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Bromidotetrakis(1*H*-2-ethyl-5-methylimidazole- κ N³)copper(II) bromide

Sylvia Godlewska, Katarzyna Baranowska, Joanna Socha and Anna Dołęga*

Department of Inorganic Chemistry, Faculty of Chemistry, Gdańsk University of Technology, 11/12 G. Narutowicz St., 80233 PL Gdańsk, Poland
Correspondence e-mail: anndoleg@pg.gda.pl

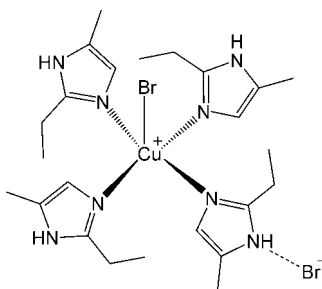
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Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; disorder in main residue; R factor = 0.027; wR factor = 0.076; data-to-parameter ratio = 13.5.

The Cu^{II} ion in the title compound, [CuBr(C₆H₁₀N₂)₄]Br, is coordinated in a square-based-pyramidal geometry by the N atoms of four imidazole ligands and a bromide anion in the apical site. Both the Cu^{II} and Br⁻ atoms lie on a crystallographic fourfold axis. In the crystal, the [CuBr(C₆H₁₀N₂)₄]⁺ complex cations are linked to the uncoordinated Br⁻ anions (site symmetry $\bar{4}$) by N—H...Br hydrogen bonds, generating a three-dimensional network. The ethyl group of the imidazole ligand was modelled as disordered over two orientations with occupancies of 0.620 (8) and 0.380 (8).

Related literature

For more copper(II) complexes with bromido and imidazole ligands, see: Godlewska *et al.* (2011); Hossaini Sadr *et al.* (2004); Li *et al.* (2007); Liu *et al.* (2007); Näther *et al.* (2002*a,b*). For the alignment of dipoles in crystalline materials, see: Anthony & Radhakrishnan (2001).



Experimental

Crystal data

[CuBr(C₆H₁₀N₂)₄]Br $M_r = 664$ Tetragonal, $P4/n$ $a = 14.0961$ (4) Å $c = 7.5236$ (4) Å $V = 1494.94$ (10) Å³ $Z = 2$ Mo $K\alpha$ radiation $\mu = 3.43$ mm⁻¹ $T = 294$ K $0.54 \times 0.45 \times 0.33$ mm

Data collection

Oxford Diffraction Xcalibur
Sapphire2 diffractometer
Absorption correction: analytical
[*CrysAlis PRO* (Oxford
Diffraction, 2006), based on
expressions derived by Clark &

Reid (1995)]

 $T_{\min} = 0.248$, $T_{\max} = 0.44$

5099 measured reflections

1395 independent reflections

898 reflections with $I > 2s(I)$ $R_{\text{int}} = 0.025$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.027$ $wR(F^2) = 0.076$ $S = 0.95$

1395 reflections

103 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.63$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.39$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-------------------------|------------|-------------------------|-------------|
| Cu1—Br1 | 2.7330 (8) | Cu1—N1 ⁱ | 2.029 (2) |
| N1 ⁱ —Cu1—N1 | 89.708 (9) | N1—Cu1—N1 ⁱⁱ | 171.81 (12) |

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

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|-------|-------------|-------------|---------------|
| N2—H2 ⁱⁱⁱ ···Br2 ⁱⁱⁱ | 0.86 | 2.63 | 3.488 (2) | 178 |

Symmetry code: (iii) $-x + 1, -y + 1, -z + 1$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2006); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6533).

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supporting information

Acta Cryst. (2011). E67, m1906 [https://doi.org/10.1107/S1600536811051117]

Bromidotetrakis(1*H*-2-ethyl-5-methylimidazole- κ N³)copper(II) bromide

Sylwia Godlewska, Katarzyna Baranowska, Joanna Socha and Anna Dołęga

S1. Comment

The composition of (I) is very similar to the bromidotetrakis(1*H*2-isopropylimidazole- κ N³)copper(II) bromide described previously (Godlewska *et al.*, 2011). However these compounds display substantially different crystal packing. Four NH \cdots Br hydrogen bonds surrounding Br2 in bromidotetrakis(1*H*2-isopropylimidazole- κ N³)copper(II) bromide are almost planar whereas the corresponding hydrogen bonds in (I) form distorted tetrahedron around Br2 and therefore build a network extending in all three directions in crystal. Complex cations [Cu(C₆H₁₀N₂)₄Br]⁺ are dipoles aligned perfectly parallel to *c* axis in a head-to-tail manner (see Fig. 2). The disorder of alkyl substituents is typical of room temperature determinations (*e.g.* Näther *et al.* (2002a), *Acta Cryst.* E58, m63-m64).

The structure of (I) is shown in Fig. 1 and packing diagram of complex dipoles is presented in Fig.2.

S2. Experimental

The title compound was prepared by adding the solution of 0.223 g (1 mmol) copper(II) bromide in 4 ml of methanol to the solution of 0.496 g (4.5 mmol) 2-ethyl-4(5)-methylimidazole in 2 ml of methanol. After a few days blue prisms were obtained by slow evaporation of solvent from the reaction mixture.

S3. Refinement

All C–H hydrogen atoms were refined as riding on carbon atoms with methyl C–H = 0.98 Å, methine C–H = 1 Å, aromatic C–H = 0.95 Å and $U_{\text{iso}}(\text{H})=1.2 U_{\text{eq}}(\text{C})$ for aromatic and methine CH and $1.5U_{\text{eq}}(\text{C})$ for methyl groups. Ethyl group of imidazole was refined as disordered between two positions with occupancies 0.620 (8)/0.380 (8).

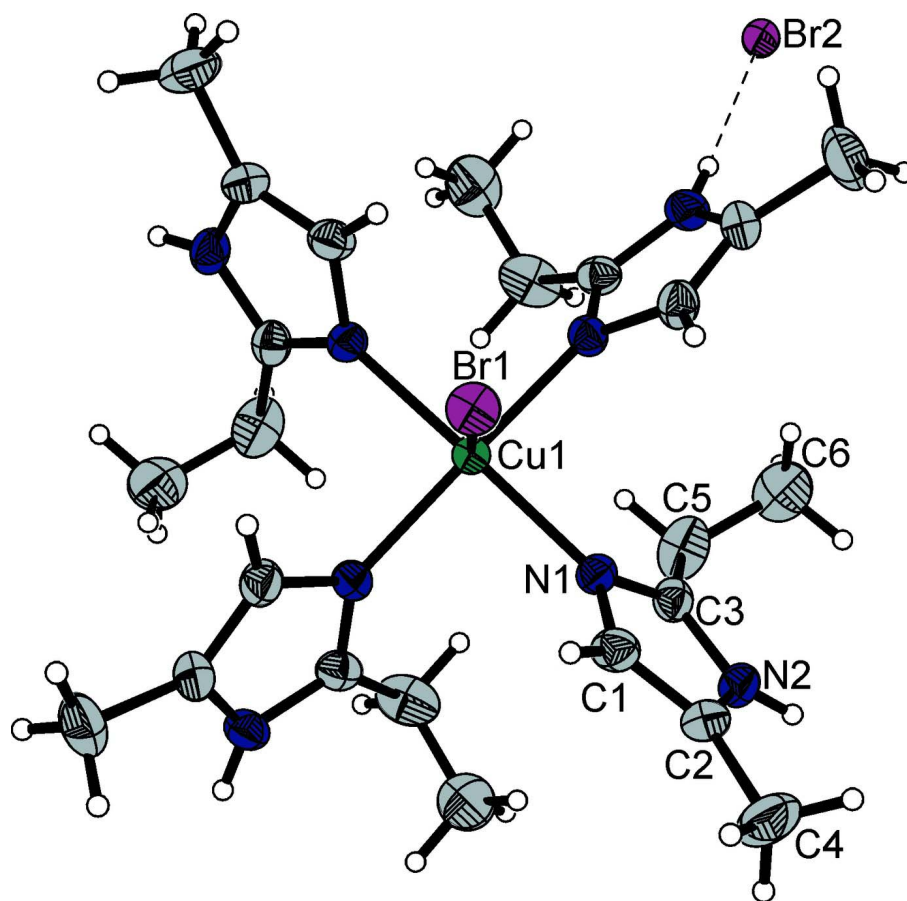


Figure 1

A view of (I), showing displacement ellipsoids drawn at the 30% probability level. Labels are given only for the independent part.

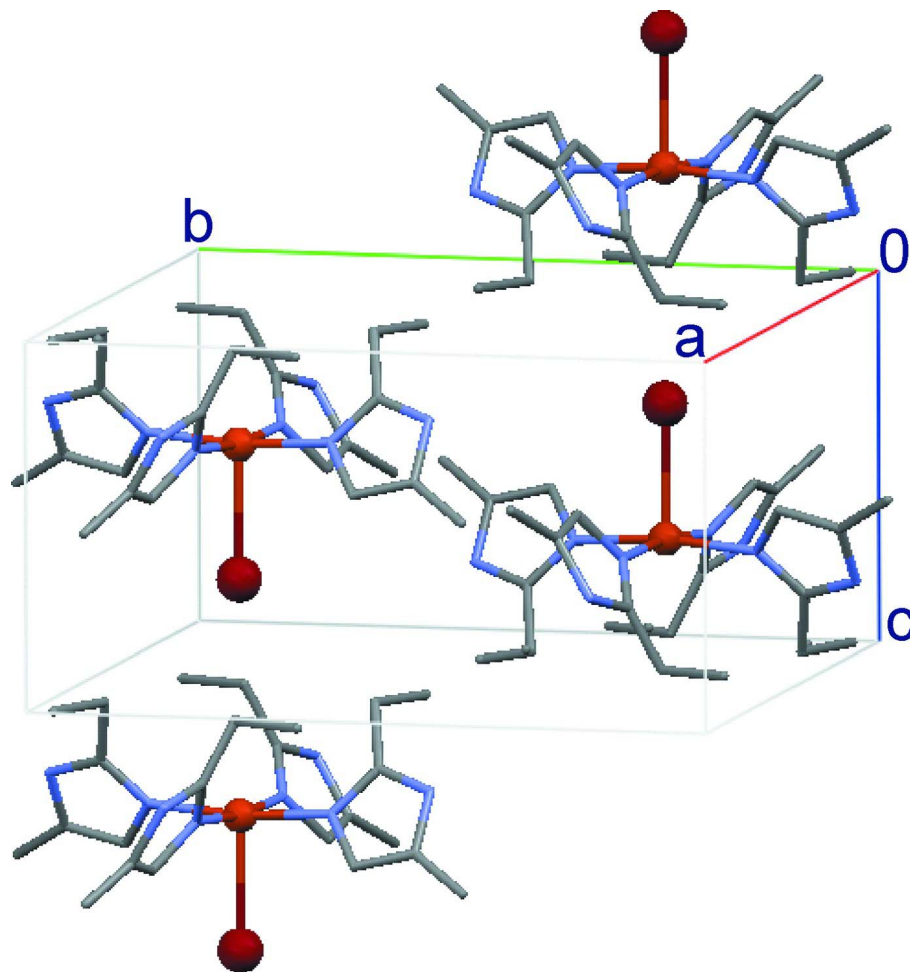


Figure 2

The packing of dipoles in crystals of (I).

Bromidotetrakis(1*H*-2-ethyl-5-methylimidazole- κ N³)copper(II) bromide

Crystal data

[CuBr(C₆H₁₀N₂)₄]₂Br

$M_r = 664$

Tetragonal, *P4/n*

Hall symbol: -*P* 4*a*

$a = 14.0961$ (4) Å

$c = 7.5236$ (4) Å

$V = 1494.94$ (10) Å³

$Z = 2$

$F(000) = 678$

Data collection

Oxford Diffraction Xcalibur Sapphire2
diffractometer

Graphite monochromator

Detector resolution: 8.1883 pixels mm⁻¹

ω scans

$D_x = 1.475$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2155 reflections

$\theta = 2.7$ – 28.8°

$\mu = 3.43$ mm⁻¹

$T = 294$ K

Prism, blue

$0.54 \times 0.45 \times 0.33$ mm

Absorption correction: analytical

[*CrysAlis PRO* (Oxford Diffraction, 2006),
based on expressions derived by Clark & Reid
(1995)]

$T_{\min} = 0.248$, $T_{\max} = 0.44$

5099 measured reflections

1395 independent reflections
 898 reflections with $I > 2s(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\text{max}} = 25.5^\circ$, $\theta_{\text{min}} = 2.7^\circ$

$h = -17 \rightarrow 10$
 $k = -17 \rightarrow 15$
 $l = -9 \rightarrow 7$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.076$
 $S = 0.95$
 1395 reflections
 103 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
 $w = 1/[\sigma^2(F_o^2) + (0.0447P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.004$
 $\Delta\rho_{\text{max}} = 0.63 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.39 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. CrysAlisPro (Oxford Diffraction Ltd., 2006) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. (Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* A51, 887-897)

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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|--------------|--------------|-------------|----------------------------------|-----------|
| Br1 | 0.25 | 0.25 | 0.31140 (7) | 0.0495 (2) | |
| Br2 | 0.75 | 0.25 | 0 | 0.05286 (19) | |
| Cu1 | 0.25 | 0.25 | 0.67466 (8) | 0.0366 (2) | |
| N1 | 0.22250 (14) | 0.39093 (14) | 0.6939 (3) | 0.0397 (5) | |
| N2 | 0.21196 (15) | 0.54003 (15) | 0.7653 (3) | 0.0486 (6) | |
| H2 | 0.2195 | 0.5922 | 0.823 | 0.058* | |
| C1 | 0.16846 (19) | 0.4385 (2) | 0.5685 (4) | 0.0481 (7) | |
| H1 | 0.141 | 0.4104 | 0.4693 | 0.058* | |
| C2 | 0.16140 (19) | 0.5299 (2) | 0.6100 (4) | 0.0520 (8) | |
| C3 | 0.24764 (19) | 0.4552 (2) | 0.8122 (4) | 0.0446 (7) | |
| C4 | 0.1150 (3) | 0.6113 (2) | 0.5178 (5) | 0.0900 (14) | |
| H4A | 0.0826 | 0.5888 | 0.4138 | 0.135* | |
| H4B | 0.1623 | 0.6568 | 0.4836 | 0.135* | |
| H4C | 0.0702 | 0.6408 | 0.5966 | 0.135* | |
| C5 | 0.2915 (9) | 0.4385 (17) | 0.980 (3) | 0.059 (3) | 0.620 (8) |
| H5A | 0.2972 | 0.3709 | 1.001 | 0.071* | 0.620 (8) |
| H5B | 0.2533 | 0.4658 | 1.0744 | 0.071* | 0.620 (8) |
| C6 | 0.3952 (5) | 0.4870 (5) | 0.9776 (9) | 0.087 (3) | 0.620 (8) |



| | | | | | |
|------|-------------|------------|-------------|-----------|-----------|
| H6A | 0.3886 | 0.5546 | 0.9672 | 0.131* | 0.620 (8) |
| H6B | 0.4307 | 0.4632 | 0.8783 | 0.131* | 0.620 (8) |
| H6C | 0.4279 | 0.4721 | 1.0859 | 0.131* | 0.620 (8) |
| C5A | 0.3233 (13) | 0.438 (2) | 0.966 (4) | 0.043 (5) | 0.380 (8) |
| H5A1 | 0.3232 | 0.3711 | 0.9977 | 0.052* | 0.380 (8) |
| H5A2 | 0.386 | 0.4535 | 0.9218 | 0.052* | 0.380 (8) |
| C6A | 0.3036 (11) | 0.4935 (7) | 1.1209 (14) | 0.123 (6) | 0.380 (8) |
| H6A1 | 0.3115 | 0.5595 | 1.0934 | 0.184* | 0.380 (8) |
| H6A2 | 0.3466 | 0.476 | 1.2143 | 0.184* | 0.380 (8) |
| H6A3 | 0.2395 | 0.4822 | 1.1588 | 0.184* | 0.380 (8) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Br1 | 0.0587 (3) | 0.0587 (3) | 0.0311 (3) | 0 | 0 | 0 |
| Br2 | 0.0394 (2) | 0.0394 (2) | 0.0798 (5) | 0 | 0 | 0 |
| Cu1 | 0.0350 (2) | 0.0350 (2) | 0.0397 (4) | 0 | 0 | 0 |
| N1 | 0.0396 (13) | 0.0367 (12) | 0.0428 (14) | 0.0018 (10) | -0.0011 (10) | -0.0029 (10) |
| N2 | 0.0519 (15) | 0.0364 (13) | 0.0576 (17) | -0.0021 (11) | 0.0071 (13) | -0.0080 (12) |
| C1 | 0.0411 (17) | 0.0519 (19) | 0.0514 (18) | 0.0037 (14) | -0.0084 (14) | -0.0031 (15) |
| C2 | 0.0455 (18) | 0.0466 (19) | 0.064 (2) | 0.0092 (14) | -0.0011 (16) | 0.0027 (16) |
| C3 | 0.0485 (18) | 0.0436 (17) | 0.0418 (17) | -0.0049 (13) | 0.0058 (14) | -0.0022 (14) |
| C4 | 0.086 (3) | 0.058 (2) | 0.127 (4) | 0.0231 (19) | -0.030 (2) | 0.007 (2) |
| C5 | 0.060 (9) | 0.070 (5) | 0.048 (6) | -0.003 (8) | -0.003 (7) | -0.007 (4) |
| C6 | 0.104 (6) | 0.079 (4) | 0.079 (6) | 0.010 (4) | -0.047 (4) | -0.021 (3) |
| C5A | 0.038 (11) | 0.060 (8) | 0.033 (8) | -0.024 (10) | -0.007 (8) | 0.007 (6) |
| C6A | 0.252 (18) | 0.065 (7) | 0.051 (7) | 0.045 (8) | -0.051 (9) | -0.023 (6) |

Geometric parameters (Å, °)

| | | | |
|---------------------------------------|------------|-----------|------------|
| Cu1—Br1 | 2.7330 (8) | C4—H4A | 0.96 |
| Cu1—N1 ⁱ | 2.029 (2) | C4—H4B | 0.96 |
| Cu1—N1 | 2.029 (2) | C4—H4C | 0.96 |
| Cu1—N1 ⁱⁱ | 2.029 (2) | C5—C6 | 1.613 (14) |
| Cu1—N1 ⁱⁱⁱ | 2.029 (2) | C5—H5A | 0.97 |
| N1—C3 | 1.319 (3) | C5—H5B | 0.97 |
| N1—C1 | 1.385 (3) | C6—H6A | 0.96 |
| N2—C3 | 1.344 (3) | C6—H6B | 0.96 |
| N2—C2 | 1.376 (4) | C6—H6C | 0.96 |
| N2—H2 | 0.86 | C5A—C6A | 1.43 (3) |
| C1—C2 | 1.330 (4) | C5A—H5A1 | 0.97 |
| C1—H1 | 0.93 | C5A—H5A2 | 0.97 |
| C2—C4 | 1.492 (4) | C6A—H6A1 | 0.96 |
| C3—C5 | 1.42 (2) | C6A—H6A2 | 0.96 |
| C3—C5A | 1.59 (3) | C6A—H6A3 | 0.96 |
| N1 ⁱ —Cu1—N1 | 89.708 (9) | N2—C3—C5A | 125.4 (12) |
| N1 ⁱ —Cu1—N1 ⁱⁱ | 89.707 (9) | C2—C4—H4A | 109.5 |

| | | | |
|---|-------------|---------------|------------|
| N1—Cu1—N1 ⁱⁱ | 171.81 (12) | C2—C4—H4B | 109.5 |
| N1 ⁱ —Cu1—N1 ⁱⁱⁱ | 171.81 (12) | H4A—C4—H4B | 109.5 |
| N1—Cu1—N1 ⁱⁱⁱ | 89.707 (9) | C2—C4—H4C | 109.5 |
| N1 ⁱⁱ —Cu1—N1 ⁱⁱⁱ | 89.708 (9) | H4A—C4—H4C | 109.5 |
| N1 ⁱ —Cu1—Br1 | 94.10 (6) | H4B—C4—H4C | 109.5 |
| N1—Cu1—Br1 | 94.10 (6) | C3—C5—C6 | 108.3 (12) |
| N1 ⁱⁱ —Cu1—Br1 | 94.10 (6) | C3—C5—H5A | 110 |
| N1 ⁱⁱⁱ —Cu1—Br1 | 94.10 (6) | C6—C5—H5A | 110 |
| C3—N1—C1 | 106.0 (2) | C3—C5—H5B | 110 |
| C3—N1—Cu1 | 132.03 (19) | C6—C5—H5B | 110 |
| C1—N1—Cu1 | 122.00 (18) | H5A—C5—H5B | 108.4 |
| C3—N2—C2 | 108.9 (2) | C6A—C5A—C3 | 112.1 (18) |
| C3—N2—H2 | 125.5 | C6A—C5A—H5A1 | 109.2 |
| C2—N2—H2 | 125.5 | C3—C5A—H5A1 | 109.2 |
| C2—C1—N1 | 110.5 (3) | C6A—C5A—H5A2 | 109.2 |
| C2—C1—H1 | 124.7 | C3—C5A—H5A2 | 109.2 |
| N1—C1—H1 | 124.7 | H5A1—C5A—H5A2 | 107.9 |
| C1—C2—N2 | 105.1 (2) | C5A—C6A—H6A1 | 109.5 |
| C1—C2—C4 | 132.0 (3) | C5A—C6A—H6A2 | 109.5 |
| N2—C2—C4 | 122.8 (3) | H6A1—C6A—H6A2 | 109.5 |
| N1—C3—N2 | 109.5 (2) | C5A—C6A—H6A3 | 109.5 |
| N1—C3—C5 | 127.0 (10) | H6A1—C6A—H6A3 | 109.5 |
| N2—C3—C5 | 122.8 (10) | H6A2—C6A—H6A3 | 109.5 |
| N1—C3—C5A | 124.3 (12) | | |

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

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------------|-------|-------------|-------------|---------------|
| N2—H2 \cdots Br2 ^{iv} | 0.86 | 2.63 | 3.488 (2) | 178 |

Symmetry code: (iv) $-x+1, -y+1, -z+1$.