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9-Amino-5,7-dibromo-1,2,3,4-tetrahydroacridine hemihydrate

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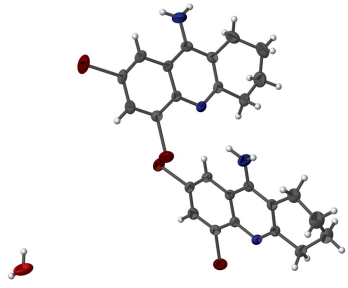
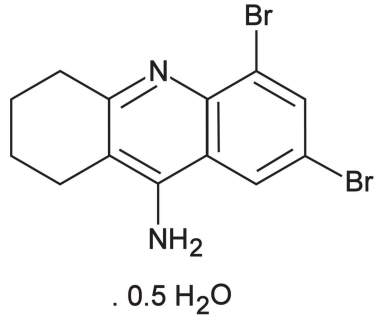
The asymmetric unit of the title compound, $C_{13}H_{12}Br_2N_2\cdot0.5H_2O$, includes two molecules of 5,7-dibromo-1,2,3,4-tetrahydroacridin-9-amine and one water molecule. In the crystal, C—H···O, N—H···N, N—H···O and O—H···N hydrogen bonds connect the molecules, forming a two-dimensional network parallel to (010). The two-dimensional sheets are further assembled into a three-dimensional structure through C—H···π and π–π stacking interactions [centroid–centroid distance = 3.719 (2) Å].

3D view



Chemical scheme



Structure description

Various synthetic methods such as the Skraup, Friedländer, Doebner-von Millet and Combes syntheses have developed due to the importance of the synthesis of bioactive heterocycles with *N* functions such as indole (Ökten *et al.*, 2015), quinoline (Ökten *et al.*, 2013), acridine (Zong *et al.*, 2006) and tacrine (Yang *et al.*, 2007). The Friedländer reaction is one of the most well known for the synthesis of polysubstituted heteroaromatic compounds (Peçanha *et al.*, 2001; Zong *et al.*, 2006; Tang *et al.*, 2012). 9-Amino-1,2,3,4-tetrahydroacridine, known as tacrine, was the first AChE inhibitor to be investigated as an AD drug (Cheng, 1994). Although beneficial effects of tacrines on AD symptoms, it exhibited several adverse effects which in some cases causes some problems (Brinton & Yamazaki, 1998). As a result of that, many other AChE inhibitors have been

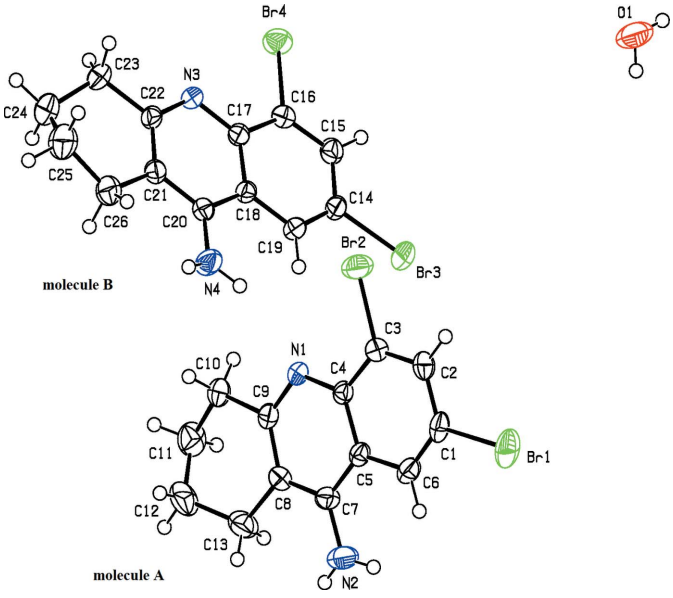


Figure 1
The asymmetric unit of the title compound, with displacement ellipsoids drawn at the 30% probability level.

studied and researchers still continue to improve the pharmacological profile of novel drug candidates (Rampa *et al.*, 2000).

Halogenated aromatics including a quinoline skeleton are used as precursors for various multifunctional heterocyclic compounds, undergoing metal–halogen exchanges (Ökten *et al.*, 2013), couplings (Zemtsova *et al.*, 2015), and metal-assisted

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

*Cg*1 is the centroid of the N3/C1/C18/C20–C22 pyridine ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*NA*···O1^{i}	0.84 (5)	2.39 (4)	3.215 (5)	168 (5)
O1—H1*O*···N3^{ii}	0.81 (4)	2.12 (3)	2.895 (4)	161 (5)
N4—H4*NB*···N1	0.88 (4)	2.36 (4)	3.207 (4)	161 (4)
C6—H6···O1^{i}	0.93	2.42	3.315 (5)	162
C25—H25*B*···*Cg*1^{iii}	0.97	2.95	3.820 (5)	151

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

substitutions (Ökten *et al.*, 2013; Eisch, 1962). In addition, this class of aromatic compounds, used as starting materials for numerous compounds with pharmacological properties, has been of interest to chemists (Zong *et al.*, 2006; Das & Parida, 2006). In this study we present the structure of 9-amino-5,7-dibromo-1,2,3,4-tetrahydroacridine hemihydrate.

As shown in Fig. 1, the asymmetric unit includes two molecules (*A* and *B*) of 9-amino-5,7-dibromo-1,2,3,4-tetrahydroacridine and a water molecule. The cyclohexane rings display a half-boat conformation, with atoms C12 and C24 as flap atoms and puckering parameters $Q_T = 0.498$ (5) Å, $\theta = 127.5$ (4)°, $\varphi = 38.6$ (6)° for ring C8–C13, and $Q_T = 0.495$ (5) Å, $\theta = 128.2$ (5)°, $\varphi = 18.7$ (6)° for ring C21–C26. The observed bond lengths are comparable to those reported for similar compounds (Glöcklhofer *et al.*, 2014; Sparrow *et al.*, 2012; Akkurt *et al.*, 2010; Çelik *et al.*, 2017).

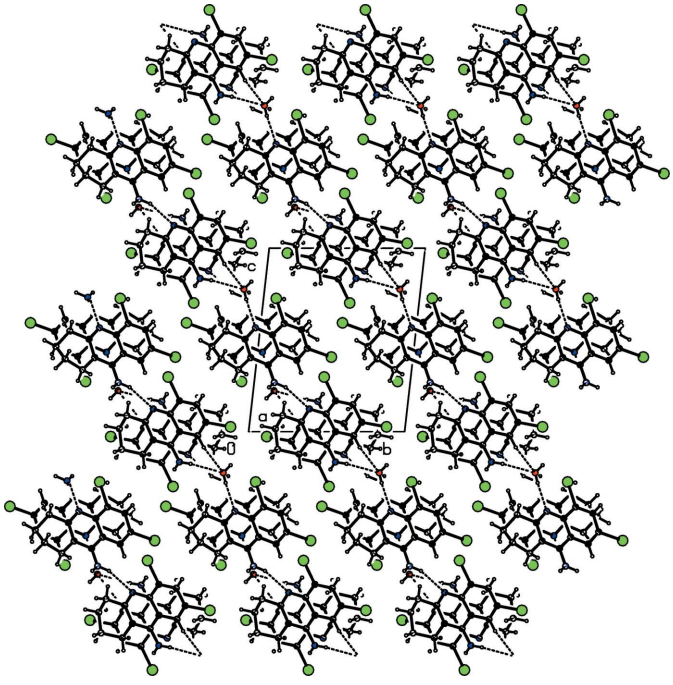


Figure 2
Crystal packing of the title compound, viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

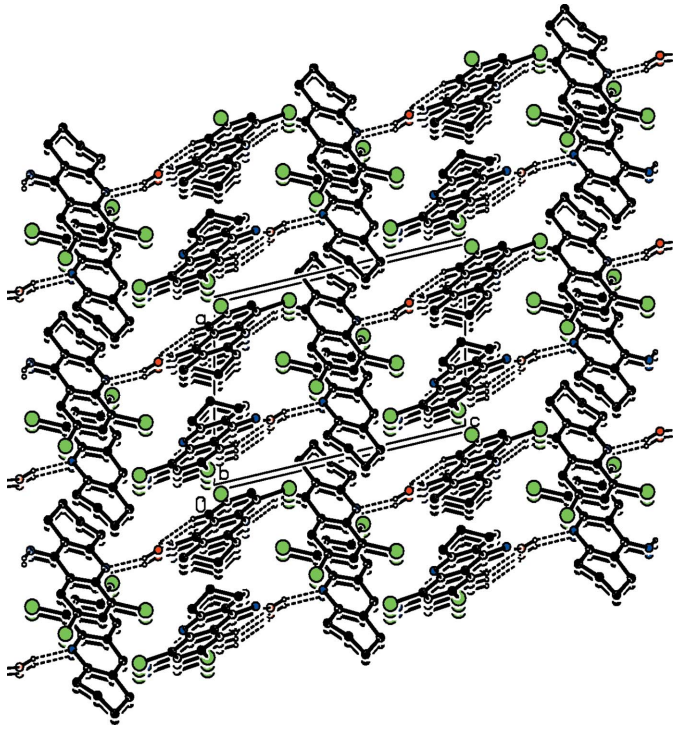


Figure 3
Crystal packing of the title compound, viewed down the *b* axis. Hydrogen bonds are shown as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{13}H_{12}Br_2N_2{\cdot}0.5H_2O$
M_r	365.05
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	296
a, b, c (Å)	9.404 (2), 11.163 (2), 13.263 (3)
α, β, γ (°)	80.607 (9), 75.713 (9), 76.407 (9)
V (Å^3)	1303.3 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	6.20
Crystal size (mm)	0.16 × 0.13 × 0.12
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2003)
T_{min}, T_{max}	0.409, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	66562, 6486, 4883
R_{int}	0.055
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.669
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.080, 1.09
No. of reflections	6486
No. of parameters	335
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.63, −0.83

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2009).

In the crystal, adjacent molecules are linked by C—H···O, N—H···N, N—H···O and O—H···N hydrogen bonds (Table 1), forming a two-dimensional network parallel to (010) (Table 1; Figs. 2 and 3). The parallel layers are then assembled into a three-dimensional network through C—H···π (Table 1) and π–π stacking interactions [$Cg\cdots Cg^{i}$ = 3.719 (2) Å; Cg is the centroid of the C1–C6 benzene ring of molecule A; symmetry code: (i) $2-x, 1-y, -z$] between the layers.

Synthesis and crystallization

According to the reported procedure (Ekiz *et al.*, 2016), 9-amino-5,7-dibromo-1,2,3,4-tetrahydroacridine was prepared by the Friedländer quinoline reaction of cyclohexanone and brominated 2-amino-3,5-dibromobenzonitrile in the presence of $InCl_3$ as Lewis acid. The recrystallization in $CHCl_3$/hexane (1:1 *v*/*v*) gave yellow block-shaped crystals suitable for X-ray analysis.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x171011 [https://doi.org/10.1107/S2414314617010112]

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9-Amino-5,7-dibromo-1,2,3,4-tetrahydroacridine hemihydrate

Crystal data

$C_{13}H_{12}Br_2N_2{\cdot}0.5H_2O$
M_r = 365.05
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 9.404 (2) Å
b = 11.163 (2) Å
c = 13.263 (3) Å
α = 80.607 (9)°
β = 75.713 (9)°
γ = 76.407 (9)°
V = 1303.3 (5) Å^3
Z = 4
$F(000)$ = 716
D_x = 1.860 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9584 reflections
θ = 3.5–28.3°
μ = 6.20 mm^{-1}
T = 296 K
Block, yellow
0.16 × 0.13 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
T_{min} = 0.409, T_{max} = 0.746
66562 measured reflections
6486 independent reflections
4883 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
θ_{max} = 28.4°, θ_{min} = 3.1°
h = −12→12
k = −14→14
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.080
S = 1.09
6486 reflections
335 parameters
3 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0191P)^2 + 2.4473P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.83 e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0038 (3)

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The observed criterion of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating -R-factor-obs etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.
The amino and water H atoms were located in a difference Fourier map and refined with $U_{iso}(H) = 1.2U_{eq}(N)$ or $1.5U_{eq}(O)$. *DFIX* instructions were used to keep the H atoms of the water molecule in place. The C-bound H atoms were included in calculated positions and treated as riding atoms, with C—H = 0.93–0.97 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.91349 (5)	0.88067 (3)	0.02649 (4)	0.0546 (2)
Br2	0.87277 (6)	0.44474 (4)	0.29818 (3)	0.0539 (1)
Br3	0.37866 (5)	0.47644 (3)	0.40689 (3)	0.0495 (1)
Br4	0.41617 (4)	0.08140 (4)	0.72633 (3)	0.0426 (1)
N1	0.7550 (3)	0.3730 (2)	0.1241 (2)	0.0273 (8)
N2	0.7120 (5)	0.5786 (3)	−0.1647 (3)	0.0515 (13)
C1	0.8727 (4)	0.7188 (3)	0.0515 (3)	0.0330 (10)
C2	0.8871 (4)	0.6491 (3)	0.1476 (3)	0.0339 (10)
C3	0.8504 (4)	0.5353 (3)	0.1682 (2)	0.0310 (10)
C4	0.7960 (3)	0.4850 (3)	0.0972 (2)	0.0251 (8)
C5	0.7853 (3)	0.5580 (3)	0.0001 (2)	0.0262 (9)
C6	0.8266 (4)	0.6763 (3)	−0.0213 (3)	0.0332 (10)
C7	0.7288 (4)	0.5106 (3)	−0.0721 (2)	0.0321 (10)
C8	0.6920 (4)	0.3941 (3)	−0.0450 (2)	0.0307 (9)
C9	0.7041 (3)	0.3311 (3)	0.0539 (2)	0.0280 (9)
C10	0.6592 (4)	0.2070 (3)	0.0881 (3)	0.0362 (11)
C11	0.5783 (5)	0.1696 (4)	0.0163 (3)	0.0508 (14)
C12	0.6505 (5)	0.1991 (4)	−0.0964 (3)	0.0559 (16)
C13	0.6399 (5)	0.3390 (4)	−0.1225 (3)	0.0462 (11)
N3	0.6966 (3)	−0.0310 (2)	0.56636 (19)	0.0277 (8)
N4	0.8774 (4)	0.1289 (3)	0.2676 (2)	0.0424 (10)
O1	0.7290 (4)	0.8667 (3)	0.7765 (2)	0.0711 (11)
C14	0.4807 (4)	0.3162 (3)	0.4538 (3)	0.0324 (10)
C15	0.4262 (4)	0.2654 (3)	0.5559 (3)	0.0339 (10)
C16	0.4985 (3)	0.1505 (3)	0.5898 (2)	0.0287 (9)
C17	0.6288 (3)	0.0828 (3)	0.5277 (2)	0.0258 (9)
C18	0.6816 (3)	0.1404 (3)	0.4257 (2)	0.0261 (9)
C19	0.6036 (4)	0.2572 (3)	0.3890 (2)	0.0308 (9)
C20	0.8175 (4)	0.0774 (3)	0.3640 (2)	0.0283 (9)
C21	0.8858 (4)	−0.0400 (3)	0.4041 (2)	0.0292 (9)
C22	0.8187 (4)	−0.0896 (3)	0.5043 (2)	0.0277 (9)
C23	0.8851 (4)	−0.2184 (3)	0.5482 (3)	0.0394 (11)
C24	0.9843 (5)	−0.2968 (4)	0.4651 (3)	0.0537 (14)
C25	1.0988 (5)	−0.2286 (4)	0.3966 (4)	0.0584 (14)
C26	1.0254 (4)	−0.1100 (3)	0.3383 (3)	0.0424 (11)
H2NA	0.727 (5)	0.651 (4)	−0.175 (4)	0.0620*
H2	0.92100	0.68000	0.19630	0.0410*

H2NB	0.678 (5)	0.552 (4)	−0.205 (4)	0.0620*
H6	0.82160	0.72350	−0.08540	0.0400*
H10A	0.59490	0.20900	0.15750	0.0440*
H10B	0.74860	0.14390	0.09290	0.0440*
H11A	0.57990	0.08130	0.03100	0.0600*
H11B	0.47450	0.21320	0.02960	0.0600*
H12A	0.60080	0.16990	−0.14080	0.0670*
H12B	0.75490	0.15690	−0.10960	0.0670*
H13A	0.70040	0.35560	−0.19190	0.0560*
H13B	0.53680	0.37890	−0.12350	0.0560*
H4NA	0.959 (5)	0.099 (4)	0.242 (3)	0.0510*
H4NB	0.842 (5)	0.205 (4)	0.242 (3)	0.0510*
H15	0.34330	0.30870	0.59940	0.0410*
H19	0.63590	0.29330	0.32140	0.0370*
H23A	0.94320	−0.21190	0.59750	0.0470*
H23B	0.80430	−0.25950	0.58630	0.0470*
H24A	1.03420	−0.37400	0.49790	0.0640*
H24B	0.92370	−0.31650	0.42290	0.0640*
H25A	1.16580	−0.28180	0.34630	0.0700*
H25B	1.15790	−0.20790	0.43920	0.0700*
H26A	1.09710	−0.05630	0.31330	0.0510*
H26B	1.00010	−0.13110	0.27770	0.0510*
H1O	0.701 (6)	0.889 (5)	0.722 (2)	0.1070*
H2O	0.667 (5)	0.909 (5)	0.818 (3)	0.1070*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0611 (3)	0.0270 (2)	0.0741 (3)	−0.0200 (2)	−0.0034 (2)	−0.0024 (2)
Br2	0.0882 (3)	0.0448 (2)	0.0405 (2)	−0.0242 (2)	−0.0337 (2)	0.0079 (2)
Br3	0.0652 (3)	0.0303 (2)	0.0496 (2)	0.0111 (2)	−0.0265 (2)	−0.0035 (2)
Br4	0.0434 (2)	0.0474 (2)	0.0309 (2)	−0.0080 (2)	−0.0006 (2)	−0.0004 (2)
N1	0.0327 (14)	0.0211 (12)	0.0274 (13)	−0.0059 (11)	−0.0067 (11)	−0.0002 (10)
N2	0.081 (3)	0.0457 (19)	0.0334 (17)	−0.0193 (19)	−0.0248 (17)	0.0077 (15)
C1	0.0310 (17)	0.0193 (14)	0.045 (2)	−0.0060 (13)	−0.0005 (14)	−0.0038 (13)
C2	0.0378 (19)	0.0269 (16)	0.0405 (19)	−0.0100 (14)	−0.0090 (15)	−0.0080 (14)
C3	0.0349 (18)	0.0290 (16)	0.0280 (16)	−0.0039 (13)	−0.0076 (13)	−0.0027 (13)
C4	0.0244 (15)	0.0219 (14)	0.0261 (15)	−0.0025 (12)	−0.0025 (12)	−0.0026 (12)
C5	0.0258 (15)	0.0220 (14)	0.0282 (16)	−0.0050 (12)	−0.0026 (12)	−0.0004 (12)
C6	0.0347 (18)	0.0255 (15)	0.0348 (18)	−0.0048 (13)	−0.0049 (14)	0.0033 (13)
C7	0.0354 (18)	0.0337 (17)	0.0247 (16)	−0.0049 (14)	−0.0052 (13)	−0.0017 (13)
C8	0.0331 (17)	0.0322 (16)	0.0269 (16)	−0.0057 (13)	−0.0051 (13)	−0.0069 (13)
C9	0.0275 (16)	0.0221 (14)	0.0320 (16)	−0.0033 (12)	−0.0034 (13)	−0.0031 (12)
C10	0.043 (2)	0.0265 (16)	0.0412 (19)	−0.0116 (14)	−0.0091 (16)	−0.0034 (14)
C11	0.057 (2)	0.042 (2)	0.061 (3)	−0.0202 (19)	−0.016 (2)	−0.0080 (19)
C12	0.074 (3)	0.051 (2)	0.055 (3)	−0.022 (2)	−0.018 (2)	−0.021 (2)
C13	0.057 (2)	0.052 (2)	0.0362 (19)	−0.0154 (19)	−0.0149 (18)	−0.0098 (17)
N3	0.0324 (14)	0.0243 (12)	0.0256 (13)	−0.0038 (11)	−0.0084 (11)	0.0002 (10)

N4	0.0477 (19)	0.0361 (17)	0.0309 (16)	−0.0018 (15)	0.0032 (14)	0.0040 (13)
O1	0.082 (2)	0.070 (2)	0.0372 (16)	0.0135 (18)	−0.0083 (16)	0.0128 (15)
C14	0.0416 (19)	0.0229 (15)	0.0349 (17)	−0.0018 (13)	−0.0174 (15)	−0.0027 (13)
C15	0.0334 (18)	0.0319 (17)	0.0353 (18)	0.0010 (14)	−0.0099 (14)	−0.0083 (14)
C16	0.0297 (16)	0.0312 (16)	0.0259 (15)	−0.0074 (13)	−0.0063 (13)	−0.0034 (13)
C17	0.0282 (16)	0.0248 (14)	0.0278 (15)	−0.0057 (12)	−0.0114 (13)	−0.0037 (12)
C18	0.0313 (16)	0.0226 (14)	0.0266 (15)	−0.0060 (12)	−0.0105 (13)	−0.0016 (12)
C19	0.0393 (18)	0.0253 (15)	0.0286 (16)	−0.0055 (13)	−0.0123 (14)	0.0005 (13)
C20	0.0341 (17)	0.0261 (15)	0.0265 (15)	−0.0076 (13)	−0.0077 (13)	−0.0040 (12)
C21	0.0305 (16)	0.0273 (15)	0.0299 (16)	−0.0022 (13)	−0.0083 (13)	−0.0061 (13)
C22	0.0323 (17)	0.0230 (14)	0.0307 (16)	−0.0033 (12)	−0.0141 (13)	−0.0033 (12)
C23	0.046 (2)	0.0288 (17)	0.0392 (19)	0.0028 (15)	−0.0147 (16)	0.0017 (15)
C24	0.064 (3)	0.035 (2)	0.056 (2)	0.0098 (19)	−0.020 (2)	−0.0065 (18)
C25	0.050 (2)	0.051 (2)	0.063 (3)	0.012 (2)	−0.010 (2)	−0.011 (2)
C26	0.040 (2)	0.0388 (19)	0.042 (2)	0.0014 (16)	−0.0038 (16)	−0.0082 (16)

Geometric parameters (Å, º)

Br1—C1	1.895 (3)	C12—H12B	0.9700
Br2—C3	1.884 (3)	C12—H12A	0.9700
Br3—C14	1.906 (3)	C13—H13B	0.9700
Br4—C16	1.899 (3)	C13—H13A	0.9700
N1—C4	1.361 (4)	N4—H4NB	0.88 (4)
N1—C9	1.335 (4)	N4—H4NA	0.78 (5)
N2—C7	1.358 (5)	C14—C15	1.401 (5)
C1—C2	1.400 (5)	C14—C19	1.358 (5)
C1—C6	1.341 (5)	C15—C16	1.365 (5)
C2—C3	1.362 (5)	C16—C17	1.422 (4)
N2—H2NA	0.84 (5)	C17—C18	1.423 (4)
N2—H2NB	0.81 (5)	C18—C20	1.431 (4)
C3—C4	1.417 (4)	C18—C19	1.412 (5)
C4—C5	1.420 (4)	C20—C21	1.399 (5)
C5—C7	1.424 (4)	C21—C26	1.507 (5)
C5—C6	1.428 (5)	C21—C22	1.408 (4)
C7—C8	1.392 (5)	C22—C23	1.510 (5)
C8—C13	1.507 (5)	C23—C24	1.508 (6)
C8—C9	1.401 (4)	C24—C25	1.497 (7)
C9—C10	1.510 (5)	C25—C26	1.525 (6)
C10—C11	1.515 (6)	O1—H1O	0.81 (4)
C11—C12	1.499 (6)	O1—H2O	0.81 (5)
C12—C13	1.528 (6)	C15—H15	0.9300
C2—H2	0.9300	C19—H19	0.9300
N3—C17	1.361 (4)	C23—H23A	0.9700
N3—C22	1.334 (4)	C23—H23B	0.9700
N4—C20	1.356 (4)	C24—H24B	0.9700
C6—H6	0.9300	C24—H24A	0.9700
C10—H10A	0.9700	C25—H25A	0.9700
C10—H10B	0.9700	C25—H25B	0.9700

C11—H11A	0.9700	C26—H26B	0.9700
C11—H11B	0.9700	C26—H26A	0.9700
C4—N1—C9	117.2 (2)	H4NA—N4—H4NB	117 (4)
Br1—C1—C2	118.4 (3)	C20—N4—H4NA	117 (3)
Br1—C1—C6	119.4 (3)	C20—N4—H4NB	123 (3)
C2—C1—C6	122.2 (3)	Br3—C14—C19	119.5 (3)
C1—C2—C3	118.7 (3)	Br3—C14—C15	117.7 (3)
H2NA—N2—H2NB	122 (5)	C15—C14—C19	122.7 (3)
C7—N2—H2NA	118 (4)	C14—C15—C16	118.0 (3)
C7—N2—H2NB	120 (3)	Br4—C16—C15	116.8 (2)
Br2—C3—C2	117.1 (3)	Br4—C16—C17	120.2 (2)
Br2—C3—C4	120.1 (2)	C15—C16—C17	123.0 (3)
C2—C3—C4	122.9 (3)	N3—C17—C18	123.3 (3)
N1—C4—C5	123.3 (3)	N3—C17—C16	120.2 (2)
N1—C4—C3	120.1 (3)	C16—C17—C18	116.6 (3)
C3—C4—C5	116.6 (3)	C17—C18—C19	120.5 (3)
C4—C5—C6	120.0 (3)	C17—C18—C20	117.6 (3)
C4—C5—C7	117.8 (3)	C19—C18—C20	121.9 (3)
C6—C5—C7	122.2 (3)	C14—C19—C18	119.2 (3)
C1—C6—C5	119.6 (3)	C18—C20—C21	118.6 (3)
C5—C7—C8	118.3 (3)	N4—C20—C21	120.5 (3)
N2—C7—C8	121.6 (3)	N4—C20—C18	120.8 (3)
N2—C7—C5	120.1 (3)	C20—C21—C22	118.3 (3)
C7—C8—C9	119.1 (3)	C20—C21—C26	119.4 (3)
C7—C8—C13	119.3 (3)	C22—C21—C26	122.3 (3)
C9—C8—C13	121.7 (3)	C21—C22—C23	119.8 (3)
C8—C9—C10	120.8 (3)	N3—C22—C21	124.8 (3)
N1—C9—C8	124.3 (3)	N3—C22—C23	115.4 (3)
N1—C9—C10	114.9 (3)	C22—C23—C24	113.1 (3)
C9—C10—C11	114.7 (3)	C23—C24—C25	110.1 (4)
C10—C11—C12	111.0 (4)	C24—C25—C26	111.5 (4)
C11—C12—C13	110.0 (3)	C21—C26—C25	113.7 (3)
C8—C13—C12	112.5 (3)	H1O—O1—H2O	104 (5)
C1—C2—H2	121.00	C14—C15—H15	121.00
C3—C2—H2	121.00	C16—C15—H15	121.00
C17—N3—C22	117.3 (2)	C18—C19—H19	120.00
C5—C6—H6	120.00	C14—C19—H19	120.00
C1—C6—H6	120.00	C22—C23—H23A	109.00
C9—C10—H10A	109.00	C22—C23—H23B	109.00
C9—C10—H10B	109.00	C24—C23—H23B	109.00
C11—C10—H10B	109.00	H23A—C23—H23B	108.00
H10A—C10—H10B	108.00	C24—C23—H23A	109.00
C11—C10—H10A	109.00	C23—C24—H24B	110.00
C10—C11—H11B	109.00	C25—C24—H24A	110.00
C12—C11—H11A	109.00	C25—C24—H24B	110.00
C12—C11—H11B	109.00	H24A—C24—H24B	108.00
H11A—C11—H11B	108.00	C23—C24—H24A	110.00

C10—C11—H11A	109.00	C24—C25—H25B	109.00
C11—C12—H12B	110.00	C26—C25—H25A	109.00
C13—C12—H12A	110.00	C24—C25—H25A	109.00
C11—C12—H12A	110.00	H25A—C25—H25B	108.00
H12A—C12—H12B	108.00	C26—C25—H25B	109.00
C13—C12—H12B	110.00	C21—C26—H26A	109.00
C8—C13—H13A	109.00	C21—C26—H26B	109.00
C8—C13—H13B	109.00	C25—C26—H26B	109.00
C12—C13—H13B	109.00	H26A—C26—H26B	108.00
H13A—C13—H13B	108.00	C25—C26—H26A	109.00
C12—C13—H13A	109.00		

C9—N1—C4—C3	179.7 (3)	C22—N3—C17—C16	−179.8 (3)
C4—N1—C9—C8	0.7 (5)	C17—N3—C22—C21	3.0 (5)
C4—N1—C9—C10	−179.6 (3)	C17—N3—C22—C23	−176.8 (3)
C9—N1—C4—C5	0.8 (4)	C22—N3—C17—C18	0.2 (5)
Br1—C1—C2—C3	176.6 (3)	Br3—C14—C15—C16	179.8 (3)
Br1—C1—C6—C5	−175.5 (3)	Br3—C14—C19—C18	177.8 (3)
C2—C1—C6—C5	2.3 (6)	C15—C14—C19—C18	−0.8 (6)
C6—C1—C2—C3	−1.2 (6)	C19—C14—C15—C16	−1.6 (6)
C1—C2—C3—Br2	179.7 (3)	C14—C15—C16—Br4	−177.3 (3)
C1—C2—C3—C4	−1.0 (6)	C14—C15—C16—C17	2.3 (5)
Br2—C3—C4—N1	2.2 (4)	Br4—C16—C17—N3	−1.1 (4)
Br2—C3—C4—C5	−178.8 (2)	Br4—C16—C17—C18	178.9 (2)
C2—C3—C4—C5	1.9 (5)	C15—C16—C17—C18	−0.6 (5)
C2—C3—C4—N1	−177.1 (3)	C15—C16—C17—N3	179.4 (3)
N1—C4—C5—C7	−0.1 (5)	N3—C17—C18—C20	−3.6 (5)
N1—C4—C5—C6	178.2 (3)	N3—C17—C18—C19	178.1 (3)
C3—C4—C5—C6	−0.8 (4)	C16—C17—C18—C19	−1.9 (4)
C3—C4—C5—C7	−179.1 (3)	C16—C17—C18—C20	176.4 (3)
C4—C5—C6—C1	−1.3 (5)	C17—C18—C19—C14	2.6 (5)
C4—C5—C7—C8	−2.1 (5)	C17—C18—C20—C21	3.9 (5)
C6—C5—C7—N2	−0.3 (5)	C19—C18—C20—N4	0.7 (5)
C6—C5—C7—C8	179.7 (3)	C19—C18—C20—C21	−177.8 (3)
C7—C5—C6—C1	177.0 (3)	C20—C18—C19—C14	−175.7 (3)
C4—C5—C7—N2	178.0 (3)	C17—C18—C20—N4	−177.6 (3)
C5—C7—C8—C9	3.4 (5)	C18—C20—C21—C22	−1.1 (5)
N2—C7—C8—C9	−176.6 (4)	N4—C20—C21—C22	−179.7 (3)
N2—C7—C8—C13	3.3 (6)	N4—C20—C21—C26	−1.1 (5)
C5—C7—C8—C13	−176.7 (3)	C18—C20—C21—C26	177.4 (3)
C7—C8—C9—C10	177.4 (3)	C20—C21—C22—C23	177.2 (3)
C13—C8—C9—N1	177.3 (3)	C26—C21—C22—N3	179.0 (3)
C7—C8—C13—C12	162.3 (4)	C20—C21—C26—C25	172.6 (3)
C9—C8—C13—C12	−17.8 (5)	C22—C21—C26—C25	−8.9 (5)
C13—C8—C9—C10	−2.4 (5)	C26—C21—C22—C23	−1.3 (5)
C7—C8—C9—N1	−2.9 (5)	C20—C21—C22—N3	−2.5 (5)
N1—C9—C10—C11	170.5 (3)	N3—C22—C23—C24	159.5 (3)
C8—C9—C10—C11	−9.8 (5)	C21—C22—C23—C24	−20.3 (5)

C9—C10—C11—C12	42.3 (5)	C22—C23—C24—C25	51.8 (5)
C10—C11—C12—C13	−62.7 (5)	C23—C24—C25—C26	−62.6 (5)
C11—C12—C13—C8	49.9 (5)	C24—C25—C26—C21	40.6 (5)

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the N3/C1/C18/C20–C22 pyridine ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*NA*···O1^{i}	0.84 (5)	2.39 (4)	3.215 (5)	168 (5)
O1—H1*O*···N3^{ii}	0.81 (4)	2.12 (3)	2.895 (4)	161 (5)
N4—H4*NB*···N1	0.88 (4)	2.36 (4)	3.207 (4)	161 (4)
C6—H6···O1^{i}	0.93	2.42	3.315 (5)	162
C25—H25*B*···*Cg*1^{iii}	0.97	2.95	3.820 (5)	151

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