IUCrData

ISSN 2414-3146

Metformindiium dibromide

Aarón Pérez-Benítez,[a] Luis E. Hernández Márquez,[a] Rosa Elena Arroyo-Carmona[a]* and Sylvain Bernès[b]*

[a]Facultad de Ciencias Químicas, Benemérita Universidad Autónoma de Puebla, Av. San Claudio y 18 Sur, 72570 Puebla, Pue., Mexico, and [b]Instituto de Física Luis Rivera Terrazas, Benemérita Universidad Autónoma de Puebla, Av. San Claudio y 18 Sur, 72570 Puebla, Pue., Mexico. *Correspondence e-mail: rosa.arroyo@correo.buap.mx, sylvain_bernes@hotmail.com

Received 31 July 2026
Accepted 2 August 2026

Edited by M. Bolte, Goethe-Universität Frankfurt, Germany

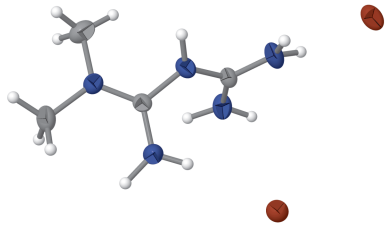
Keywords: crystal structure; metformin; dibromide salt; hydrogen bonds; QTAIM.

CCDC reference: 2578518

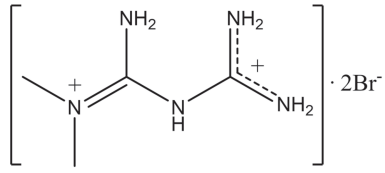
Structural data: full structural data are available from iucrdata.iucr.org

The crystal structure of the title salt, $C_4H_{13}N_5^{2+}\cdot 2Br^-$, is reported in space group $P2_1/c$, with $Z = 4$. Unexpectedly, this crystal is not isomorphous to the dichloride analogue, which has been reported in space group $P2_1$ ($Z = 2$). This originates from the shift of one halide anion in the asymmetric unit, which modifies the network of N—H···halide hydrogen bonds. For the here-reported structure, centrosymmetric $R_4^2(8)$ ring motifs are formed, affording a one-dimensional structure along [100], and the network is further expanded to a three-dimensional structure including larger ring motifs. This report is an example of a routine refinement carried out using now well-established techniques of quantum crystallography.

3D view



Chemical scheme



Structure description

In a recent article, Hill & Boeré (2025) argue in favour of wider application of quantum crystallography methods in routine chemical crystallography. Nowadays, experimental data quality is enough, even at room temperature, to fit the observed structure factors against non-spherical features of the electronic density map $\rho(\mathbf{r})$. As a result, refined structures are closer to those expected from neutron diffraction data. Most significantly, accurate positions for H atoms can be obtained, frequently with anisotropic displacement parameters. Such a precision is inherently unachievable in the context of an IAM (Independent Atom Model), since structure factors only include spherical scattering factors. In fact, the default *SFAC* command in *SHELXL* still refers to Cromer–Mann scattering factors for neutral atoms, taken from the 1992 edition of the *International Tables* (Wilson & Geist, 1992; Sheldrick, 2015*b*). In opposition, the 'Hirshfeld Atom Refinement' approach (HAR; Capelli *et al.*, 2014; Kleemiss *et al.*, 2021) uses non-spherical form factors for each atom in the model. The computed map $\rho(\mathbf{r})$ is then suitable for studying atoms, bonds, and lone pairs, using the concepts devised by Richard Bader in the

Table 1
Bond lengths (Å) and valence angles (°) observed in dication H_2Mf^{2+} for the dichloride (Xia, 2023) and dibromide salts.

Parameter	$H_2Mf^{2+}\cdot 2Cl^-$ [a]	$H_2Mf^{2+}\cdot 2Br^-$/ *SHELXL* [b]	$H_2Mf^{2+}\cdot 2Br^-$/ *NoSpherA2* [c]
Bonds			
N1—C1	1.473 (4)	1.463 (3)	1.455 (3)
N1—C2	1.469 (4)	1.462 (4)	1.459 (4)
N1—C3	1.335 (4)	1.304 (3)	1.309 (3)
N2—C3	1.321 (4)	1.315 (3)	1.315 (3)
N3—C3	1.386 (3)	1.392 (3)	1.392 (3)
N3—C4	1.378 (3)	1.362 (3)	1.362 (3)
N4—C4	1.325 (4)	1.306 (4)	1.309 (4)
N5—C4	1.310 (4)	1.304 (4)	1.311 (3)
Angles			
C1—N1—C2	115.7 (3)	115.1 (3)	115.2 (3)
C1—N1—C3	122.9 (2)	123.2 (2)	123.3 (3)
C2—N1—C3	120.0 (3)	120.9 (2)	120.7 (2)
N1—C3—N2	123.3 (2)	123.6 (2)	123.5 (2)
N1—C3—N3	118.2 (2)	119.5 (2)	119.2 (2)
N2—C3—N3	118.3 (3)	116.8 (2)	117.3 (2)
C3—N3—C4	125.0 (2)	124.8 (2)	124.4 (2)
N3—C4—N4	118.1 (3)	118.0 (3)	117.9 (3)
N3—C4—N5	120.4 (3)	119.5 (2)	119.6 (2)
N4—C4—N5	121.6 (3)	122.5 (3)	122.4 (3)
Torsion angles			
N1—C3—N3—C4	−139.2 (3)	−133.1 (3)	−133.4 (2)
N2—C3—N3—C4	45.6 (4)	49.7 (4)	49.6 (3)

Notes: (*a*) Xia (2023); (*b*) *SHELXL* refinement: isotropic H atoms; free coordinates and displacement parameters for all atoms (152 parameters, R_1 = 3.14% for observed reflections, wR_2 = 7.84% for all reflections); (*c*) refinement details in Table 3.

QTAIM theory (Quantum Theory of Atoms in Molecules; Bader, 2005). Indeed, some such 'routine' structures have already been published in repository journals like *Acta Cryst. C* or *IUCrData* (*e.g.* Jones, 2025; Samson *et al.*, 2025). We report here the HAR refinement for a new metforminium(2+) salt.

The title compound, abbreviated $H_2Mf^{2+}\cdot 2Br^-$, is the dibromide salt of metformin [IUPAC name: [amino(dimethylimino)methyl](diaminomethylidene)ammonium dibromide]. Metformin, Mf, is the first-line oral medication used to lower blood sugar in patients diagnosed with type-2 diabetes, and is sold in form of chlorhydrate, $HMf^+\cdot Cl^-$. On the other hand, the monocation HMf^+ and dication H_2Mf^{2+} have been used as counter-ions for vanadium clusters, which are also probed as medication against diabetes (*e.g.* Polito-Lucas *et al.*, 2021; Chatkon *et al.*, 2022).

The here reported crystal structure for $H_2Mf^{2+}\cdot 2Br^-$ is not isostructural to $H_2Mf^{2+}\cdot 2Cl^-$ (Xia, 2023; Hitchings *et al.*, 2025). The dichloride salt crystallizes in space group $P2_1$, with Z = 2, while the dibromide salt gives crystals in space group $P2_1/c$, with Z = 4 (Fig. 1). Metrics for the dication H_2Mf^{2+} are however similar in both salts, and its twisted conformation is maintained, regardless of the counter-ion (Table 1). An overlay between both dications gives an rms deviation of 0.06 Å. The introduction of a *c* glide plane in the case of the dibromide salt should thus result from different positions of the halide ions in the asymmetric units. In turn, these positions should determine different networks of hydrogen bonds. This is indeed the case, as shown in Fig. 2: the halide ions interact directly with the guanidine moiety of H_2Mf^{2+}, through charge-assisted $(Cl^-/Br^-)\cdots(H_2N)^+$ contacts. Cl1/Br1 ions have the

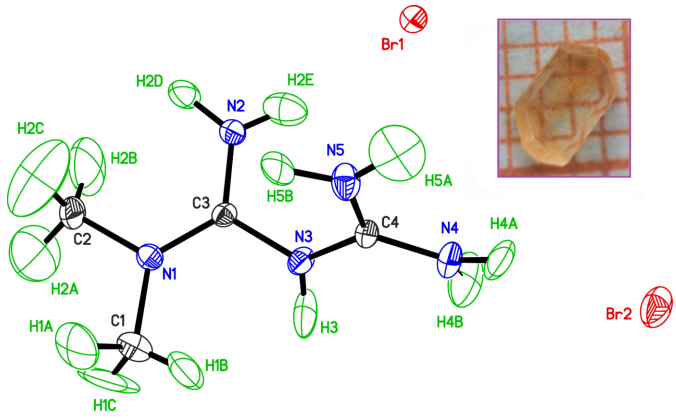


Figure 1
Molecular structure of the title compound, with displacement ellipsoids at 30% probability level. The asymmetric unit and the labelling scheme are those adopted by Xia (2023) in the dichloride analogue. The inset shows a representative crystal with a maximum dimension of *ca*. 4 mm, obtained by evaporation of an aqueous solution.

same position in the asymmetric units, and behave as acceptors with H2*E* as donor (Table 2, entry 1). The key difference relates for Cl2/Br2 position: in the dichloride salt, Cl2 gives a double-acceptor hydrogen bond, with H4*A* and H5*A* as donors (Fig. 2, top). In the case of the dibromide salt, only one

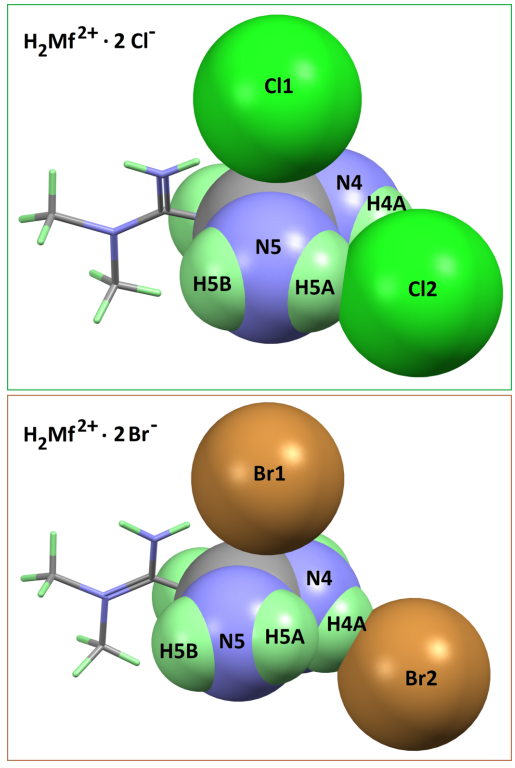


Figure 2
Comparison of the asymmetric units for $H_2Mf^{2+}\cdot 2Cl^-$ (Xia, 2023; space group $P2_1$; top) and $H_2Mf^{2+}\cdot 2Br^-$ (this work; space group $P2_1/c$; bottom). The guanidine moiety in the cation and halides ions are shown using a spacefill representation (Macrae *et al.*, 2020).

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2E···Br1	0.89 (5)	2.46 (4)	3.343 (3)	168 (3)
N4—H4A···Br2	0.91 (5)	2.48 (4)	3.355 (3)	163 (3)
N2—H2D···Br1^{i}	0.99 (4)	2.45 (4)	3.341 (3)	149 (3)
N3—H3···Br1^{ii}	0.94 (4)	2.42 (4)	3.321 (2)	160 (4)
N4—H4B···Br1^{iii}	1.01 (5)	2.48 (5)	3.350 (3)	144 (4)
N5—H5A···Br2^{iv}	0.90 (5)	2.49 (5)	3.346 (3)	157 (5)
N5—H5B···Br2^{v}	0.99 (4)	2.34 (4)	3.322 (3)	172 (3)

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

hydrogen bond is formed, N4—H4A···Br2 (Fig. 2, bottom; Table 2, entry 2).

This difference for the position of one anion is reflected in different supramolecular features. The smallest ring motifs found in $H_2Mf^{2+}\cdot 2Br^-$ have graph set $R_4^2(8)$ and are centrosymmetric. Cations are connected through these rings, forming a one-dimensional network oriented along [100]. The remaining amine groups, N3 and N5, give other efficient N—H···Br interactions, to build a complex three-dimensional framework (Fig. 3). A different image is obtained in the case of the dichloride salt: the bifurcated hydrogen bond including Cl2 affords an $R_2^1(6)$ ring motif, which is not present in the dibromide salt. The complete crystal structure is essentially diperiodic, and expands to a three-dimensional framework, documented in the supplementary information file available from the *CrystEngComm* article (Hitchings *et al.*, 2025; see Table S5 and Figure S3).

Synthesis and crystallization

The title compound was synthesized by reacting at room temperature 3.4 g (20.5 mmol) of metforminium chloride dissolved in 15 ml of distilled water, with 6 ml of 48% HBr (53.0 mmol). After 15 min. of magnetic stirring, the solvent was evaporated at ambient conditions for about three weeks, to yield large polyhedric colourless single crystals (Fig. 1, inset).

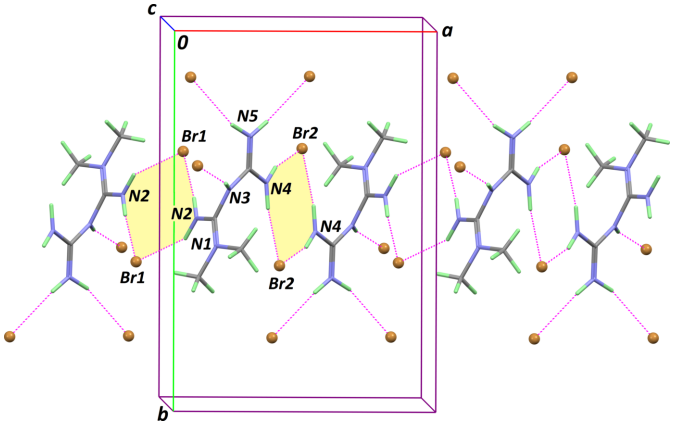


Figure 3
Part of the crystal structure of the title compound, emphasizing $R_4^2(8)$ rings building the one-dimensional framework (yellow areas). Br atom interactions with N3 and N5 afford a three-dimensional supramolecular structure.

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_4H_{13}N_5^{2+}\cdot 2Br^-$
M_r	290.99
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	295
a, b, c (Å)	10.3335 (3), 15.0443 (4), 6.4977 (2)
β (°)	95.427 (2)
V (Å^3)	1005.61 (5)
Z	4
Radiation type	Ag $K\alpha$, λ = 0.56083 Å
μ (mm^{-1})	4.29
Crystal size (mm)	0.29 × 0.20 × 0.07
Data collection	
Diffractometer	Stoe Stadivari
Absorption correction	Multi-scan (*LANA*; Folkers-Karlsson *et al.*, 2026)
T_{min}, T_{max}	0.288, 0.741
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	31050, 3212, 2465
R_{int}	0.031
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.725
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.070, 1.04
No. of reflections	3212
No. of parameters	217
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.85, −0.57

Computer programs: *X-AREA Pilatus3SV* (Stoe, 2025), *X-AREA Recipe* (Folkers-Karlsson *et al.*, 2026), *X-AREA Integrate3D* and *LANA* (Folkers-Karlsson *et al.*, 2026), *SHELXT2018/2* (Sheldrick, 2015*a*), *OLEX2.refine* (Bourhis *et al.*, 2015), *XP* in *SHELXTL-Plus* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The structure was first refined with *SHELXL* (Sheldrick, 2015*b*) and then with *OLEX2.refine* using the GUI *OLEX2* (Bourhis *et al.*, 2015; Dolomanov *et al.*, 2009). Further refinements were carried out using *NoSpherA2* in the same GUI (Kleemiss *et al.*, 2021) and *ORCA* for DFT computations (Neese, 2022). The last cycles for refining non-spherical scattering factors were based on a tetrameric model, $[C_4H_{13}N_5Br_2]_4$, in order to take in account non-covalent bonds, using the PBE0 functional in conjunction with the def2-TZVPD basis set, including the DKH2 correction for relativistic effects. Coordinates and anisotropic displacement parameters were refined for all atoms, without restraints nor constraints. A batch of 12 cycles of refinement for this 96-atom model including 568 electrons is completed in a few hours on an unsophisticated desktop PC (i7–6700 CPU @3.40 GHz, 8 threads, 8 Gb RAM).

Funding information

Funding for this research was provided by: Vicerrectoría de Investigación y Estudios de Posgrado, BUAP (grant No.

00118-PVG/2026; studentship to Luis E. Hernández-Márquez (Program Haciendo Ciencia en la BUAP Primavera 2026)); Consejo Nacional de Ciencia y Tecnología (grant No. 268178).

References

Bader, R. F. W. (2005). *Monatsh. Chem.* **136**, 819–854.

Bourhis, L. J., Dolomanov, O. V., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2015). *Acta Cryst.* A**71**, 59–75.

Capelli, S. C., Bürgi, H.-B., Dittrich, B., Grabowsky, S. & Jayatilaka, D. (2014). *IUCrJ* **1**, 361–379.

Chatkon, A., Haller, J. P. & Haller, K. J. (2022). *Acta Cryst.* B**78**, 798–808.

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

Folkers-Karlsson, L. C., Celani, P., Hahn, F. & Richter, J. (2026). *Z. Kristallogr.* **241**, 41–51.

Hill, N. D. D. & Boeré, R. T. (2025). *Chem. Methods* **5**, e202400052.

Hitchings, T. J., School Project Students, Shepherd, A., Alfredsson, M. & Saines, P. J. (2025). *CrystEngComm* **27**, 7785–7791.

Jones, P. G. (2025). *Acta Cryst.* C**81**, 455–461.

Kleemiss, F., Dolomanov, O. V., Bodensteiner, M., Peyerimhoff, N., Midgley, L., Bourhis, L. J., Genoni, A., Malaspina, L. A., Jayatilaka, D., Spencer, J. L., White, F., Grundkötter-Stock, B., Steinhauer, S., Lentz, D., Puschmann, H. & Grabowsky, S. (2021). *Chem. Sci.* **12**, 1675–1692.

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.

Neese, F. (2022). *WIREs Comput. Mol. Sci.* **12**, e1606.

Polito-Lucas, J. A., Núñez-Ávila, J. A., Bernès, S. & Pérez-Benítez, A. (2021). *IUCrData* **6**, x210634.

Samson, L., Banwart, L., Silwal, S. & Bond, M. R. (2025). *IUCrData* **10**, x250747.

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

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

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

Stoe (2025). *X-AREA Pilatus3SV*. Stoe & Cie, Darmstadt, Germany.

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

Wilson, A. J. C. & Geist, V. (1992). *International Tables for Crystallography* Vol. C, *Mathematical, Physical and Chemical Tables*. Dordrecht, Boston, London: Kluwer Academic Publishers.

Xia, Y.-P. (2023). *Z. Kristallogr. New Cryst. Struct.* **238**, 799–800.

full crystallographic data

IUCrData (2026). **11**, x260791 [https://doi.org/10.1107/S2414314626007911]

Metformindiium dibromide

Aarón Pérez-Benítez, Luis E. Hernández Márquez, Rosa Elena Arroyo-Carmona and Sylvain Bernès

[Amino(dimethyliminio)methyl](diaminomethylidene)ammonium dibromide

Crystal data

$C_4H_{13}N_5^{2+}\cdot 2Br^-$
M_r = 290.99
Monoclinic, $P2_1/c$
a = 10.3335 (3) Å
b = 15.0443 (4) Å
c = 6.4977 (2) Å
β = 95.427 (2)°
V = 1005.61 (5) Å^3
Z = 4
$F(000)$ = 569.890
D_x = 1.922 Mg m^{-3}
Ag $K\alpha$ radiation, λ = 0.56083 Å
Cell parameters from 22061 reflections
θ = 2.7–29.9°
μ = 4.29 mm^{-1}
T = 295 K
Plate, colourless
0.29 × 0.2 × 0.07 mm

Data collection

Stoe Stadivari diffractometer
Radiation source: Sealed X-ray tube, Axo Astix-f Microfocus source
Graded multilayer mirror monochromator
Detector resolution: 5.81 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*LANA*;Folkers-Karlsson *et al*., 2026)
T_{min} = 0.288, T_{max} = 0.741
31050 measured reflections
3212 independent reflections
2465 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 24.0°, θ_{min} = 2.7°
h = −14→14
k = −21→21
l = −9→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.070
S = 1.04
3212 reflections
217 parameters
0 restraints
0 constraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0267P)^2 + 1.1908P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.85 e Å^{-3}
$\Delta\rho_{min}$ = −0.57 e Å^{-3}

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

	x	y	z	U_{iso}*/U_{eq}
Br1	0.90769 (3)	0.642983 (18)	−0.06038 (4)	0.03418 (8)
Br2	0.44558 (3)	0.85428 (2)	0.28006 (5)	0.04693 (9)
N1	0.81449 (19)	0.41933 (14)	0.5843 (3)	0.0288 (4)

N2	0.8743 (3)	0.48014 (19)	0.2806 (4)	0.0341 (5)
H2D	0.916 (4)	0.426 (3)	0.231 (5)	0.048 (10)
H2E	0.881 (4)	0.529 (3)	0.205 (6)	0.061 (12)
N3	0.7614 (2)	0.56611 (16)	0.4982 (3)	0.0307 (5)
H3	0.783 (4)	0.585 (3)	0.635 (7)	0.065 (12)
N4	0.6770 (3)	0.70012 (18)	0.3858 (5)	0.0377 (5)
H4A	0.612 (4)	0.736 (3)	0.330 (7)	0.058 (12)
H4B	0.749 (4)	0.735 (3)	0.465 (8)	0.079 (15)
N5	0.6060 (3)	0.5722 (2)	0.2185 (4)	0.0354 (5)
H5A	0.568 (3)	0.608 (4)	0.118 (8)	0.078 (15)
H5B	0.600 (4)	0.506 (3)	0.215 (5)	0.046 (10)
C1	0.7302 (4)	0.4179 (3)	0.7514 (6)	0.0441 (7)
H1A	0.671 (5)	0.360 (3)	0.730 (7)	0.080 (15)
H1B	0.675 (5)	0.468 (3)	0.748 (7)	0.102 (18)
H1C	0.780 (5)	0.402 (4)	0.878 (6)	0.12 (2)
C2	0.8806 (4)	0.3358 (2)	0.5493 (6)	0.0424 (7)
H2A	0.910 (6)	0.306 (4)	0.683 (8)	0.13 (2)
H2B	0.964 (7)	0.343 (3)	0.475 (12)	0.14 (3)
H2C	0.824 (5)	0.295 (4)	0.451 (12)	0.15 (3)
C3	0.8168 (2)	0.48498 (16)	0.4524 (3)	0.0241 (4)
C4	0.6799 (2)	0.61371 (16)	0.3628 (4)	0.0257 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.03867 (13)	0.03190 (14)	0.03194 (12)	0.00332 (10)	0.00313 (9)	−0.00091 (10)
Br2	0.05447 (18)	0.04031 (17)	0.04234 (15)	0.01947 (13)	−0.01468 (12)	−0.00801 (12)
N1	0.0322 (10)	0.0297 (11)	0.0238 (9)	0.0024 (8)	−0.0007 (7)	0.0022 (8)
N2	0.0430 (13)	0.0310 (13)	0.0294 (11)	0.0084 (11)	0.0104 (10)	0.0042 (10)
H2D	0.06 (3)	0.05 (3)	0.04 (2)	0.03 (2)	0.017 (19)	0.01 (2)
H2E	0.06 (3)	0.08 (3)	0.05 (3)	−0.02 (2)	0.01 (2)	0.00 (2)
N3	0.0358 (11)	0.0285 (11)	0.0262 (10)	0.0087 (9)	−0.0055 (8)	−0.0039 (9)
H3	0.08 (3)	0.03 (2)	0.09 (3)	0.01 (2)	−0.01 (3)	0.01 (2)
N4	0.0376 (13)	0.0237 (12)	0.0518 (16)	0.0065 (10)	0.0042 (11)	0.0007 (11)
H4A	0.08 (3)	0.02 (2)	0.08 (3)	0.01 (2)	0.03 (2)	−0.01 (2)
H4B	0.06 (3)	0.06 (3)	0.11 (4)	0.03 (3)	−0.03 (3)	0.00 (3)
N5	0.0348 (12)	0.0298 (13)	0.0391 (13)	0.0012 (10)	−0.0091 (10)	0.0038 (11)
H5A	0.02 (2)	0.11 (4)	0.11 (4)	0.00 (2)	0.02 (2)	0.01 (3)
H5B	0.07 (3)	0.04 (2)	0.019 (18)	0.00 (2)	−0.016 (17)	0.007 (17)
C1	0.0488 (18)	0.052 (2)	0.0331 (15)	−0.0020 (16)	0.0106 (13)	0.0068 (15)
H1A	0.09 (3)	0.07 (3)	0.08 (3)	−0.05 (3)	0.02 (3)	0.00 (2)
H1B	0.16 (4)	0.07 (3)	0.09 (3)	0.05 (3)	0.08 (3)	0.05 (3)
H1C	0.15 (5)	0.18 (6)	0.04 (2)	0.03 (4)	0.06 (3)	0.03 (3)
C2	0.057 (2)	0.0293 (15)	0.0398 (16)	0.0100 (14)	0.0006 (14)	0.0062 (12)
H2A	0.17 (6)	0.12 (5)	0.09 (4)	0.04 (4)	−0.04 (4)	0.03 (4)
H2B	0.17 (6)	0.07 (4)	0.18 (6)	0.06 (4)	0.07 (6)	0.05 (4)
H2C	0.06 (3)	0.12 (5)	0.25 (7)	−0.01 (3)	−0.04 (4)	−0.09 (5)
C3	0.0247 (10)	0.0249 (11)	0.0219 (9)	0.0021 (8)	−0.0015 (8)	−0.0024 (8)

C4	0.0262 (10)	0.0215 (10)	0.0293 (10)	0.0036 (9)	0.0020 (8)	0.0008 (9)

Geometric parameters (Å, º)

N1—C1	1.455 (3)	N4—C4	1.309 (4)
N1—C2	1.459 (4)	N5—H5A	0.90 (5)
N1—C3	1.309 (3)	N5—H5B	0.99 (4)
N2—H2D	0.99 (4)	N5—C4	1.311 (3)
N2—H2E	0.89 (5)	C1—H1A	1.06 (4)
N2—C3	1.315 (3)	C1—H1B	0.95 (4)
N3—H3	0.94 (4)	C1—H1C	0.96 (5)
N3—C3	1.392 (3)	C2—H2A	1.00 (5)
N3—C4	1.362 (3)	C2—H2B	1.04 (6)
N4—H4A	0.91 (5)	C2—H2C	1.02 (5)
N4—H4B	1.01 (5)		
C2—N1—C1	115.2 (3)	H1B—C1—H1A	108 (4)
C3—N1—C1	123.3 (3)	H1C—C1—N1	109 (3)
C3—N1—C2	120.7 (2)	H1C—C1—H1A	99 (4)
H2E—N2—H2D	116 (3)	H1C—C1—H1B	120 (4)
C3—N2—H2D	125 (2)	H2A—C2—N1	111 (3)
C3—N2—H2E	119 (3)	H2B—C2—N1	114 (3)
C3—N3—H3	114 (2)	H2B—C2—H2A	105 (5)
C4—N3—H3	122 (2)	H2C—C2—N1	111 (3)
C4—N3—C3	124.4 (2)	H2C—C2—H2A	113 (5)
H4B—N4—H4A	113 (4)	H2C—C2—H2B	103 (5)
C4—N4—H4A	125 (3)	N2—C3—N1	123.5 (2)
C4—N4—H4B	123 (2)	N3—C3—N1	119.2 (2)
H5B—N5—H5A	123 (4)	N3—C3—N2	117.3 (2)
C4—N5—H5A	115 (3)	N4—C4—N3	117.9 (3)
C4—N5—H5B	121.7 (19)	N5—C4—N3	119.6 (2)
H1A—C1—N1	107 (2)	N5—C4—N4	122.4 (3)
H1B—C1—N1	112 (2)		
N1—C3—N3—C4	−133.4 (2)	N2—C3—N3—C4	49.6 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*E*···Br1	0.89 (5)	2.46 (4)	3.343 (3)	168 (3)
N4—H4*A*···Br2	0.91 (5)	2.48 (4)	3.355 (3)	163 (3)
N2—H2*D*···Br1^{i}	0.99 (4)	2.45 (4)	3.341 (3)	149 (3)
N3—H3···Br1^{ii}	0.94 (4)	2.42 (4)	3.321 (2)	160 (4)
N4—H4*A*···N4^{iii}	0.91 (5)	3.18 (4)	3.579 (2)	109 (3)
N4—H4*B*···Br1^{iv}	1.01 (5)	2.48 (5)	3.350 (3)	144 (4)
N4—H4*B*···N4^{iv}	1.01 (5)	3.06 (5)	3.579 (2)	113 (3)
N5—H5*A*···Br2^{iii}	0.90 (5)	2.49 (5)	3.346 (3)	157 (5)
N5—H5*B*···Br2^{v}	0.99 (4)	2.34 (4)	3.322 (3)	172 (3)

C1—H1*A*···N5^{vi}	1.06 (4)	3.08 (5)	3.501 (5)	104 (3)
C1—H1*B*···N3	0.95 (4)	2.43 (4)	2.808 (5)	104 (3)
C1—H1*B*···N5^{vi}	0.95 (4)	2.99 (5)	3.501 (5)	115 (4)
C2—H2*A*···Br1^{vii}	1.00 (5)	3.24 (6)	3.630 (3)	105 (4)

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