

Redetermination of (*E*)-*N,N'*-bis(4-bromophenyl)formamidinium

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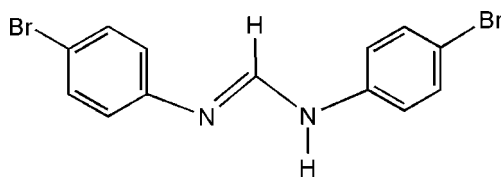
Received 1 April 2011; accepted 10 April 2011

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.048; wR factor = 0.114; data-to-parameter ratio = 16.8.

In comparison with the previous structural study [Anulewicz *et al.* (1991). *Pol. J. Chem.* **65**, 465–471], for which only the coordinates of all non-H atoms and of some H atoms were reported, the current redetermination of the title compound, $\text{C}_{13}\text{H}_{10}\text{Br}_2\text{N}_2$, additionally reports anisotropic displacement parameters for all non-H atoms and the coordinates of all H atoms, accompanied by higher accuracy of the geometric parameters. Two independent half-molecules are present in the asymmetric unit, which are completed by a twofold rotation axis as symmetry element. In the crystal, intermolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds link the molecules into dimers. Linear chains parallel to $[102]$ are formed by intermolecular $\text{Br}\cdots\text{Br}$ interactions of $3.4328(7)$ Å between two Br atoms of adjacent molecules. The dihedral angles between the benzene rings are $50.05(15)$ and $75.61(11)^\circ$ in the two independent molecules. Owing to the twofold symmetry of the molecules, H atoms attached to the N atoms are only half-occupied, leading to them being disordered over two positions of equal occupancy.

Related literature

For the previous structure determination, see: Anulewicz *et al.* (1991). For $\text{Br}\cdots\text{Br}$ interactions, see: Fujiwara *et al.* (2006); Reddy *et al.* (1996). For $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds, see: Del Bene & Elguero (2006); Grotjahn *et al.* (2000); Thar & Kirchner (2006).



Experimental

Crystal data

$\text{C}_{13}\text{H}_{10}\text{Br}_2\text{N}_2$	$V = 2666.9(9)$ Å ³
$M_r = 354.05$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 11.563(2)$ Å	$\mu = 6.06$ mm ⁻¹
$b = 23.447(5)$ Å	$T = 293$ K
$c = 9.881(2)$ Å	$0.15 \times 0.07 \times 0.06$ mm
$\beta = 95.43(3)^\circ$	

Data collection

Bruker SMART CCD diffractometer	5954 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	2611 independent reflections
$T_{\min} = 0.403$, $T_{\max} = 0.695$	1715 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$	155 parameters
$wR(F^2) = 0.114$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\max} = 0.48$ e Å ⁻³
2611 reflections	$\Delta\rho_{\min} = -0.91$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H2A}\cdots\text{N2}^{\text{i}}$	0.85	2.12	2.964(4)	180
$\text{N2}-\text{H3A}\cdots\text{N1}^{\text{ii}}$	0.88	2.12	2.964(4)	161

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

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP (Sheldrick, 2008) and DIAMOND (Brandenburg, 1999); software used to prepare material for publication: SHELXL97.

This work was supported by the National Natural Scientific Foundation of China (No.20741004/B010303).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2476).

References

- Anulewicz, R., Krygowski, T. M., Jaroszevska-Manaj, J. & Pniewska, B. (1991). *Pol. J. Chem.* **65**, 465–471.
- Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruker. (2001). *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker. (2004). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Del Bene, J. E. & Elguero, J. (2006). *J. Phys. Chem. A*, **110**, 7496–7502.
- Fujiwara, H., Hayashi, T., Sugimoto, T., Nakazumi, H., Noguchi, S., Li, L., Yokogawa, K., Yasuzuka, S., Murata, K. & Mori, T. (2006). *Inorg. Chem.* **45**, 5712–5714.
- Grotjahn, D. B., Combs, D., Van, S., Aguirre, G. & Ortega, F. (2000). *Inorg. Chem.* **39**, 2080–2086.
- Reddy, D. S., Craig, D. C. & Desiraju, G. R. (1996). *J. Am. Chem. Soc.* **118**, 4090–4093.
- Sheldrick, G. M. (2004). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Thar, J. & Kirchner, B. (2006). *J. Phys. Chem. A*, **110**, 4229–4237.

supporting information

Acta Cryst. (2011). E67, o1159 [https://doi.org/10.1107/S1600536811013419]

Redetermination of (*E*)-*N,N'*-bis(4-bromophenyl)formamidine

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S1. Comment

With the determination of reliable intermolecular distances, Br $\cdots$ Br interactions (Fujiwara *et al.*, 2006; Reddy *et al.*, 1996) and N—H $\cdots$ N hydrogen bonding (Del Bene & Elguero, 2006; Grotjahn *et al.* 2000; Thar & Kirchner, 2006) became important criteria in the description of supramolecular chemistry and in applied crystal engineering. The title compound C₁₃H₁₀Br₂N₂, (I), has been determined previously by Anulewicz *et al.* (1991). However, in that study only coordinates of all non-H atoms and of some H atoms were given. The present re-determination additionally reports anisotropic displacement parameters for all non-H atoms and the coordinates of all H atoms, accompanied by higher accuracy of all geometric parameters.

In (I) two independent half-molecules are present in the asymmetric unit which are completed by a twofold rotation axis as symmetry element that runs to the central C—H groups (C1—H1 and C2—H2, respectively). One molecule is displayed in Fig. 1. The dihedral angles between the two benzene rings in the individual molecules are 50.05 (15) ° for the first and 75.61 (11) ° for the second molecule.

In the crystal, intermolecular N—H $\cdots$ N hydrogen bonds link the individual molecules into dimers (Fig. 2). Linear chains parallel to [102] are formed by intermolecular Br $\cdots$ Br interactions of 3.4328 (7) Å between two bromine atoms of adjacent molecules (Fig. 3). This interaction is significantly less than the van der Waals contact of 3.90 Å (Reddy *et al.*, 1996; Fujiwara *et al.*, 2006), hence making this interaction important for consolidation of the crystal packing.

S2. Experimental

The title compound was synthesized by the following reaction. 17.202 g (0.1 mol) of 4-bromobenzenamine and 8.33 ml (0.05 mol) of triethyl orthoformate were combined in a round-bottom flask equipped with a distillation tube and heated at 160 until the distillation of ethanol ceased. The retained solid was washed with ether, and dried under a dynamic vacuum to yield 16.10 g of white solid, (91%). 0.04 g of the white solid was dissolved in THF (3 ml) and the solution was layered with hexane. Colourless needle-shaped crystals formed after several days. ¹HNMR(CDCl₃, p.p.m.): 8.08(s, 1H, —NCHN—), 7.43(d, 2H, aromatic), 7.40(d, 2H, aromatic), 6.93(d, 2H, aromatic), 6.91(d, 2H, aromatic). Anal. Calcd. C₁₃H₁₀Br₂N₂: C, 44.10; H, 2.85; N, 7.91; Found: C, 43.83; H, 2.69; N, 8.02.

S3. Refinement

H atoms attached to C atoms were positioned geometrically with C—H = 0.93 (CH), and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms attached to N atoms were found from difference Fourier maps and were fixed. They were refined with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. Owing to the 2 symmetry of the molecules, the H atoms attached to the N atoms are only half-occupied, leading to being disordered over two positions of equal occupancy.

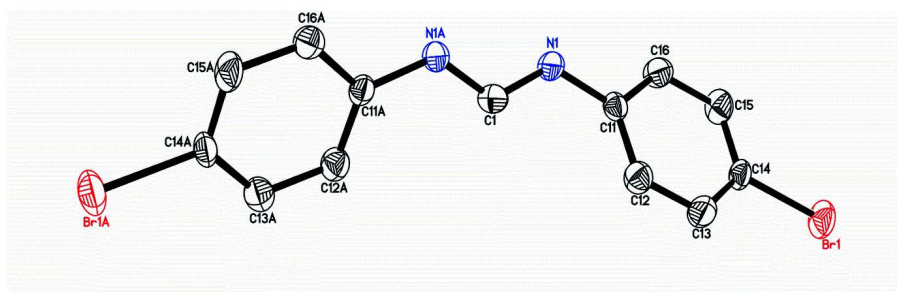


Figure 1

Molecular structure of one of the two molecules of (I) drawn with displacement ellipsoids at the 30% probability level.
[Symmetry code A) $-x+1, y, -z+1/2$.]

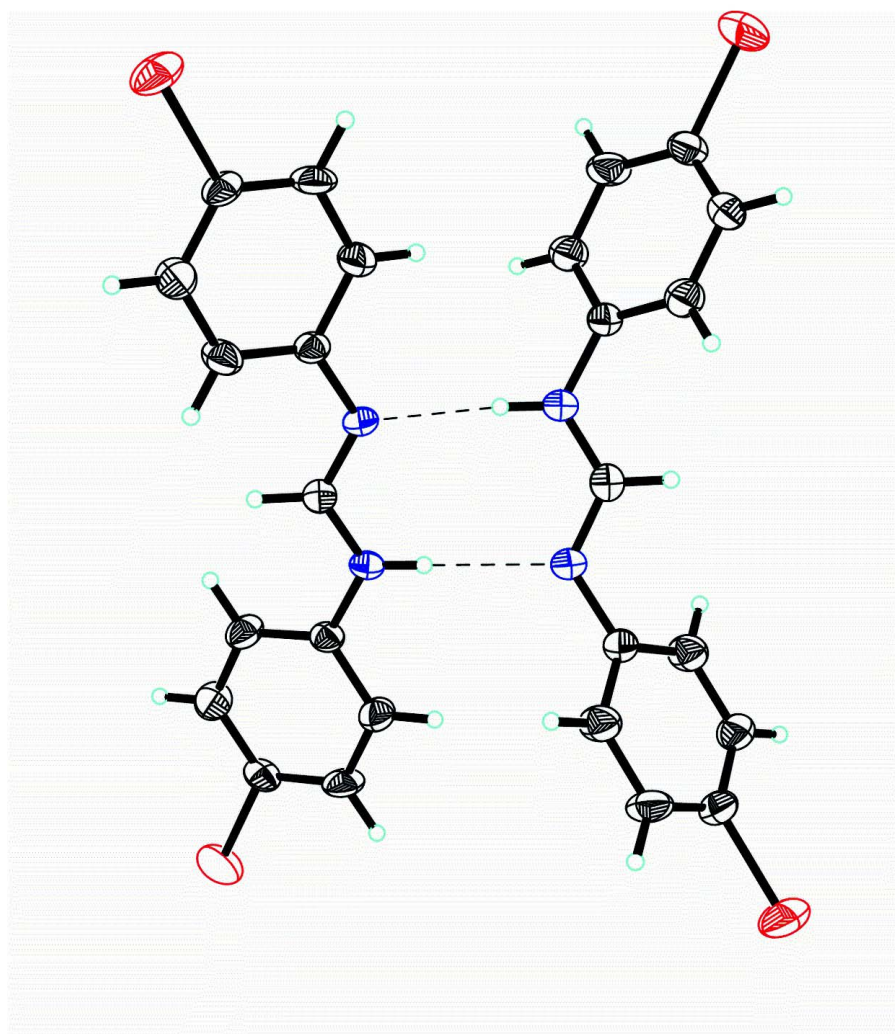


Figure 2

A dimer formed by intermolecular N–H···N hydrogen bonds.

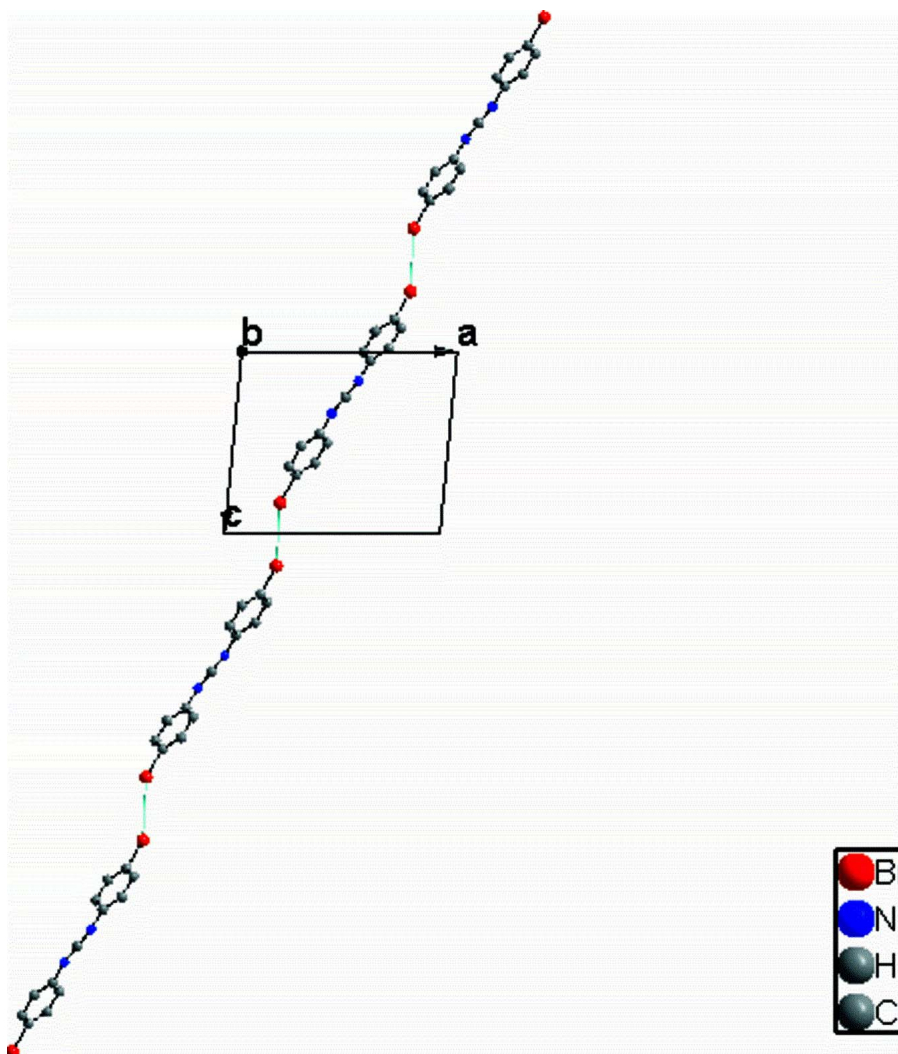


Figure 3

Part of an one-dimensional linear chain of the title compound, viewed along [010]. Br···Br interactions are drawn with blue dashed lines.

(*E*)-*N,N'*-bis(4-bromophenyl)formamidine

Crystal data

$C_{13}H_{10}Br_2N_2$

$M_r = 354.05$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 11.563\ (2)\ \text{\AA}$

$b = 23.447\ (5)\ \text{\AA}$

$c = 9.881\ (2)\ \text{\AA}$

$\beta = 95.43\ (3)^\circ$

$V = 2666.9\ (9)\ \text{\AA}^3$

$Z = 8$

$F(000) = 1376$

$D_x = 1.764\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 4303 reflections

$\theta = 2.5\text{--}26.7^\circ$

$\mu = 6.06\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Needle, colourless

$0.15 \times 0.07 \times 0.06\ \text{mm}$

Data collection

Bruker SMART CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2004)
 $T_{\min} = 0.403$, $T_{\max} = 0.695$

5954 measured reflections
 2611 independent reflections
 1715 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.061$
 $\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 1.7^\circ$
 $h = -12 \rightarrow 14$
 $k = -26 \rightarrow 28$
 $l = -12 \rightarrow 11$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.114$
 $S = 1.00$
 2611 reflections
 155 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0533P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.48 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.90 \text{ e } \text{\AA}^{-3}$

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness 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 threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Br1	0.24399 (5)	0.73912 (2)	0.82770 (5)	0.0708 (2)	
N1	0.4449 (3)	0.63281 (13)	0.3396 (3)	0.0429 (8)	
H2A	0.4352	0.5975	0.3271	0.052*	0.50
C1	0.5000	0.6600 (2)	0.2500	0.0428 (13)	
H1	0.5000	0.6997	0.2500	0.051*	
C11	0.3994 (4)	0.65996 (16)	0.4505 (4)	0.0404 (9)	
C12	0.4347 (4)	0.71277 (17)	0.4995 (4)	0.0525 (11)	
H12A	0.4903	0.7329	0.4570	0.063*	
C13	0.3885 (4)	0.73617 (18)	0.6108 (5)	0.0569 (11)	
H13A	0.4131	0.7719	0.6428	0.068*	
C14	0.3065 (4)	0.70681 (17)	0.6738 (4)	0.0459 (10)	
C15	0.2716 (4)	0.65412 (19)	0.6293 (4)	0.0560 (11)	
H15A	0.2171	0.6340	0.6737	0.067*	
C16	0.3177 (4)	0.63066 (17)	0.5178 (4)	0.0546 (11)	
H16A	0.2935	0.5947	0.4873	0.066*	
Br2	0.02928 (6)	0.61567 (3)	1.05388 (8)	0.1036 (3)	

N2	0.4121 (3)	0.49146 (13)	0.7963 (3)	0.0507 (8)	0.50
H3A	0.4085	0.4541	0.7936	0.061*	
C2	0.5000	0.5180 (2)	0.7500	0.0520 (15)	
H2B	0.5000	0.5577	0.7500	0.062*	
C21	0.3242 (4)	0.52137 (16)	0.8556 (4)	0.0455 (10)	
C22	0.2110 (4)	0.50352 (19)	0.8320 (5)	0.0588 (12)	
H32A	0.1933	0.4723	0.7758	0.071*	
C23	0.1229 (4)	0.53143 (19)	0.8908 (5)	0.0635 (12)	
H33A	0.0466	0.5189	0.8746	0.076*	
C24	0.1488 (4)	0.57764 (18)	0.9729 (5)	0.0561 (11)	
C25	0.2603 (4)	0.59524 (19)	0.9991 (4)	0.0584 (12)	
H35A	0.2774	0.6264	1.0557	0.070*	
C26	0.3483 (4)	0.56719 (17)	0.9422 (4)	0.0561 (11)	
H36A	0.4247	0.5791	0.9621	0.067*	

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0872 (4)	0.0873 (4)	0.0409 (3)	0.0246 (3)	0.0215 (2)	−0.0074 (2)
N1	0.046 (2)	0.0446 (17)	0.0413 (18)	0.0019 (15)	0.0199 (15)	−0.0018 (14)
C1	0.040 (3)	0.042 (3)	0.047 (3)	0.000	0.006 (3)	0.000
C11	0.044 (2)	0.046 (2)	0.033 (2)	0.0046 (18)	0.0111 (17)	0.0051 (17)
C12	0.059 (3)	0.056 (2)	0.045 (2)	−0.014 (2)	0.017 (2)	−0.001 (2)
C13	0.070 (3)	0.056 (2)	0.046 (3)	−0.009 (2)	0.012 (2)	−0.007 (2)
C14	0.056 (3)	0.055 (2)	0.028 (2)	0.010 (2)	0.0129 (18)	−0.0038 (18)
C15	0.053 (3)	0.073 (3)	0.047 (2)	−0.005 (2)	0.029 (2)	0.000 (2)
C16	0.064 (3)	0.051 (2)	0.053 (3)	−0.009 (2)	0.025 (2)	−0.003 (2)
Br2	0.0764 (5)	0.0940 (5)	0.1485 (7)	0.0149 (3)	0.0538 (4)	−0.0264 (4)
N2	0.046 (2)	0.0459 (18)	0.063 (2)	0.0002 (16)	0.0217 (17)	−0.0012 (17)
C2	0.055 (4)	0.043 (3)	0.059 (4)	0.000	0.011 (3)	0.000
C21	0.047 (3)	0.044 (2)	0.047 (2)	0.0014 (18)	0.0127 (19)	0.0011 (18)
C22	0.049 (3)	0.061 (3)	0.067 (3)	−0.010 (2)	0.014 (2)	−0.019 (2)
C23	0.035 (3)	0.078 (3)	0.079 (3)	−0.006 (2)	0.014 (2)	−0.016 (3)
C24	0.052 (3)	0.057 (3)	0.062 (3)	0.011 (2)	0.019 (2)	0.000 (2)
C25	0.057 (3)	0.053 (3)	0.067 (3)	0.000 (2)	0.017 (2)	−0.014 (2)
C26	0.047 (3)	0.059 (3)	0.061 (3)	−0.007 (2)	0.005 (2)	−0.010 (2)

Geometric parameters ($\text{\AA}$, $^\circ$)

Br1—C14	1.901 (4)	Br2—C24	1.886 (4)
N1—C1	1.305 (4)	N2—C2	1.311 (4)
N1—C11	1.412 (5)	N2—C21	1.407 (5)
N1—H2A	0.8422	N2—H3A	0.8763
C1—N1 ⁱ	1.305 (4)	C2—N2 ⁱⁱ	1.311 (4)
C1—H1	0.9300	C2—H2B	0.9300
C11—C12	1.377 (5)	C21—C22	1.373 (6)
C11—C16	1.388 (6)	C21—C26	1.385 (5)
C12—C13	1.381 (6)	C22—C23	1.383 (6)

C12—H12A	0.9300	C22—H32A	0.9300
C13—C14	1.369 (6)	C23—C24	1.369 (6)
C13—H13A	0.9300	C23—H33A	0.9300
C14—C15	1.360 (6)	C24—C25	1.355 (6)
C15—C16	1.383 (6)	C25—C26	1.375 (6)
C15—H15A	0.9300	C25—H35A	0.9300
C16—H16A	0.9300	C26—H36A	0.9300
C1—N1—C11	123.2 (3)	C2—N2—C21	121.5 (3)
C1—N1—H2A	116.6	C2—N2—H3A	120.0
C11—N1—H2A	120.1	C21—N2—H3A	118.5
N1 ⁱ —C1—N1	121.4 (5)	N2 ⁱⁱ —C2—N2	123.3 (5)
N1 ⁱ —C1—H1	119.3	N2 ⁱⁱ —C2—H2B	118.4
N1—C1—H1	119.3	N2—C2—H2B	118.4
C12—C11—C16	118.0 (4)	C22—C21—C26	118.3 (4)
C12—C11—N1	123.9 (4)	C22—C21—N2	119.4 (3)
C16—C11—N1	118.0 (3)	C26—C21—N2	122.2 (4)
C11—C12—C13	120.9 (4)	C21—C22—C23	120.8 (4)
C11—C12—H12A	119.6	C21—C22—H32A	119.6
C13—C12—H12A	119.6	C23—C22—H32A	119.6
C14—C13—C12	120.0 (4)	C24—C23—C22	119.6 (4)
C14—C13—H13A	120.0	C24—C23—H33A	120.2
C12—C13—H13A	120.0	C22—C23—H33A	120.2
C15—C14—C13	120.5 (4)	C25—C24—C23	120.3 (4)
C15—C14—Br1	119.8 (3)	C25—C24—Br2	119.8 (3)
C13—C14—Br1	119.7 (3)	C23—C24—Br2	119.8 (3)
C14—C15—C16	119.6 (4)	C24—C25—C26	120.2 (4)
C14—C15—H15A	120.2	C24—C25—H35A	119.9
C16—C15—H15A	120.2	C26—C25—H35A	119.9
C15—C16—C11	121.1 (4)	C25—C26—C21	120.7 (4)
C15—C16—H16A	119.5	C25—C26—H36A	119.7
C11—C16—H16A	119.5	C21—C26—H36A	119.7

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

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H2A $\cdots$ N2 ⁱⁱⁱ	0.85	2.12	2.964 (4)	180
N2—H3A $\cdots$ N1 ^{iv}	0.88	2.12	2.964 (4)	161

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