525612	0.023*
H5	0.217 (8)	0.134 (2)	0.5193 (13)	0.023*
H6A	−0.002 (8)	0.099 (2)	0.6194 (14)	0.029*
H3A	0.189 (9)	0.247 (2)	0.4323 (14)	0.029*
H6B	0.249 (9)	0.164 (2)	0.6242 (14)	0.029*
H2A	0.340 (8)	0.080 (2)	0.4114 (13)	0.023*
H3B	−0.094 (10)	0.192 (2)	0.4303 (14)	0.029*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br2	0.02599 (13)	0.02054 (11)	0.01841 (11)	0.00436 (10)	0.00240 (9)	−0.00398 (9)
N5	0.0309 (11)	0.0166 (9)	0.0112 (8)	0.0065 (8)	−0.0005 (8)	−0.0007 (7)
N4	0.0197 (10)	0.0138 (8)	0.0149 (8)	−0.0018 (8)	−0.0008 (8)	−0.0004 (6)
Br1	0.02350 (12)	0.02039 (11)	0.01847 (11)	0.00379 (9)	0.00074 (9)	0.00649 (8)
N2	0.0451 (14)	0.0163 (9)	0.0143 (9)	0.0125 (10)	0.0005 (9)	0.0026 (8)
N1	0.0174 (9)	0.0136 (8)	0.0138 (8)	−0.0005 (7)	−0.0022 (8)	−0.0009 (7)
N6	0.0234 (10)	0.0186 (9)	0.0136 (8)	0.0000 (8)	0.0019 (8)	−0.0032 (7)

C3	0.0215 (11)	0.0202 (10)	0.0209 (11)	0.0004 (9)	0.0017 (10)	−0.0061 (8)
C8	0.0198 (10)	0.0191 (10)	0.0205 (10)	−0.0022 (10)	−0.0067 (9)	0.0048 (9)
N3	0.0271 (12)	0.0169 (9)	0.0154 (9)	0.0034 (8)	−0.0009 (8)	0.0001 (7)
C9	0.0193 (11)	0.0183 (10)	0.0138 (9)	−0.0035 (9)	−0.0016 (9)	0.0005 (8)
C5	0.0205 (11)	0.0130 (10)	0.0177 (10)	−0.0023 (8)	−0.0040 (8)	−0.0006 (8)
C1	0.0146 (10)	0.0146 (9)	0.0165 (10)	−0.0007 (8)	−0.0020 (9)	0.0020 (8)
C4	0.0218 (12)	0.0139 (9)	0.0223 (11)	−0.0004 (8)	−0.0007 (9)	−0.0017 (8)
C2	0.0214 (12)	0.0232 (11)	0.0146 (10)	−0.0016 (9)	0.0003 (9)	−0.0005 (8)
C6	0.0163 (10)	0.0160 (10)	0.0157 (10)	−0.0016 (8)	0.0006 (9)	−0.0037 (8)
C10	0.0165 (10)	0.0142 (9)	0.0156 (10)	−0.0027 (8)	−0.0016 (9)	−0.0010 (8)
C7	0.0189 (11)	0.0141 (10)	0.0252 (11)	0.0005 (9)	−0.0027 (9)	0.0006 (8)

Geometric parameters (Å, º)

Br2—C6	1.917 (2)	C5—C4	1.411 (3)
N5—N6	1.410 (3)	C1—C2	1.376 (3)
N5—C10	1.351 (3)	C6—C7	1.379 (3)
N4—C6	1.318 (3)	N2—H2A	0.80 (3)
N4—C10	1.356 (3)	N3—H3A	0.85 (3)
Br1—C1	1.917 (2)	N3—H3B	0.84 (4)
N2—N3	1.409 (3)	N5—H5	0.86 (3)
N2—C5	1.356 (3)	N6—H6A	0.87 (3)
N1—C5	1.346 (3)	N6—H6B	0.82 (3)
N1—C1	1.321 (3)	C2—H2	0.95
C3—C4	1.370 (3)	C3—H3	0.95
C3—C2	1.403 (3)	C4—H4	0.95
C8—C9	1.382 (3)	C7—H7	0.95
C8—C7	1.389 (3)	C8—H8	0.95
C9—C10	1.410 (3)	C9—H9	0.95
C10—N5—N6	124.36 (19)	N3—N2—H2A	117 (2)
C6—N4—C10	116.81 (19)	C5—N2—H2A	120 (2)
C5—N2—N3	122.2 (2)	N2—N3—H3A	106 (2)
C1—N1—C5	116.46 (19)	N2—N3—H3B	107 (2)
C4—C3—C2	120.2 (2)	H3A—N3—H3B	108 (3)
C9—C8—C7	120.8 (2)	N6—N5—H5	114 (2)
C8—C9—C10	118.1 (2)	C10—N5—H5	121 (2)
N2—C5—C4	120.3 (2)	N5—N6—H6A	114 (2)
N1—C5—N2	117.3 (2)	N5—N6—H6B	114 (2)
N1—C5—C4	122.3 (2)	H6A—N6—H6B	107 (3)
N1—C1—Br1	114.48 (16)	C1—C2—H2	122
N1—C1—C2	126.9 (2)	C3—C2—H2	122
C2—C1—Br1	118.63 (17)	C2—C3—H3	120
C3—C4—C5	118.5 (2)	C4—C3—H3	120
C1—C2—C3	115.7 (2)	C3—C4—H4	121
N4—C6—Br2	114.58 (16)	C5—C4—H4	121
N4—C6—C7	126.7 (2)	C6—C7—H7	122
C7—C6—Br2	118.69 (17)	C8—C7—H7	122

N5—C10—N4	114.20 (19)	C7—C8—H8	120
N5—C10—C9	123.9 (2)	C9—C8—H8	120
N4—C10—C9	121.9 (2)	C8—C9—H9	121
C6—C7—C8	115.7 (2)	C10—C9—H9	121

C5—N1—C1—Br1	−177.25 (16)	C10—N4—C6—Br2	−178.79 (16)
C5—N1—C1—C2	1.4 (4)	C10—N4—C6—C7	1.2 (4)
C1—N1—C5—N2	177.1 (2)	C6—N4—C10—N5	179.1 (2)
C1—N1—C5—C4	−1.3 (3)	C6—N4—C10—C9	−0.7 (3)
N3—N2—C5—N1	5.4 (3)	N6—N5—C10—N4	171.0 (2)
N3—N2—C5—C4	−176.2 (2)	N6—N5—C10—C9	−9.2 (4)
Br1—C1—C2—C3	177.84 (18)	Br2—C6—C7—C8	179.49 (17)
N1—C1—C2—C3	−0.8 (4)	N4—C6—C7—C8	−0.5 (4)
C1—C2—C3—C4	0.0 (4)	C6—C7—C8—C9	−0.7 (3)
C2—C3—C4—C5	0.0 (4)	C7—C8—C9—C10	1.1 (3)
C3—C4—C5—N1	0.7 (4)	C8—C9—C10—N4	−0.3 (3)
C3—C4—C5—N2	−177.6 (2)	C8—C9—C10—N5	179.9 (2)
C5—N2—N3—H3A	−54 (2)	C10—N5—N6—H6A	−45 (2)
C5—N2—N3—H3B	61 (2)	C10—N5—N6—H6B	77 (2)
H2A—N2—N3—H3A	137 (3)	H5—N5—N6—H6A	121 (3)
H2A—N2—N3—H3B	−109 (3)	H5—N5—N6—H6B	−117 (3)
H2A—N2—C5—N1	174 (3)	H5—N5—C10—N4	6 (2)
H2A—N2—C5—C4	−7 (3)	H5—N5—C10—C9	−174 (2)
Br1—C1—C2—H2	−2	Br2—C6—C7—H7	−1
N1—C1—C2—H2	179	N4—C6—C7—H7	180
C1—C2—C3—H3	−180	C6—C7—C8—H8	179
H2—C2—C3—C4	−180	H7—C7—C8—C9	179
H2—C2—C3—H3	0	H7—C7—C8—H8	−1
C2—C3—C4—H4	180	C7—C8—C9—H9	−179
H3—C3—C4—C5	180	H8—C8—C9—C10	−179
H3—C3—C4—H4	0	H8—C8—C9—H9	1
H4—C4—C5—N1	−179	H9—C9—C10—N4	180
C1—N1—C9—H9B	176	H9—C9—C10—N5	0
H4—C4—C5—N2	2		

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2A⋯N4	0.80 (3)	2.36 (3)	3.058 (3)	146 (3)
N3—H3A⋯N6[i]	0.85 (3)	2.43 (3)	3.212 (3)	154 (3)
N3—H3A⋯N5[ii]	0.85 (3)	2.67 (3)	3.149 (3)	117 (3)
N3—H3B⋯N2[iii]	0.84 (4)	2.74 (4)	3.543 (3)	161 (3)
N3—H3B⋯N6[ii]	0.84 (4)	2.69 (3)	3.183 (3)	119 (2)
N5—H5⋯N3	0.86 (3)	2.06 (3)	2.913 (3)	173 (3)
N6—H6B⋯N1[i]	0.82 (3)	2.46 (3)	3.257 (3)	164 (3)

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