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Crystal structure and Hirshfeld surface analysis of 1,4-diazabicyclo[2.2.2]octanediium bis(tribromide)

Dmytro A. Haleliuk,[a]* Laurentiu Baltag,[b] Dina D. Naumova,[a] Valeriia O. Zozulia[a] and Sofiia V. Partsevska[a]

[a]Department of Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrska str. 64/13, 01601 Kyiv, Ukraine, and [b]'Petru Poni' Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41-A, 700487 Iaşi, Romania. *Correspondence e-mail: galelukd@knu.ua

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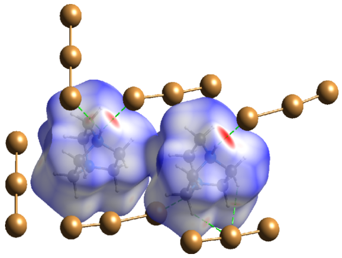
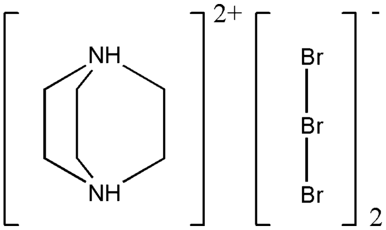
The crystal structure of the title salt, 1,4-diazabicyclo[2.2.2]octanediium bis(tribromide), $(C_6H_{14}N_2)[Br_3]_2$, consists of diprotonated 1,4-diazabicyclo[2.2.2]octanediium (or triethylenediamine) cations, which are separated by $[Br_3]^-$ anions. Br···Br contacts between polybromide anions generate supramolecular two-dimensional layers propagating along the *bc* plane. Organic cations are accommodated inside anionic layers and interact with tribromide anions through N—H···Br contacts. The structure is additionally stabilized by weak C—H···Br interactions linking the organic cations and $[Br_3]^-$. Hirshfeld surface analysis and associated fingerprint plots reveal that the main contributions to the crystal packing are provided by Br···H interactions (84.8%), followed by less chemically meaningful H···H (15.2%) contacts. As a novel example of a tribromide salt, the reported compound is of interest toward its potential use in organic synthesis as a regioselective brominating agent, in oxidation chemistry, and in materials processing involving metal dissolution and recovery.



1. Chemical context

Halogens represent a highly adaptable group of elements with numerous significant applications. Among their distinctive features is the ability to generate interhalogen species, as well as polyhalogen ions. Within this class, polyhalide anions – particularly those containing iodine – have been the subject of sustained interest for more than a century. A broad variety of these compounds has been identified and structurally characterized (Svensson & Kloo, 2003). Lighter halogens, however, tend to produce comparatively fewer polyhalide anions, a trend largely attributed to their higher volatility relative to iodine. Nonetheless, several polybromide species have been reported since the first systematic study by Chattaway and Hoyle in 1923 (Chattaway & Hoyle, 1923), including monoanions ($[Br_3]^-$, $[Br_5]^-$, $[Br_7]^-$, $[Br_9]^-$ and $[Br_{11}]^-$) and dianions ($[Br_4]^{2-}$, $[Br_6]^{2-}$, $[Br_8]^{2-}$ and $[Br_{10}]^{2-}$) (Sonnenberg *et al.*, 2020).



One of the most relevant applications of tribromide anions is their role as mild brominating reagents. In organic synthesis, tribromides serve as mild brominating agents with high

Table 1
Geometric paramerets of polybromide anions (Å, °).

	Br—Br	Br—Br—Br
Br1—Br2—Br3	2.5429 (9); 2.5780 (9)	179.51 (3)
Br4—Br5—Br6	2.8805 (9); 2.3582 (9)	174.15 (3)
Br7—Br8—Br7^{i}	2.5612 (6)	180
Br9—Br10—Br9^{ii}	2.5405 (7)	175.78 (5)

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

regioselectivity, while nonabromide anions, such as [NPr$_4$][Br$_9$], provide enhanced chemo- and stereoselectivity compared to Br$_2$ (Beck *et al.*, 2014). Tribromide complexes have been successfully applied as selective oxidizing agents. For example, the [DBUH][Br$_3$] complex (where DBUH = 1,8-diazabicyclo[5.4.0]undec-7-enium) was shown to promote efficient oxidations of sulfides to sulfoxides and of alcohols to carbonyl compounds under mild conditions, delivering high selectivity and avoiding over-oxidation (Bakavoli *et al.*, 2010*a*, 2010*b*). Polyhalide-based ionic liquids, such as [HMIM][Br$_9$] (where HMIM = 1-hexyl-3-methylimidazolium), combine low viscosity with strong oxidizing ability (Sonnenberg *et al.*, 2020). These liquids have been successfully employed for the oxidative dissolution and recovery of metals and alloys (Van Den Bossche *et al.*, 2018).

In the present communication, we report on a new polybromide compound containing the tribromide anion, (C$_6$H$_{14}$N$_2$)[Br$_3$]$_2$, its synthesis, crystal structure and Hirshfeld surface analysis.

2. Structural commentary

The title compound crystalizes in the monoclinic space group *C*2/*c*. It consists of diprotonated 1,4-diazabicyclo[2.2.2]octanediium (or triethylenediamine) cations separated by [Br$_3$]$^-$ anions (Fig. 1). The symmetry-independent unit contains 1.5 organic cation and9 Br atoms.

The Br—Br bond lengths are summarized in Table 1. Two symmetric and two asymmetric [Br$_3$]$^-$ anions are present in the structure. The Br4—Br5—Br6 anion exhibits two markedly different Br—Br distances, 2.8805 (9) and 2.3582 (9) Å, while in Br1—Br2—Br3, Br7—Br8—Br7^{i} and Br9—Br10—Br9^{ii}, the bond lengths are similar (Table 1).

The symmetric tribromide anion is best described as a delocalized three-centre four-electron (3c-4e) unit (Br—Br—Br)$^-$, in which the additional electron density is shared across the three Br atoms, giving peripheral Br—Br interactions of comparable half-bond character. In contrast, an asymmetric tribromide anion exhibits localization of the bonding: one Br—Br distance is relatively short, approaching that of a conventional single/partial single bond, while the other is elongated and weak, essentially representing a halogen-bond-type contact rather than a typical covalent bond. Such asymmetric trihalides are well documented in the polyhalide literature, and structural surveys reveal a wide distribution of Br—Br distances (Pichierri, 2011).

The angles between the Br atoms lie in the range between 174.15 (3) (for Br4—Br5—Br6) and 180.00° (for Br7—Br8—Br7^{i}) (Table 1). This range is also characteristic for other tribromide compounds listed in the *Database survey* section.

The charge of the tribromide anions is balanced by one fully independent asymmetric 1,4-diazabicyclo[2.2.2]octanediium dication and one half of a symmetry-generated cation, both diprotonated. The C—C bond lengths fall in the range 1.530 (7)–1.545 (7) Å and the C—N bond lengths are 1.480 (7)–1.499 (7) Å. These values are typical for diprotonated triethylenediamine cations and are consistent with previous reports (Andrzejewski *et al.*, 2011).

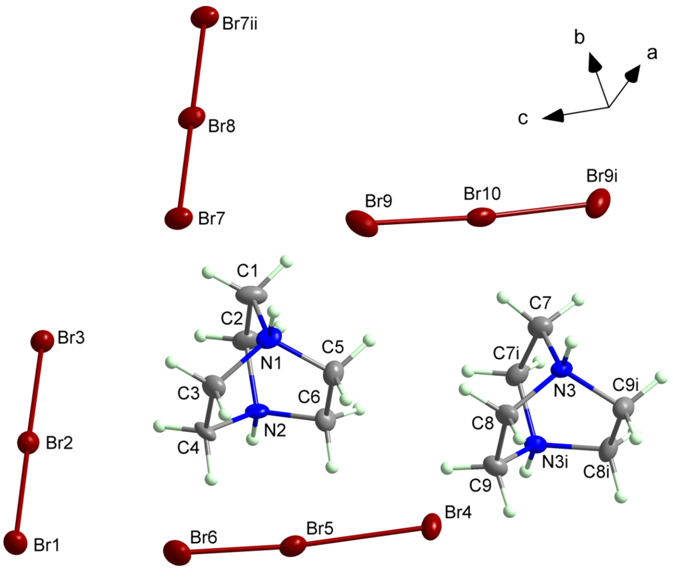


Figure 1
A fragment of the crystal structure of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x + 1, y, -z + \frac{1}{2}$; (ii) $-x + 1, -y + 2, -z + 1$.]

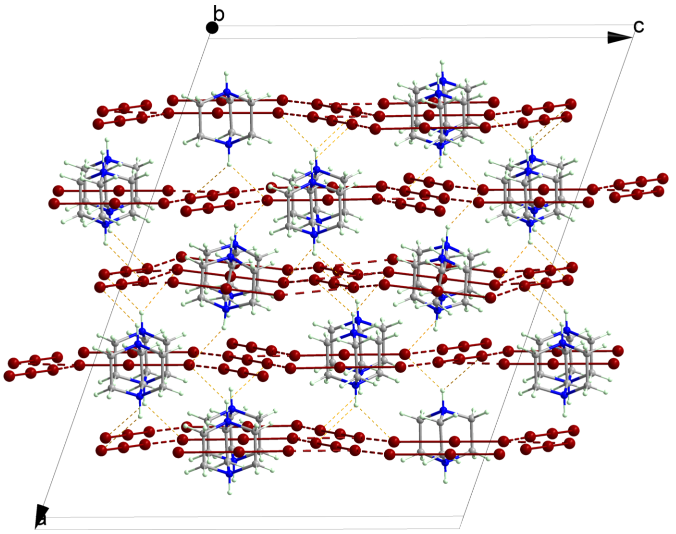


Figure 2
The crystal structure of the title compound in a view along the *bc* plane. Hydrogen bonds between organic cations and polybromide anions are shown as orange dashed lines. Br···Br contacts between [Br$_3$]$^-$ anions are shown as red dashed lines.

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯Br7	0.89 (5)	2.87 (2)	3.491 (4)	128 (1)
N1—H1⋯Br9	0.89 (5)	2.66 (5)	3.386 (5)	138 (3)
N2—H2⋯Br3^{i}	0.95 (5)	2.90 (4)	3.526 (5)	125 (1)
N2—H2⋯Br4^{ii}	0.95 (5)	2.51 (2)	3.256 (4)	136 (2)
N3—H3⋯Br4^{iii}	0.89 (5)	2.46 (5)	3.209 (5)	142 (3)

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

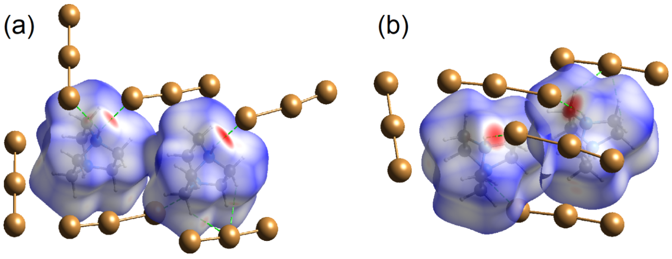


Figure 3
(*a*)/(*b*) Hirshfeld surface of the 1,4-diazabicyclo[2.2.2]octanediium cation. Neighbouring Br atoms are shown in ball-and-stick mode for clarity. The surface regions with the strongest intermolecular interactions are shown in red.

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_6H_{14}N_2^{2+}\cdot 2Br_3^-$
M_r	593.65
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	180
a, *b*, *c* (Å)	24.7979 (7), 8.9860 (2), 20.1594 (6)
β (°)	109.675 (3)
V (Å^3)	4229.9 (2)
Z	12
Radiation type	Mo *K*α
μ (mm^{-1})	17.06
Crystal size (mm)	0.19 × 0.13 × 0.1
Data collection	
Diffractometer	Rigaku Xcalibur Eos
Absorption correction	Analytical (*CrysAlis PRO*; Rigaku OD, 2024)
T_{min}, T_{max}	0.101, 0.276
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18451, 5033, 3541
R_{int}	0.062
(sin θ/λ)$_{max}$ (Å^{-1})	0.693
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.061, 1.04
No. of reflections	5033
No. of parameters	196
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.85, −0.83

Computer programs: *CrysAlis PRO* (Rigaku OD, 2024), *SHELXT2018* (Sheldrick, 2015*a*), *SHELXL2019* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

3. Supramolecular features

The polybromide anions form multiple intermolecular Br⋯Br contacts ensuring the creation of supramolecular two-dimensional layers which propagate along the *bc* plane (Fig. 2). All the supramolecular Br⋯Br contacts (3.5378 Å on average) are smaller than the sum of the van der Waals radii of 3.7 Å for Br atoms. The organic cations are located inside anionic layers and are connected with tribromide anions through N—H⋯Br contacts (Fig. 2 and Table 2). In particular, some of the N—H⋯Br hydrogen bonds exhibit significantly shorter H⋯Br distances compared to others. Such a close approach of the hydrogen-bond donors to one end of the tribromide anion stabilizes charge localization, resulting in the elongation of one Br—Br bond and the shortening of the other. This effect is particularly pronounced for the Br4—Br5—Br6 anion, while its influence on the Br9—Br10—Br9^{ii} [symmetry code: (ii) $-x+1, y, -z+\frac{1}{2}$] anion is less substantial.

In addition, there are weak C—H⋯Br contacts between the organic cations and $[Br_3]^-$ that provide additional stabilization of the structure.

4. Hirshfeld surface analysis

Hirshfeld surface analysis and two-dimensional fingerprint plots of the title compound were generated using *CrystalExplorer* (Spackman *et al.*, 2021).

The Hirshfeld surface analysis of the 1,4-diazabicyclo[2.2.2]octanediium cation highlights a pronounced N—H⋯Br hydrogen bond with a neighbouring tribromide anion, visualized as an intense red spot (d_{norm} plot; Fig. 3).

In addition, weaker C—H⋯Br contacts are observed. The relative contributions of these interactions to the crystal packing are depicted in the two-dimensional Hirshfeld fingerprint plots (Fig. 4).

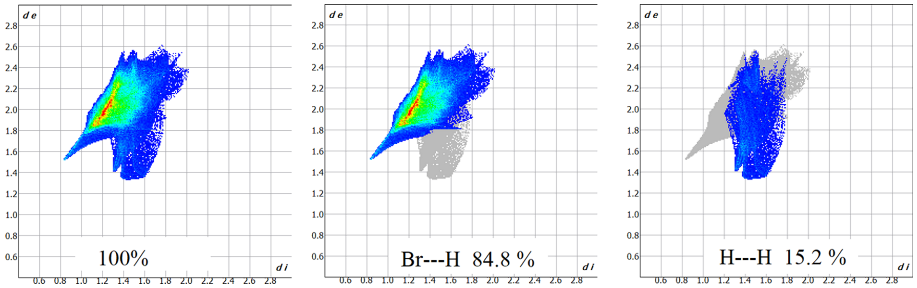


Figure 4
Fingerprint plots for 1,4-diazabicyclo[2.2.2]octanediium, showing the overall (100%), Br⋯H (84.8%) and H⋯H (15.2%) contributions. The d_e and d_i values are the distances to the closest external and internal atoms, respectively, from a given point to the Hirshfeld surface.

Acta Cryst. (2025). E**81**, 1067–1070 Haleliuk *et al.* • $C_6H_{14}N_2^{2+}\cdot 2Br_3^-$ **1069**

Among them, Br···H interactions provide the largest contribution (84.8%), followed by H···H (15.2%) contacts, which, though originating from the terminal positions of H atoms, are chemically insignificant.

5. Database survey

A search of the tribromide anion in the Cambridge Structural Database (CSD, Version 6.00, last update April 2025; Groom *et al.*, 2016) revealed 312 crystal structures. A search of the monoprotonated DABCO cation revealed 375 crystal structures and a search of the diprotonated DABCO cation revealed 581 crystal structures. The closest analogues to the title compound were found to be bis(1,4-diazoniabicyclo[2.2.2]-octane) bis(1-aza-4-azoniabicyclo[2.2.2]octane) tetrakis(tribromide) dibromides [DAHGUO (Allwood *et al.*, 1985) and DAHGUO01 (Heravi *et al.*, 2005)], both of which contain the diprotonated DABCO cation. There is also quinuclidinium tribromide (REKBIS; Robertson *et al.*, 1997) with a similar bicyclic cation.

6. Synthesis and crystallization

DABCO (0.5 mmol) was mixed with $PbBr_2$ (0.1 mmol) in 3 ml of HBr (48%). Bromine (1 mmol) was then added dropwise. The mixture was stirred for 4 h and the product was collected upon cooling of the solution. After filtration, light-orange crystals were obtained. They were separated and kept under Paratone oil until the diffraction experiment.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Methylene H atoms were positioned geometrically and refined with riding coordinates [$U_{iso}(H) = 1.2U_{eq}(C)$]. H atoms of the N—H groups were positioned geometrically and refined with riding coordinates and stretchable bonds [$U_{iso}(H) = 1.2U_{eq}(N)$].

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References

Allwood, B. L., Moysak, P. I., Rzepa, H. S. & Williams, D. J. (1985). *J. Chem. Soc. Chem. Commun.* pp. 1127–1129.

Andrzejewski, M., Olejniczak, A. & Katrusiak, A. (2011). *Cryst. Growth Des.* **11**, 4892–4899.

Bakavoli, M., Kakhky, A. M., Shiri, A., Ghabdian, M., Davoodnia, A., Eshghi, H. & Khatami, M. (2010*a*). *Chin. Chem. Lett.* **21**, 651–655.

Bakavoli, M., Rahimizadeh, M., Eshghi, H., Shiri, A., Ebrahimpour, Z. & Takjoo, R. (2010*b*). *Bull. Korean Chem. Soc.* **31**, 949–952.

Beck, T. M., Haller, H., Streuff, J. & Riedel, S. (2014). *Synthesis* **46**, 740–747.

Chattaway, F. D. & Hoyle, G. (1923). *J. Chem. Soc. Trans.* **123**, 654–662.

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

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

Heravi, M. M., Derikvand, F., Ghassemzadeh, M. & Neumüller, B. (2005). *Tetrahedron Lett.* **46**, 6243–6245.

Pichierri, F. (2011). *Chem. Phys. Lett.* **515**, 116–121.

Rigaku OD (2024). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, Oxfordshire, England.

Robertson, K. N., Bakshi, P. K., Cameron, T. S. & Knop, O. (1997). *Z. Anorg. Allg. Chem.* **623**, 104–114.

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

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

Sonnenberg, K., Mann, L., Redeker, F. A., Schmidt, B. & Riedel, S. (2020). *Angew. Chem.* **132**, 5506–5535.

Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). *J. Appl. Cryst.* **54**, 1006–1011.

Svensson, P. H. & Kloo, L. (2003). *Chem. Rev.* **103**, 1649–1684.

Van den Bossche, A., De Witte, E., Dehaen, W. & Binnemans, K. (2018). *Green Chem.* **20**, 3327–3338.

1070 Haleliuk *et al.* • $C_6H_{14}N_2^{2+}\cdot 2Br_3^-$ *Acta Cryst.* (2025). E**81**, 1067–1070

supporting information

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Computing details

1,4-Diazabicyclo[2.2.2]octanediium bis(tribromide)

Crystal data

$C_6H_{14}N_2^{2+}\cdot 2Br_3^-$
$M_r = 593.65$
Monoclinic, $C2/c$
$a = 24.7979\ (7)$ Å
$b = 8.9860\ (2)$ Å
$c = 20.1594\ (6)$ Å
$\beta = 109.675\ (3)°$
$V = 4229.9\ (2)$ Å^3
$Z = 12$

$F(000) = 3288$
$D_x = 2.797$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3922 reflections
$\theta = 2.3–28.1°$
$\mu = 17.06$ mm^{-1}
$T = 180$ K
Prism, clear light orange
0.19 × 0.13 × 0.1 mm

Data collection

Rigaku Xcalibur Eos diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.1593 pixels mm^{-1}
ω scans
Absorption correction: analytical (CrysAlis PRO; Rigaku OD, 2024)

$T_{\min} = 0.101$, $T_{\max} = 0.276$
18451 measured reflections
5033 independent reflections
3541 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.062$
$\theta_{\max} = 29.5°$, $\theta_{\min} = 1.7°$
$h = -32 \rightarrow 33$
$k = -11 \rightarrow 11$
$l = -26 \rightarrow 27$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.061$
$S = 1.04$
5033 reflections
196 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0062P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.85$ e Å^{-3}
$\Delta\rho_{\min} = -0.83$ e Å^{-3}
Extinction correction: SHELXL2019 (Sheldrick, 2015*b*), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.000083 (3)

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	$U_{\rm iso}$*/$U_{\rm eq}$
Br2	0.33244 (2)	0.50575 (7)	0.64045 (3)	0.02256 (15)
Br3	0.33170 (2)	0.77017 (7)	0.59054 (3)	0.02278 (15)
Br10	0.500000	0.60990 (9)	0.250000	0.0252 (2)
Br5	0.33242 (2)	0.11522 (7)	0.41626 (3)	0.02463 (16)
Br4	0.33268 (2)	0.10617 (7)	0.27353 (3)	0.02476 (16)
Br8	0.500000	1.000000	0.500000	0.0249 (2)
Br1	0.33315 (3)	0.24402 (7)	0.68869 (3)	0.02580 (16)
Br7	0.50095 (2)	0.73650 (7)	0.54881 (3)	0.02625 (16)
Br6	0.33155 (3)	0.14927 (7)	0.53188 (3)	0.03047 (17)
Br9	0.51368 (3)	0.62030 (8)	0.38060 (3)	0.03385 (18)
N2	0.28257 (18)	0.5789 (5)	0.3643 (2)	0.0167 (11)
H2	0.242 (2)	0.5785 (5)	0.3461 (9)	0.020*
N3	0.55301 (19)	0.0763 (5)	0.2665 (2)	0.0167 (11)
H3	0.591 (2)	0.0763 (5)	0.2778 (7)	0.020*
N1	0.38870 (18)	0.5790 (5)	0.4120 (2)	0.0194 (12)
H1	0.427 (2)	0.5794 (5)	0.4287 (9)	0.023*
C4	0.3012 (2)	0.5139 (6)	0.4374 (3)	0.0180 (14)
H4A	0.286087	0.411521	0.435981	0.022*
H4B	0.286299	0.575026	0.468271	0.022*
C3	0.3673 (2)	0.5120 (7)	0.4661 (3)	0.0230 (15)
H3A	0.381497	0.569881	0.510404	0.028*
H3B	0.381323	0.408464	0.476170	0.028*
C8	0.5380 (2)	0.0047 (6)	0.3243 (3)	0.0217 (14)
H8A	0.552330	0.065723	0.367606	0.026*
H8B	0.555898	−0.094974	0.334504	0.026*
C6	0.3041 (2)	0.4874 (7)	0.3175 (3)	0.0219 (14)
H6A	0.289743	0.527505	0.268904	0.026*
H6B	0.290410	0.383638	0.316405	0.026*
C9	0.4724 (2)	−0.0094 (6)	0.3011 (3)	0.0225 (15)
H9A	0.461046	−0.115398	0.293658	0.027*
H9B	0.458416	0.031316	0.337972	0.027*
C1	0.3681 (2)	0.7365 (7)	0.3979 (3)	0.0280 (16)
H1A	0.384404	0.783387	0.364353	0.034*
H1B	0.380795	0.794392	0.442216	0.034*
C7	0.53241 (19)	0.2334 (7)	0.2562 (3)	0.0232 (15)
H7A	0.539921	0.277607	0.215221	0.028*
H7B	0.552795	0.293208	0.298496	0.028*
C2	0.3027 (2)	0.7363 (6)	0.3668 (3)	0.0244 (15)
H2A	0.286432	0.797200	0.396380	0.029*

H2B	0.290034	0.779202	0.318716	0.029*
C5	0.3697 (2)	0.4911 (6)	0.3457 (3)	0.0224 (15)
H5A	0.385023	0.388602	0.354820	0.027*
H5B	0.384278	0.537359	0.310429	0.027*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br2	0.0212 (3)	0.0242 (4)	0.0228 (3)	−0.0002 (2)	0.0080 (3)	−0.0020 (3)
Br3	0.0228 (3)	0.0212 (4)	0.0239 (3)	0.0001 (3)	0.0073 (3)	−0.0004 (3)
Br10	0.0196 (5)	0.0144 (5)	0.0410 (6)	0.000	0.0095 (4)	0.000
Br5	0.0242 (3)	0.0164 (4)	0.0312 (4)	−0.0003 (3)	0.0066 (3)	−0.0011 (3)
Br4	0.0168 (3)	0.0360 (4)	0.0208 (3)	0.0009 (3)	0.0055 (3)	−0.0078 (3)
Br8	0.0213 (5)	0.0226 (5)	0.0258 (5)	−0.0005 (4)	0.0011 (4)	0.0001 (4)
Br1	0.0301 (4)	0.0237 (4)	0.0251 (4)	0.0009 (3)	0.0112 (3)	0.0023 (3)
Br7	0.0259 (4)	0.0223 (4)	0.0255 (4)	−0.0020 (3)	0.0019 (3)	0.0036 (3)
Br6	0.0344 (4)	0.0294 (4)	0.0271 (4)	−0.0008 (3)	0.0097 (3)	0.0086 (3)
Br9	0.0235 (4)	0.0420 (5)	0.0351 (4)	0.0002 (3)	0.0086 (3)	0.0158 (4)
N2	0.010 (2)	0.015 (3)	0.022 (3)	−0.0036 (19)	0.002 (2)	0.001 (2)
N3	0.013 (2)	0.014 (3)	0.023 (3)	−0.001 (2)	0.006 (2)	−0.002 (2)
N1	0.009 (2)	0.021 (3)	0.022 (3)	0.002 (2)	−0.003 (2)	0.000 (2)
C4	0.013 (3)	0.026 (4)	0.016 (3)	−0.003 (2)	0.006 (3)	0.007 (3)
C3	0.024 (4)	0.026 (4)	0.018 (3)	−0.001 (3)	0.005 (3)	0.005 (3)
C8	0.025 (4)	0.022 (4)	0.017 (3)	−0.003 (3)	0.005 (3)	0.005 (3)
C6	0.018 (3)	0.025 (4)	0.023 (4)	0.002 (3)	0.009 (3)	−0.002 (3)
C9	0.021 (3)	0.022 (4)	0.026 (4)	0.000 (3)	0.010 (3)	0.005 (3)
C1	0.021 (4)	0.020 (4)	0.040 (4)	−0.003 (3)	0.007 (3)	0.005 (3)
C7	0.024 (3)	0.020 (4)	0.023 (4)	0.000 (3)	0.005 (3)	0.004 (3)
C2	0.027 (4)	0.014 (4)	0.030 (4)	0.000 (3)	0.008 (3)	0.002 (3)
C5	0.022 (3)	0.025 (4)	0.020 (3)	0.003 (3)	0.006 (3)	−0.003 (3)

Geometric parameters (Å, º)

Br2—Br3	2.5780 (9)	C4—C3	1.545 (7)
Br2—Br1	2.5429 (9)	C3—H3A	0.9900
Br10—Br9	2.5405 (7)	C3—H3B	0.9900
Br10—Br9$^{\rm i}$	2.5405 (7)	C8—H8A	0.9900
Br5—Br4	2.8805 (9)	C8—H8B	0.9900
Br5—Br6	2.3582 (9)	C8—C9	1.539 (7)
Br8—Br7	2.5612 (6)	C6—H6A	0.9900
Br8—Br7$^{\rm ii}$	2.5612 (6)	C6—H6B	0.9900
N2—H2	0.95 (5)	C6—C5	1.533 (7)
N2—C4	1.505 (6)	C9—H9A	0.9900
N2—C6	1.480 (7)	C9—H9B	0.9900
N2—C2	1.496 (7)	C1—H1A	0.9900
N3—H3	0.88 (5)	C1—H1B	0.9900
N3—C8	1.485 (6)	C1—C2	1.530 (7)
N3—C9$^{\rm i}$	1.506 (6)	C7—C7$^{\rm i}$	1.541 (9)

N3—C7	1.491 (7)	C7—H7A	0.9900
N1—H1	0.89 (5)	C7—H7B	0.9900
N1—C3	1.491 (7)	C2—H2A	0.9900
N1—C1	1.499 (7)	C2—H2B	0.9900
N1—C5	1.486 (6)	C5—H5A	0.9900
C4—H4A	0.9900	C5—H5B	0.9900
C4—H4B	0.9900		

Br1—Br2—Br3	179.5	Br7—Br8—Br7	180.0
Br4—Br5—Br6	174.2	Br9—Br10—Br9	175.8

N2—C4—C3—N1	1.6 (6)	C6—N2—C2—C1	−62.5 (6)
N2—C6—C5—N1	2.8 (6)	C9$^{\text{i}}$—N3—C8—C9	−55.4 (5)
N3—C8—C9—N3$^{\text{i}}$	−9.0 (6)	C9$^{\text{i}}$—N3—C7—C7$^{\text{i}}$	66.9 (7)
N1—C1—C2—N2	2.2 (7)	C1—N1—C3—C4	60.6 (5)
C4—N2—C6—C5	−63.0 (6)	C1—N1—C5—C6	−62.4 (6)
C4—N2—C2—C1	60.4 (6)	C7—N3—C8—C9	66.5 (5)
C3—N1—C1—C2	−63.4 (6)	C2—N2—C4—C3	−62.8 (5)
C3—N1—C5—C6	59.5 (6)	C2—N2—C6—C5	59.7 (6)
C8—N3—C7—C7$^{\text{i}}$	−55.3 (7)	C5—N1—C3—C4	−61.7 (6)
C6—N2—C4—C3	60.4 (5)	C5—N1—C1—C2	59.4 (6)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Br7	0.89 (5)	2.87 (2)	3.491 (4)	128 (1)
N1—H1···Br9	0.89 (5)	2.66 (5)	3.386 (5)	138 (3)
N2—H2···Br3$^{\text{iii}}$	0.95 (5)	2.90 (4)	3.526 (5)	125 (1)
N2—H2···Br4$^{\text{iv}}$	0.95 (5)	2.51 (2)	3.256 (4)	136 (2)
N3—H3···Br4$^{\text{i}}$	0.89 (5)	2.46 (5)	3.209 (5)	142 (3)

Symmetry codes: (i) −*x*+1, *y*, −*z*+1/2; (iii) −*x*+1/2, −*y*+3/2, −*z*+1; (iv) −*x*+1/2, *y*+1/2, −*z*+1/2.