Crystal structure and halogen–hydrogen bonding of a Delépine reaction intermediate

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The reaction of 1,5-dibromopentane with urotropine results in crystals of the title molecular salt, 5-bromourotropinium bromide [systematic name: 1-(5-bromopentyl)-3,5,7-triaza-1-azoniatricyclo[3.3.1.1^{3,7}]decane bromide], $C_{11}H_{22}BrN_4^+ \cdot Br^-$ (**1**), crystallizing in space group $P2_1/n$. The packing in compound **1** is directed mainly by H$\cdots$H van der Waals interactions and C—H$\cdots$Br hydrogen bonds, as revealed by Hirshfeld surface analysis. Comparison with literature examples of alkylurotropinium halides shows that the interactions in **1** are consistent with those in other bromides and simple chloride and iodide species.

1. Chemical context

Urotropine, $C_6H_{12}N_4$ (also known as hexamethylenetetramine, hmta) and its salts are widely used in chemical organic synthesis (Blažević *et al.*, 1979), as precursors for explosives (Fried *et al.*, 2001) and as pharmaceuticals (Lo *et al.*, 2014).

The Delépine reaction is a classic synthetic route to produce primary amines (Delépine, 1895, 1897). Alkyl or aryl halides are reacted with hmta to form a quaternary ammonium salt, followed by acid hydrolysis to give a primary amine. A major advantage of this reaction over other routes is that the formation of the quaternary urotropinium cation prevents further alkylation and high yields are possible (Galat & Elion, 1939). We recently made an attempt to find a cost-effective route to synthesize 1,5-diaminopentane (cadaverine) from 1,5-dibromopentane. On an industrial scale, this is produced by bacterial decarboxylation of lysine (Ma *et al.* 2017; Wang *et al.*, 2018). Attempts to react 1,5-dibromopentane with hmta in the presence of NaI in ethanol (modified from Galat & Elion, 1939) led to the crystallization of a monosubstituted product, 5-bromourotropinium bromide, $C_{11}H_{22}BrN_4^+ \cdot Br^-$ (**1**), the structure and supramolecular features of which are presented here.
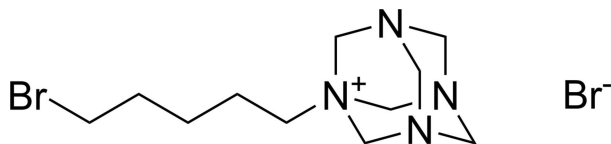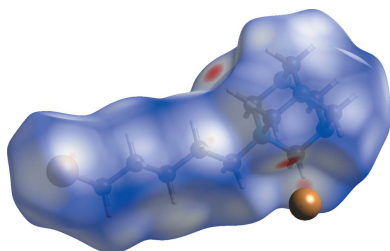
2. Structural commentary

Compound **1** crystallizes in the centrosymmetric monoclinic space group $P2_1/n$. The asymmetric unit of **1** (Fig. 1) contains one $C_{11}H_{22}BrN_4^+$ *N*-(5-bromopentyl)urotropinium cation and one bromide anion. The pentyl chain is in the all-*trans*
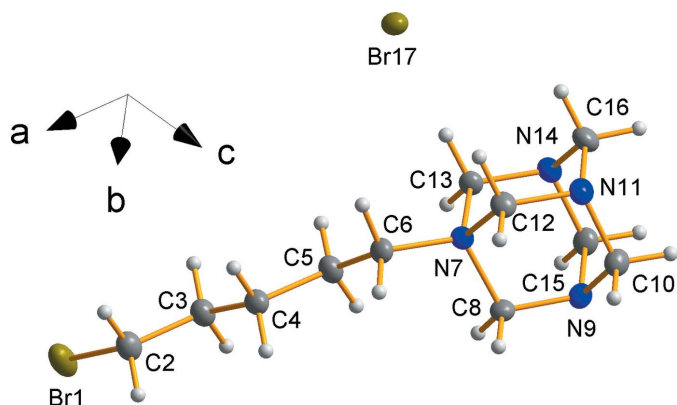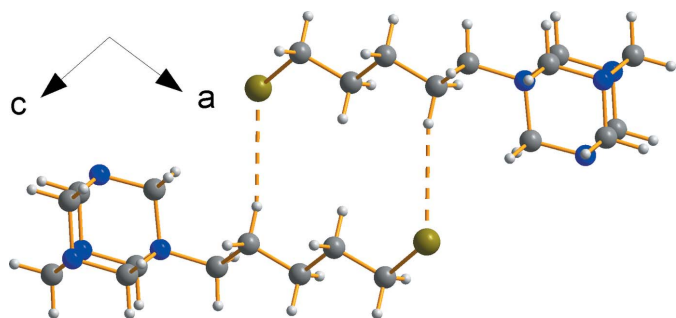
Figure 1
Asymmetric unit of compound **1**. Hydrogen atom labels are omitted for clarity. Displacement ellipsoids are at the 50% probability level.

configuration, unlike its hexyl relative (Reddy *et al.*, 1994), which displays an anticlinal configuration between C4 and C6 of the hexyl chain (torsion angle = 133°).

3. Supramolecular features

The three-dimensional structure of **1** features C—H$\cdots$Br$^-$ and C—H$\cdots$Br—C interactions (Table 1). Hirshfeld surface

Figure 2
Dimerization of 5-bromopentylurotropinium cations through C—H$\cdots$Br—C bonds.
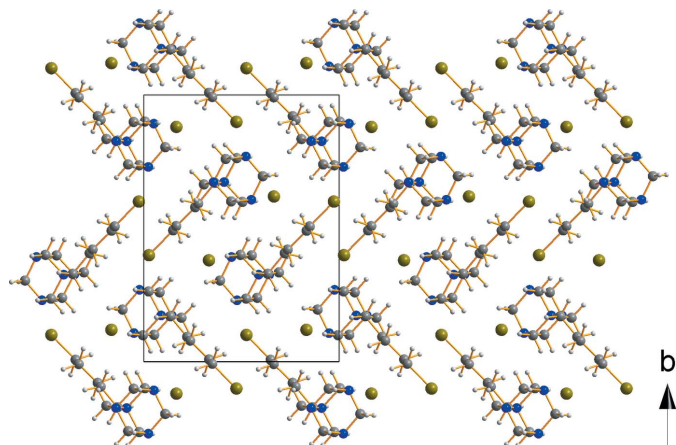
Figure 3
View of the crystal packing of compound **1** looking down the *a* axis.

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

| D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C12—H12$A\cdots$Br17	0.99	2.91	3.800 (2)	150
C13—H13$B\cdots$Br17	0.99	2.77	3.689 (2)	155
C15—H15$A\cdots$Br17^{i}	0.99	2.92	3.844 (3)	156
C8—H8$B\cdots$Br17^{ii}	0.99	2.82	3.777 (2)	162
C6—H6$B\cdots$Br17^{iii}	0.99	2.86	3.819 (2)	163
C5—H5$B\cdots$Br1^{iv}	0.99	3.00	3.960 (3)	163

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

analysis of the urotropinium cation (see below for further details) reveals that the bromide anion, Br17, accepts C—H$\cdots$Br hydrogen bonds from H12A and H13B [H$\cdots$Br = 2.91 and 2.77 Å, respectively] within the asymmetric unit and forms bonds to H6$B(\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$, 2.92 Å), H8$B$ ($\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$, 2.82 Å) and H15$A(-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$, 2.86 Å). C—H$\cdots$Br—C bonds are also seen from H5B to Br1($1 - x, 1 - y, -z$) at the end of the pentyl chain, linking neighbouring cations into an inversion dimer with an H$\cdots$Br distance of 3.00 Å (Fig. 2).

The overall packing (Fig. 3) is similar to the hexyl compound.

4. Hirshfeld surface analysis and two-dimensional fingerprint plots

The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and two-dimensional fingerprint plots (McKinnon *et al.*, 2007) were calculated using *Crystal Explorer 17* (Turner *et al.*, 2017). The surface was calculated for the 5-bromopentyl-urotropinium cation (Fig. 4) in order to differentiate the contribution of the alkylbromine and bromide components to the overall bonding picture. In the d_{norm} plot (Fig. 5a), white surface areas represent contacts at the sum of van der Waals radii, red is shorter (close contact) and blue is longer (long contact).
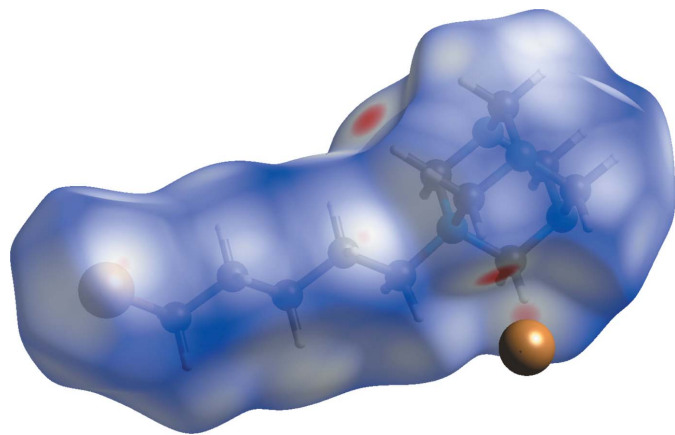
Figure 4
Hirshfeld surface of the 5-bromopentylurotropinium cation in compound **1** with the bromide anion shown. Surface plotted for d_{norm} in the range −0.1755 to 1.3045 a.u.
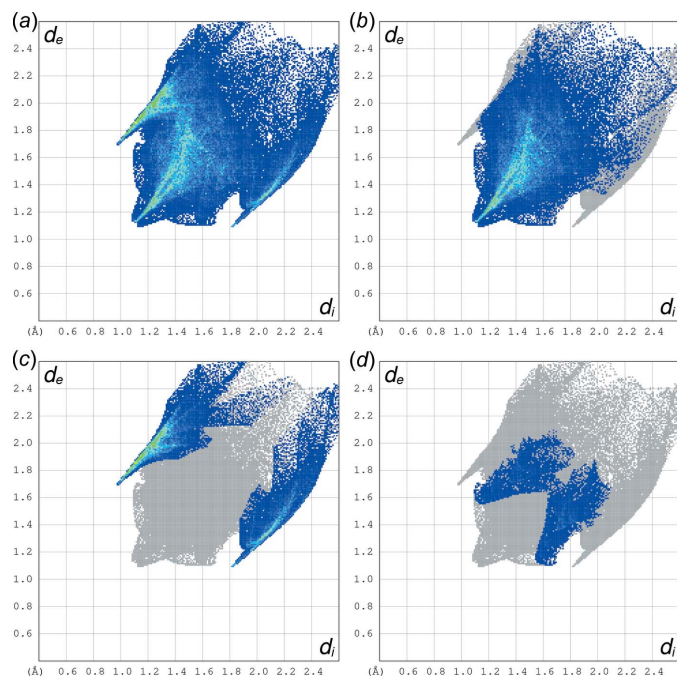
Figure 5
Two-dimensional fingerprint plots for compound **1**, showing (*a*) all interactions, (*b*) H⋯H, (*c*) H⋯Br and (*d*) H⋯N subsets.

The Hirshfeld surface primarily consists of H⋯H van der Waals interactions (59.6%, Fig. 5*b*) with the next major contributor being H⋯Br (31.0%, Fig. 5*c*) with a small N⋯H component (9.4%, Fig. 5*d*). The interaction of H and the alkylbromine residue accounts for 12.6% of the surface (bottom right of Fig. 5*c*), leaving the remaining 18.4% as H⋯Br^{-} hydrogen bonds to the bromide ions (top left of Fig. 5*c*), as detailed above.

5. Database survey

Surprisingly few discrete alkylurotropinium salts have been submitted to the Cambridge Structural Database (version 5.41, May 2020 update 2, Groom *et al.*, 2016), given that the salts are reported to crystallize in most cases. There are 48 in total, 17 of which are halide or polyiodide salts. In the remainder, the alkylurotropinium exists as a counter-ion to complex anions or is a bridging species in a coordination polymer. Of the 17, only six are bromide salts (refcode BUXZEZ, Qingchuan *et al.* 1983; CAQVUO, Aniol *et al.*, 2017; CEXLOG, Mak, 1984; GINHAN, Betz & Klüfers, 2007; YOYWEO and YOYWIS, Reddy *et al.*, 1994).

A close relative to compound **1** is 6-bromohexyl-urotropinium bromide, C$_{12}$H$_{24}$BrN$_4$$^+$·Br$^-$ (YOYWIS; Reddy *et al.*, 1994), which is isostructural, also crystallizing in space group *P*2$_1$/*n*. As mentioned above, this displays an anticlinal torsion angle in the alkyl chain, but presents very similar H⋯Br$^-$ interactions and overall packing. For the purposes of comparison, the partial structure CIF in the CSD was completed in *OLEX2* to add in the hydrogen atoms present in the original publication, and Hirshfeld surface analysis also undertaken. A potential difficulty in this structure is the

Table 2
Experimental details.

Crystal data	
Chemical formula	C$_{11}$H$_{22}$BrN$_4$$^+$·Br$^-$
M_r	370.14
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	8.7897 (2), 14.8937 (3), 11.1294 (2)
β (°)	101.742 (2)
V (Å^3)	1426.47 (5)
Z	4
Radiation type	Cu *K*α
μ (mm^{-1})	7.09
Crystal size (mm)	0.08 × 0.06 × 0.05
Data collection	
Diffractometer	Rigaku Oxford Diffraction Super-Nova, Dual, Cu at zero, Atlas
Absorption correction	Gaussian (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.698, 0.788
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22370, 2992, 2652
R_{int}	0.040
(sin θ/λ)$_{max}$ (Å^{-1})	0.632
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.025, 0.063, 1.04
No. of reflections	2992
No. of parameters	154
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.53, −0.64

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Berndt, 1999) and *OLEX2* (Dolomanov *et al.*, 2009).

presence of a possible disorder in the hexyl chain (atom C10 has a markedly larger U_{eq} value than its neighbours, plus hydrogen atoms on C10 come into closer than van der Waals contact with hydrogen atoms on neighbouring C10 atoms in the crystal). However, the interactions between hydrogen and bromide account for a similar percentage of the overall Hirshfeld surface (16.6% in YOYWIS *versus* 18.4% in compound **1**).

Direct comparisons with BUXZEZ (Yang *et al.*, 1983) are difficult because of the disorder around the allyl group while the remaining compounds have other significant intermolecular interactions such as hydrogen bonds formed to bromide by a water molecule (CEXLOG, GINHAN) or from a carboxylic acid (YOYWEO). Similar interactions to compound **1** can be seen where chloride is the halide anion: BIDBIZ (Shao *et al.*, 1982) shows hydrogen bonds from the benzylurotropinium cation to the chloride anion, accounting for 12.2% of the interaction surface. Polyiodide compounds appear not to show C—H⋯I interactions in the same manner as the above bromide and chloride compounds, but a methylurotropinium monoiodide compound (VOBCIY; Ribár *et al.*, 1991) displays similar interactions to **1** with H⋯I hydrogen bonds forming 15.5% of the Hirshfeld surface.

6. Synthesis and crystallization

Uroptropine (11.0 mmol, 1.542 g) and NaI (90.95 mmol, 1.648 g) were dissolved in ethanol and 1,5-dibromopentane

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(5.00 mmol, 0.595 ml) was added. Clear block-like crystals appeared after 8 days, which were found to be a mixture of compound **1** and [Na(H$_2$O)$_4$(hmta)]$_2$Br$_2$·2H$_2$O (Kruszynski *et al.*, 2012), which precluded further analysis, given the instability of hmta adducts to recrystallization.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms were positioned geometrically (C—H = 0.99 Å) and refined as riding atoms with U_{iso}(H) = 1.2U_{eq}(C).

References

Aniol, A., Mallick, B., Winter, M. & Feigel, M. (2017). *J. Mol. Struct.* **1141**, 451–456.

Betz, R. & Klüfers, P. (2007). *Acta Cryst.* E**63**, o4279.

Blažević, N., Kolbah, D., Belin, B., Šunjić, V. & Kajfež, F. (1979). *Synthesis*, pp. 161–176.

Brandenburg, K. & Berndt, M. (1999). *DIAMOND.* Crystal Impact GbR, Bonn, Germany.

Delépine, M. (1895). *Bull. Soc. Chim. Paris*, **13**, 352–355.

Delépine, M. (1897). *Bull. Soc. Chim. Paris*, **17**, 292–295.

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

Fried, L. E., Manaa, M. R., Pagoria, P. F. & Simpson, R. L. (2001). *Annu. Rev. Mater. Res.* **31**, 291–321.

Galat, A. & Elion, G. (1939). *J. Am. Chem. Soc.* **61**, 3585–3586.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Kruszynski, R., Sieranski, T., Bilinska, A., Bernat, T. & Czubacka, E. (2012). *Struct. Chem.* **23**, 1643–1656.

Lo, T. S., Hammer, K. D. P., Zegarra, M. & Cho, W. C. S. (2014). *Expert Rev. Anti Infect. Ther.* **12**, 549–554.

Ma, W., Chen, K., Li, Y., Hao, N., Wang, X. & Ouyang, P. (2017). *Engineering*, **3**, 308–317.

Mak, T. C. W. (1984). *Inorg. Chem.* **23**, 620–622.

McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* 3814–3816.

Qingchuan, Y., Meicheng, S. & Minxie, Q. (1983). *Huaxue Xuebao*, **41**, 176–178.

Reddy, D. S., Panneerselvam, K., Shimoni, L., Carrell, H. L. & Desiraju, G. R. (1994). *J. Mol. Struct.* **327**, 113–120.

Ribár, B., Mészáros, C., Vladimirov, S., Živanov-Stakić, D. & Golič, L. (1991). *Acta Cryst.* C**47**, 1987–1989.

Rigaku OD (2015). *CrysAlis PRO Software System*. Rigaku Oxford Diffraction, Yarnton, England.

Shao, M., Wang, L., Zheng, X. & Tang, Y. (1982). *Acta Chim. Sinica*, **40**, 223–232.

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

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

Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.

Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17.5*. The University of Western Australia.

Wang, J., Lu, X., Ying, H., Ma, W., Xu, S., Wang, X., Chen, K. & Ouyang, P. (2018). *Front. Microbiol.* **9**, 1312.

Yang, Q., Shao, M. & Qian, M. (1983). *Acta Chim. Sinica*, **41**, 176-181.

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: ShelXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

1-(5-Bromopentyl)-3,5,7-triaza-1-azoniatricyclo[3.3.1.1^{3,7}]decane bromide

Crystal data

$C_{11}H_{22}BrN_4^+·Br^-$	$F(000) = 744$
$M_r = 370.14$	$D_x = 1.724$ Mg m^{-3}
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
$a = 8.7897$ (2) Å	Cell parameters from 10133 reflections
$b = 14.8937$ (3) Å	$\theta = 5.0–76.7°$
$c = 11.1294$ (2) Å	$\mu = 7.09$ mm^{-1}
$\beta = 101.742$ (2)°	$T = 100$ K
$V = 1426.47$ (5) Å^3	Block, colourless
$Z = 4$	$0.08 × 0.06 × 0.05$ mm

Data collection

Rigaku Oxford Diffraction SuperNova, Dual, Cu at zero, Atlas diffractometer	22370 measured reflections
	2992 independent reflections
	2652 reflections with $I > 2\sigma(I)$
Detector resolution: 10.3196 pixels mm^{-1}	$R_{int} = 0.040$
ω scans	$\theta_{max} = 76.9°$, $\theta_{min} = 5.0°$
Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2015)	$h = -9 \rightarrow 11$
	$k = -18 \rightarrow 17$
$T_{min} = 0.698$, $T_{max} = 0.788$	$l = -13 \rightarrow 14$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.025$	H-atom parameters constrained
$wR(F^2) = 0.063$	$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2 + 1.7861P]$
$S = 1.04$	where $P = (F_o^2 + 2F_c^2)/3$
2992 reflections	$(\Delta/\sigma)_{max} = 0.001$
154 parameters	$\Delta\rho_{max} = 0.53$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.64$ e Å^{-3}
Primary atom site location: dual	

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 ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br17	0.26207 (3)	0.11960 (2)	0.16658 (2)	0.02528 (8)
Br1	0.83401 (3)	0.60049 (2)	0.02566 (3)	0.03427 (9)
N14	0.0484 (2)	0.32690 (14)	0.35699 (18)	0.0220 (4)
N9	0.1817 (2)	0.39262 (14)	0.55095 (18)	0.0209 (4)
N7	0.3320 (2)	0.32645 (13)	0.41148 (17)	0.0185 (4)
N11	0.1807 (2)	0.23044 (14)	0.52273 (19)	0.0233 (4)
C13	0.1875 (3)	0.33503 (16)	0.3076 (2)	0.0204 (4)
H13A	0.188486	0.393964	0.266600	0.024*
H13B	0.189079	0.287431	0.245757	0.024*
C8	0.3233 (3)	0.40058 (15)	0.5049 (2)	0.0200 (4)
H8A	0.413960	0.396114	0.573916	0.024*
H8B	0.326628	0.459996	0.465655	0.024*
C12	0.3222 (3)	0.23654 (16)	0.4761 (2)	0.0222 (5)
H12A	0.325576	0.186875	0.417548	0.027*
H12B	0.412836	0.230205	0.544750	0.027*
C4	0.6585 (3)	0.42073 (17)	0.2631 (2)	0.0228 (5)
H4A	0.723264	0.440004	0.342377	0.027*
H4B	0.700757	0.363271	0.239322	0.027*
C3	0.6661 (3)	0.49142 (17)	0.1656 (2)	0.0250 (5)
H3A	0.601900	0.471674	0.086368	0.030*
H3B	0.622209	0.548478	0.189060	0.030*
C6	0.4807 (3)	0.32939 (16)	0.3650 (2)	0.0216 (5)
H6A	0.491918	0.272273	0.322120	0.026*
H6B	0.568745	0.333678	0.436101	0.026*
C2	0.8312 (3)	0.50736 (18)	0.1499 (2)	0.0267 (5)
H2A	0.874916	0.450893	0.124359	0.032*
H2B	0.896396	0.526437	0.229127	0.032*
C16	0.0478 (3)	0.23966 (17)	0.4192 (2)	0.0261 (5)
H16A	−0.049980	0.233470	0.449665	0.031*
H16B	0.051124	0.190783	0.359514	0.031*
C5	0.4915 (3)	0.40688 (17)	0.2780 (2)	0.0241 (5)
H5A	0.453165	0.462523	0.310466	0.029*
H5B	0.424587	0.394188	0.196898	0.029*
C15	0.0467 (3)	0.39888 (16)	0.4473 (2)	0.0228 (5)
H15A	−0.050356	0.394968	0.479113	0.027*
H15B	0.048158	0.457856	0.406527	0.027*
C10	0.1763 (3)	0.30439 (16)	0.6095 (2)	0.0237 (5)
H10A	0.265689	0.298837	0.679369	0.028*
H10B	0.079868	0.299928	0.642209	0.028*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br17	0.02347 (13)	0.02523 (14)	0.02747 (13)	−0.00279 (9)	0.00593 (9)	−0.00790 (9)
Br1	0.02808 (14)	0.04267 (18)	0.03123 (15)	−0.00985 (11)	0.00409 (11)	0.00965 (11)
N14	0.0176 (9)	0.0237 (11)	0.0244 (10)	−0.0014 (7)	0.0038 (7)	0.0001 (8)
N9	0.0214 (9)	0.0215 (10)	0.0205 (9)	0.0016 (7)	0.0060 (7)	−0.0001 (7)
N7	0.0169 (9)	0.0173 (9)	0.0213 (9)	0.0007 (7)	0.0039 (7)	−0.0005 (7)
N11	0.0257 (10)	0.0193 (10)	0.0264 (10)	−0.0008 (8)	0.0092 (8)	0.0013 (8)
C13	0.0169 (10)	0.0237 (12)	0.0197 (10)	−0.0002 (8)	0.0018 (8)	−0.0002 (9)
C8	0.0212 (11)	0.0167 (11)	0.0220 (10)	−0.0005 (8)	0.0045 (8)	−0.0026 (8)
C12	0.0233 (11)	0.0167 (11)	0.0269 (12)	0.0019 (8)	0.0062 (9)	0.0013 (9)
C4	0.0191 (11)	0.0231 (12)	0.0268 (11)	0.0003 (9)	0.0063 (9)	−0.0024 (9)
C3	0.0218 (11)	0.0274 (13)	0.0264 (12)	−0.0019 (9)	0.0060 (9)	0.0011 (10)
C6	0.0178 (10)	0.0233 (12)	0.0248 (11)	0.0010 (8)	0.0069 (8)	−0.0023 (9)
C2	0.0248 (12)	0.0293 (13)	0.0264 (12)	−0.0019 (10)	0.0063 (9)	0.0037 (10)
C16	0.0233 (12)	0.0246 (13)	0.0308 (13)	−0.0067 (9)	0.0062 (10)	−0.0015 (10)
C5	0.0185 (11)	0.0273 (13)	0.0266 (12)	−0.0009 (9)	0.0050 (9)	0.0019 (9)
C15	0.0199 (11)	0.0239 (12)	0.0250 (11)	0.0049 (9)	0.0054 (9)	0.0012 (9)
C10	0.0269 (12)	0.0224 (12)	0.0230 (11)	0.0012 (9)	0.0077 (9)	0.0021 (9)

Geometric parameters (Å, º)

Br1—C2	1.962 (3)	C4—H4A	0.9900
N14—C13	1.444 (3)	C4—H4B	0.9900
N14—C16	1.473 (3)	C4—C3	1.523 (3)
N14—C15	1.472 (3)	C4—C5	1.525 (3)
N9—C8	1.444 (3)	C3—H3A	0.9900
N9—C15	1.480 (3)	C3—H3B	0.9900
N9—C10	1.472 (3)	C3—C2	1.515 (3)
N7—C13	1.539 (3)	C6—H6A	0.9900
N7—C8	1.529 (3)	C6—H6B	0.9900
N7—C12	1.530 (3)	C6—C5	1.522 (3)
N7—C6	1.501 (3)	C2—H2A	0.9900
N11—C12	1.445 (3)	C2—H2B	0.9900
N11—C16	1.471 (3)	C16—H16A	0.9900
N11—C10	1.471 (3)	C16—H16B	0.9900
C13—H13A	0.9900	C5—H5A	0.9900
C13—H13B	0.9900	C5—H5B	0.9900
C8—H8A	0.9900	C15—H15A	0.9900
C8—H8B	0.9900	C15—H15B	0.9900
C12—H12A	0.9900	C10—H10A	0.9900
C12—H12B	0.9900	C10—H10B	0.9900
C13—N14—C16	109.72 (19)	H3A—C3—H3B	107.9
C13—N14—C15	109.01 (18)	C2—C3—C4	111.8 (2)
C15—N14—C16	108.66 (19)	C2—C3—H3A	109.2
C8—N9—C15	109.30 (18)	C2—C3—H3B	109.2

C8—N9—C10	109.79 (18)	N7—C6—H6A	108.7
C10—N9—C15	107.96 (19)	N7—C6—H6B	108.7
C8—N7—C13	107.64 (17)	N7—C6—C5	114.37 (19)
C8—N7—C12	107.27 (17)	H6A—C6—H6B	107.6
C12—N7—C13	107.99 (17)	C5—C6—H6A	108.7
C6—N7—C13	112.44 (17)	C5—C6—H6B	108.7
C6—N7—C8	112.39 (17)	Br1—C2—H2A	109.7
C6—N7—C12	108.89 (17)	Br1—C2—H2B	109.7
C12—N11—C16	108.50 (19)	C3—C2—Br1	109.96 (17)
C12—N11—C10	109.20 (19)	C3—C2—H2A	109.7
C10—N11—C16	108.76 (19)	C3—C2—H2B	109.7
N14—C13—N7	109.89 (18)	H2A—C2—H2B	108.2
N14—C13—H13A	109.7	N14—C16—H16A	109.2
N14—C13—H13B	109.7	N14—C16—H16B	109.2
N7—C13—H13A	109.7	N11—C16—N14	111.85 (19)
N7—C13—H13B	109.7	N11—C16—H16A	109.2
H13A—C13—H13B	108.2	N11—C16—H16B	109.2
N9—C8—N7	110.37 (18)	H16A—C16—H16B	107.9
N9—C8—H8A	109.6	C4—C5—H5A	109.4
N9—C8—H8B	109.6	C4—C5—H5B	109.4
N7—C8—H8A	109.6	C6—C5—C4	111.0 (2)
N7—C8—H8B	109.6	C6—C5—H5A	109.4
H8A—C8—H8B	108.1	C6—C5—H5B	109.4
N7—C12—H12A	109.4	H5A—C5—H5B	108.0
N7—C12—H12B	109.4	N14—C15—N9	111.64 (19)
N11—C12—N7	111.02 (18)	N14—C15—H15A	109.3
N11—C12—H12A	109.4	N14—C15—H15B	109.3
N11—C12—H12B	109.4	N9—C15—H15A	109.3
H12A—C12—H12B	108.0	N9—C15—H15B	109.3
H4A—C4—H4B	108.1	H15A—C15—H15B	108.0
C3—C4—H4A	109.5	N9—C10—H10A	109.3
C3—C4—H4B	109.5	N9—C10—H10B	109.3
C3—C4—C5	110.7 (2)	N11—C10—N9	111.71 (19)
C5—C4—H4A	109.5	N11—C10—H10A	109.3
C5—C4—H4B	109.5	N11—C10—H10B	109.3
C4—C3—H3A	109.2	H10A—C10—H10B	107.9
C4—C3—H3B	109.2		
N7—C6—C5—C4	164.35 (19)	C3—C4—C5—C6	173.8 (2)
C13—N14—C16—N11	61.4 (3)	C6—N7—C13—N14	176.92 (19)
C13—N14—C15—N9	−61.1 (2)	C6—N7—C8—N9	−177.46 (18)
C13—N7—C8—N9	58.2 (2)	C6—N7—C12—N11	179.94 (19)
C13—N7—C12—N11	−57.7 (2)	C16—N14—C13—N7	−58.7 (2)
C13—N7—C6—C5	49.2 (3)	C16—N14—C15—N9	58.4 (2)
C8—N9—C15—N14	60.4 (2)	C16—N11—C12—N7	59.3 (2)
C8—N9—C10—N11	−60.0 (2)	C16—N11—C10—N9	−58.7 (2)
C8—N7—C13—N14	−58.8 (2)	C5—C4—C3—C2	179.3 (2)
C8—N7—C12—N11	58.1 (2)	C15—N14—C13—N7	60.2 (2)

C8—N7—C6—C5	−72.4 (2)	C15—N14—C16—N11	−57.7 (2)
C12—N7—C13—N14	56.8 (2)	C15—N9—C8—N7	−58.9 (2)
C12—N7—C8—N9	−57.8 (2)	C15—N9—C10—N11	59.0 (2)
C12—N7—C6—C5	168.85 (19)	C10—N9—C8—N7	59.3 (2)
C12—N11—C16—N14	−60.9 (3)	C10—N9—C15—N14	−59.0 (2)
C12—N11—C10—N9	59.5 (2)	C10—N11—C12—N7	−59.1 (2)
C4—C3—C2—Br1	−178.93 (17)	C10—N11—C16—N14	57.8 (2)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12*A*···Br17	0.99	2.91	3.800 (2)	150
C13—H13*B*···Br17	0.99	2.77	3.689 (2)	155
C15—H15*A*···Br17[i]	0.99	2.92	3.844 (3)	156
C8—H8*B*···Br17[ii]	0.99	2.82	3.777 (2)	162
C6—H6*B*···Br17[iii]	0.99	2.86	3.819 (2)	163
C5—H5*B*···Br1[iv]	0.99	3.00	3.960 (3)	163

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