Crystal structure and Hirshfeld surface analysis of 2-(4-bromophenyl)-4-methyl-6-oxo-1-phenyl-1,6-dihydropyridine-3-carbonitrile

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In the title compound, C19H13BrN2O, the pyridine ring is essentially planar [maximum deviation = 0.024 (4) Å for the N atom] and makes dihedral angles of 74.6 (2) and 65.8 (2)°, respectively, with the phenyl and bromophenyl rings, which subtend a dihedral angle of 63.1 (2)°. In the crystal, molecules are connected along the c-axis direction via C—Br···π interactions, generating zigzag chains parallel to the (010) plane. C—H···N and C—H···O hydrogen-bonding interactions further connect the molecules, forming a three-dimensional network and reinforcing the molecular packing. Hirshfeld surface analysis indicates that the most important contributions to the crystal packing are from H···H (36.2%), C···H/H···C (21.6%), N···H/H···N (12.2%), and Br···H/H···Br (10.8%) interactions.

1. Chemical context

C—C and C—N bond-forming reactions are a cornerstone of organic synthesis, materials science and medicinal chemistry (Zubkov et al., 2018; Shikhaliyev et al., 2019; Viswanathan et al., 2019; Gurbanov et al., 2020). Nitrogen heterocycles, particularly those including the 2-pyridone core, play a key role in medicinal chemistry and natural product synthesis (Sośnicki & Idzik, 2019; Duruskari et al., 2020; Sangwan et al., 2022). We report herein the synthesis of 2-pyridone, 2, on the basis of a one-step reaction of acetoacetanilide with 3-(4-bromophenyl)-3-oxopropanenitrile (Path B). Under two-step reaction conditions (Fig. 1), the interaction of acetocacetanilide with 3-oxo-3-phenylpropanenitrile led to the formation of another 2-pyridone, 1 (Path A), reported in the literature (Wardakhan & Agami, 2001).

Figure 1
The reaction of acetocacetanilide with 3-oxo-3-arylpropanenitriles.
Thus, in the framework of our ongoing structural studies (Naghiyev et al., 2020, 2021, 2022; Khalilov et al., 2022), we report the crystal structure and Hirshfeld surface analysis of the title compound, 2-(4-bromophenyl)-4-methyl-6-oxo-1-phenyl-1,6-dihydropyridine-3-carbonitrile.

2. Structural commentary

In the title compound, (Fig. 2), the pyridine ring (N1/C2–C6) is largely planar [maximum deviation = 0.024 (4) Å for N1]. The phenyl and bromophenyl groups are linked to the central pyridine ring in an equatorial arrangement. The pyridine ring subtends dihedral angles of 74.6 (2) and 65.8 (2)° with the phenyl (C7–C12) and bromophenyl (C15–C20) rings, which in turn make a dihedral angle of 63.1 (2)° with each other.

3. Supramolecular features and Hirshfeld surface analysis

Fig. 3 shows a general view of the C—H ⋯ N, C—H ⋯ O hydrogen bonds (Table 1) and C—Br ⋯ π interactions in the unit cell of the title compound. In the crystal, molecules are joined along the c-axis direction by C—Br ⋯ π interactions [C18—Br1 ⋯ Cg1iv; C18—Br1 = 1.944 (4) Å, Br1 ⋯ Cg1iv = 3.4788 (18) Å, C18—Br1 ⋯ Cg1iv = 100.50 (13)°; Cg1 is the centroid of the N1/C2–C6 pyridine ring; symmetry code: (iv) x+3/2, y+1/2, z]. generating zigzag chains parallel to the (010) plane (Figs. 4 and 5). C—H ⋯ N and C—H ⋯ O hydrogen bonds link these molecules, establishing a three-dimensional network and strengthening the molecular packing.

CrystalExplorer17.5 (Turner et al., 2017) was used to analyse and visualize the intermolecular interactions of the title compound. Fig. 6a,b depicts the front and back sides of the Hirshfeld surface plotted over dnorm in the range of 0.2437 to 1.2589 a.u. The red spots on the Hirshfeld surface indicate C—H ⋯ N and C—H ⋯ O interactions (Table 1).

The overall two-dimensional fingerprint plot for the title compound and those delineated into H—H (36.2%, Fig. 7b), C—H—H—C (21.6%, Fig. 7c), N—H—H—N (12.2%, Fig. 7d), and Br—H—H—Br (10.8%, Fig. 7e) interactions, as well as

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

| D—H ⋯ A     | D—H | H ⋯ A | D ⋯ A | D—H ⋯ A |
|-------------|-----|-------|-------|---------|
| C16—H16 ⋯ N2i | 0.95 | 2.55  | 3.234 (6) | 129 |
| C17—H17 ⋯ O1ii | 0.95 | 2.56  | 3.342 (6) | 140 |
| C20—H20 ⋯ O1iii | 0.95 | 2.40  | 3.256 (6) | 150 |

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

Figure 2
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

Figure 3
A general view of the C—H ⋯ N, C—H ⋯ O hydrogen bonds and C—Br ⋯ π interactions of the title compound. Symmetry codes: (i) x+1/2, −y+1/2, z−1; (ii) −x+1/2, y+1/2, z+1/2; (iii) −x+1, −y+1, z+1/2; (iv) x, −y+1/2, z.
their relative contributions to the Hirshfeld surface, are shown in Fig. 7, while Tables 1 and 2 provide data on the distinct intermolecular contacts. The remaining weak interactions (contribution percentages) are O···H/H···O (7.2%), Br···C/

Figure 4
Packing view of the title compound along the a axis showing the C—Br···π interactions as dashed lines.

Figure 5
Packing view of the title compound along the b axis with the C—Br···π interactions indicated by dashed lines.

Figure 7
The two-dimensional fingerprint plots of the title compound, showing (a) all interactions, and delineated into (b) H···H, (c) C···H/H···C, (d) N···H/H···N and (e) Br···H/H···Br interactions. [d_e and d_i represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

C···Br (3.6%), C···C (3.0%), Br·N/N·Br (2.2%), O···C/

Figure 6
(a) Front and (b) back sides of the three-dimensional Hirshfeld surface of the title compound mapped over d_ww, with a fixed colour scale of −0.2437 to 1.2589 a.u.

C···Br (3.6%), C···C (3.0%), Br·N/N·Br (2.2%), O···C/

Figure 4
Packing view of the title compound along the a axis showing the C—Br···π interactions as dashed lines.

Figure 5
Packing view of the title compound along the b axis with the C—Br···π interactions indicated by dashed lines.
4. Database survey

A search of the Cambridge Structural Database (CSD version 5.42, updated September 2021; Groom et al., 2016) for the basic skeleton of 6-oxo-1,6-dihydropyridine gave five compounds very similar to the title compound.

The cations in the crystal of FONDO01 (Pérez-Aguirre et al., 2015) interact with the anions through O—H⋯O and N—H⋯O hydrogen bonds, forming a three-dimensional supramolecular network.

In the crystal of SECPUN (Thanigaimani et al., 2012), an N—H⋯O hydrogen bond connects the cation and anion, while a pair of N—H⋯O hydrogen bonds connects the two anions with an \( R_2^2(8) \) ring motif. Weak N—H⋯O and C—H⋯O hydrogen bonds connect the aggregates, forming a three-dimensional network.

The ion pairs in the crystal of SUYXIU (Hemamalini & Fun, 2010) are linked by O⋯H⋯O, N—H⋯O, N—H⋯Br and C—H⋯O hydrogen bonds, producing a two-dimensional network parallel to the bc plane.

In the crystal of XOZCUL (Shishkina et al., 2009), the pyridine-3-carboxylate molecules form layers parallel to (010), which are linked by hydrogen bonds mediated by the bridging solvate molecules.

The asymmetric unit of GIHCOQ (Gupta et al., 2007) contains four molecules. The compound forms hydrogen-bonded sheets parallel to the [001] direction via intermolecular N—H⋯O and O—H⋯O hydrogen bonds. Each sheet is made up of linked dimers generated by \( R_2^2(8) \) N—H⋯O hydrogen-bonded motifs. Intermolecular N—H⋯O and O—H⋯O hydrogen bonds generate sheets parallel to the [001] direction. Each sheet is made up of linked dimers formed by N—H⋯O hydrogen bonds with \( R_2^2(8) \) motifs.

5. Synthesis and crystallization

To a solution of 3-(4-bromophenyl)-3-oxopropanenitrile (1.14 g; 5.1 mmol) and acetooaceticilide (0.92 g; 5.2 mmol) in methanol (25 mL), methylpyperazine (3 drops) was added and the mixture was stirred at room temperature for 48 h. Then 15 mL of methanol were removed from the reaction mixture, which was left overnight. The precipitated crystals were separated by filtration and recrystallized from ethanol/water (1:1) solution (yield 49%; m.p. 484–485 K).

\(^1\)H NMR (300 MHz, DMSO-\( d_6 \); ppm): 2.21 (s, 3H, CH\(_3\)); 6.61 (s, 1H, \( \equiv CH \)); 7.19–7.89 (m, 9H, 9Ar—H). \(^{13}\)C NMR (75 MHz, DMSO-\( d_6 \); ppm): 20.58 (CH\(_3\)).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All C-bound H atoms were placed at calculated positions and refined using a riding model, with C—H = 0.95 Å for aromatic H atoms and 0.98 Å for methyl H atoms, and with \( U_{iso}(H) = 1.2 \) or 1.5\( U_{eq}(C) \). Owing to poor agreement between observed and calculated intensities, nineteen outliers (8 4 0, 17 3 2, 15 8 2, 0 10 8, 5 3 2, 0 12 4, 4 11 3, 3 5 0, 18 5 2, 2 0 7, 5 3 2, 18 2 5, 15 8 2, 0 10 8, 5 3 2, 0 12 4, 17 6 1) were omitted in the final cycles of refinement.

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AB and ANK; resources, AB, VNK and EVD; supervision, ANK and MA.

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Crystal structure and Hirshfeld surface analysis of 2-(4-bromophenyl)-4-methyl-6-oxo-1-phenyl-1,6-dihydropyridine-3-carbonitrile

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Computing details

Data collection: CrysAlis PRO (Rigaku OD, 2021); cell refinement: CrysAlis PRO (Rigaku OD, 2021); data reduction: CrysAlis PRO (Rigaku OD, 2021); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: PLATON (Spek, 2020).

2-(4-Bromophenyl)-4-methyl-6-oxo-1-phenyl-1,6-dihydropyridine-3-carbonitrile

Crystal data

C_{19}H_{13}BrN_{2}O  
Mr = 365.21  
Orthorhombic, Pna2_1  
a = 15.58979 (16) Å  
b = 10.33883 (10) Å  
c = 9.91195 (9) Å  
V = 1597.61 (3) Å³  
Z = 4  
F(000) = 736

Data collection

XtaLAB Synergy, Dualflex, HyPix  
diffactometer  
Radiation source: micro-focus sealed X-ray tube  
φ and ω scans  
Absorption correction: multi-scan  
(CrysAlisPro; Rigaku OD, 2021)  
T_{min} = 0.413, T_{max} = 0.462  
45325 measured reflections

Refinement

Refinement on F^2  
Least-squares matrix: full  
R[F^2 > 2σ(F^2)] = 0.037  
wR(F^2) = 0.099  
S = 1.05  
3359 reflections  
209 parameters  
1 restraint  
Primary atom site location: difference Fourier map  
Secondary atom site location: difference Fourier map  
Hydrogen site location: inferred from neighbouring sites  
H-atom parameters constrained  
w = 1/σ^2(Fo)^2 + (0.0658P)^2 + 1.8045P  
where P = (Fo^2 + 2Fc^2)/3
\((\Delta/\sigma)_{\text{max}} < 0.001\)
\(\Delta \rho_{\text{max}} = 1.27 \text{ e Å}^{-3}\)
\(\Delta \rho_{\text{min}} = -0.89 \text{ e Å}^{-3}\)

**Absolute structure**: Flack \(x\) determined using 1531 quotients \([I^+]-[I^-])/([I^+]+[I^-])\) (Parsons et al., 2013).

**Absolute structure parameter**: \(-0.012 (18)\)

**Special details**

**Experimental.** CrysAlisPro 1.171.41.117a (Rigaku OD, 2021) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

**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 (Å²)**

| Atom | \(x\)  | \(y\)  | \(z\)  | \(U_{eq}\)  |
|------|-------|-------|-------|-----------|
| Br1  | 0.84710 (3) | -0.04550 (4) | 0.63282 (7) | 0.02494 (16) |
| O1   | 0.4307 (2)  | 0.4948 (4)  | 0.3074 (4)  | 0.0278 (7)   |
| N1   | 0.5437 (2)  | 0.4161 (4)  | 0.4275 (4)  | 0.0188 (7)   |
| N2   | 0.7885 (2)  | 0.6147 (4)  | 0.6339 (5)  | 0.0294 (7)   |
| C2   | 0.4948 (3)  | 0.5231 (5)  | 0.3709 (4)  | 0.0216 (10)  |
| C3   | 0.5263 (3)  | 0.6562 (5)  | 0.3980 (4)  | 0.0238 (9)   |
| H3   | 0.4934      | 0.7271      | 0.3657      | 0.029*       |
| C4   | 0.5993 (3)  | 0.6812 (4)  | 0.4665 (4)  | 0.0215 (8)   |
| C5   | 0.6468 (3)  | 0.5678 (5)  | 0.5140 (5)  | 0.0222 (10)  |
| C6   | 0.6185 (3)  | 0.4373 (4)  | 0.4937 (4)  | 0.0188 (8)   |
| C7   | 0.5051 (3)  | 0.2830 (4)  | 0.4247 (4)  | 0.0205 (8)   |
| C8   | 0.4705 (3)  | 0.2349 (5)  | 0.5395 (5)  | 0.0237 (9)   |
| H8   | 0.4733      | 0.2837      | 0.6205      | 0.028*       |
| C9   | 0.4295 (3)  | 0.1103 (5)  | 0.5393 (5)  | 0.0263 (9)   |
| H9   | 0.4052      | 0.0789      | 0.6209      | 0.032*       |
| C10  | 0.4243 (3)  | 0.0354 (5)  | 0.4255 (5)  | 0.0268 (10)  |
| H10  | 0.3970      | -0.0467     | 0.4261      | 0.032*       |
| C11  | 0.4602 (3)  | 0.0848 (5)  | 0.3123 (5)  | 0.0290 (10)  |
| H11  | 0.4587      | 0.0354      | 0.2315      | 0.035*       |
| C12  | 0.5005 (3)  | 0.2097 (5)  | 0.3110 (5)  | 0.0260 (9)   |
| H12  | 0.5243      | 0.2417      | 0.2293      | 0.031*       |
| C13  | 0.6315 (3)  | 0.8212 (5)  | 0.4893 (5)  | 0.0274 (10)  |
| H13A | 0.5887      | 0.8824      | 0.4551      | 0.041*       |
| H13B | 0.6857      | 0.8338      | 0.4412      | 0.041*       |
| H13C | 0.6403      | 0.8359      | 0.5859      | 0.041*       |
| C14  | 0.7262 (3)  | 0.5907 (4)  | 0.5820 (5)  | 0.0233 (9)   |
| C15  | 0.6711 (3)  | 0.3187 (4)  | 0.5311 (4)  | 0.0174 (8)   |
| C16  | 0.7071 (3)  | 0.2397 (4)  | 0.4329 (4)  | 0.0201 (8)   |
| H16  | 0.6956      | 0.2589      | 0.3409      | 0.024*       |
| C17  | 0.7600 (3)  | 0.1318 (4)  | 0.4629 (4)  | 0.0214 (8)   |
| H17  | 0.7843      | 0.0813      | 0.3924      | 0.026*       |
| C18  | 0.7751 (3)  | 0.1027 (4)  | 0.5913 (4)  | 0.0205 (8)   |
| C19  | 0.7397 (3)  | 0.1793 (5)  | 0.6909 (4)  | 0.0232 (9)   |
### Atomic displacement parameters (Å²)

|   | $U_{11}$  | $U_{22}$  | $U_{33}$  | $U_{12}$  | $U_{13}$  | $U_{23}$  |
|---|----------|----------|----------|----------|----------|----------|
| Br1 | 0.0283 (2) | 0.0232 (3) | 0.0233 (2) | 0.00633 (14) | −0.0028 (2) | 0.0055 (2) |
| O1 | 0.0269 (16) | 0.0306 (17) | 0.0260 (16) | 0.0013 (15) | −0.0068 (13) | 0.0022 (14) |
| N1 | 0.0179 (16) | 0.0204 (18) | 0.0182 (17) | 0.0037 (15) | −0.0015 (13) | 0.0042 (14) |
| N2 | 0.0286 (17) | 0.0326 (19) | 0.0270 (17) | 0.0030 (14) | −0.003 (2) | −0.009 (2) |
| C2 | 0.0214 (19) | 0.027 (3) | 0.016 (2) | 0.0027 (19) | 0.0010 (16) | 0.0020 (17) |
| C3 | 0.024 (2) | 0.024 (2) | 0.024 (2) | 0.0070 (18) | 0.0013 (16) | 0.0046 (18) |
| C4 | 0.026 (2) | 0.020 (2) | 0.0187 (19) | 0.0013 (17) | 0.0017 (16) | −0.0013 (15) |
| C5 | 0.024 (2) | 0.024 (2) | 0.019 (2) | 0.0049 (16) | −0.0004 (16) | −0.0031 (18) |
| C6 | 0.021 (2) | 0.023 (2) | 0.0128 (18) | 0.0052 (17) | 0.0003 (15) | 0.0013 (15) |
| C7 | 0.0197 (19) | 0.022 (2) | 0.019 (2) | 0.0020 (17) | −0.0003 (15) | 0.0009 (17) |
| C8 | 0.023 (2) | 0.029 (2) | 0.0188 (18) | 0.0036 (17) | 0.0015 (16) | 0.0010 (17) |
| C9 | 0.027 (2) | 0.028 (2) | 0.023 (2) | 0.0004 (18) | 0.0009 (17) | 0.0042 (18) |
| C10 | 0.026 (2) | 0.023 (2) | 0.031 (3) | 0.0001 (17) | 0.0013 (19) | −0.0009 (18) |
| C11 | 0.033 (2) | 0.028 (2) | 0.026 (2) | 0.001 (2) | 0.0016 (19) | −0.004 (2) |
| C12 | 0.027 (2) | 0.033 (3) | 0.0172 (19) | −0.0010 (19) | 0.0026 (16) | −0.0004 (18) |
| C13 | 0.031 (2) | 0.020 (2) | 0.031 (2) | 0.0041 (19) | −0.0016 (19) | 0.0007 (18) |
| C14 | 0.029 (2) | 0.021 (2) | 0.0199 (18) | 0.0020 (18) | 0.0007 (16) | −0.0028 (17) |
| C15 | 0.0170 (17) | 0.017 (2) | 0.018 (2) | 0.0035 (16) | −0.0027 (15) | −0.0001 (16) |
| C16 | 0.025 (2) | 0.022 (2) | 0.0131 (18) | 0.0017 (16) | 0.0016 (15) | 0.0015 (15) |
| C17 | 0.0219 (19) | 0.025 (2) | 0.0174 (19) | 0.0030 (16) | 0.0019 (15) | −0.0021 (16) |
| C18 | 0.0228 (19) | 0.019 (2) | 0.0196 (19) | 0.0006 (16) | −0.0029 (14) | 0.0030 (15) |
| C19 | 0.026 (2) | 0.028 (2) | 0.0150 (18) | 0.0051 (18) | −0.0014 (16) | −0.0002 (17) |
| C20 | 0.028 (2) | 0.027 (2) | 0.014 (2) | 0.0015 (17) | −0.0006 (15) | −0.0017 (15) |

### Geometric parameters (Å, °)

|     | Bond Length (Å) | Angle (°)        |
|-----|----------------|-----------------|
| Br1—C18 | 1.944 (4)      | C9—H9 0.9500    |
| O1—C2 | 1.217 (6)      | C10—C11 1.354 (7) |
| N1—C6 | 1.356 (6)      | C10—H10 0.9500  |
| N1—C7 | 1.456 (6)      | C11—C12 1.436 (7) |
| N1—C7 | 1.503 (6)      | C11—H11 0.9500  |
| N2—C14 | 1.127 (6)     | C12—H12 0.9500  |
| C2—C3 | 1.485 (7)      | C13—H13A 0.9800 |
| C3—C4 | 1.352 (7)      | C13—H13B 0.9800 |
| C3—H3 | 0.9500        | C13—H13C 0.9800 |
| C4—C5 | 1.464 (7)      | C15—C20 1.342 (6) |
| C4—C13 | 1.548 (6)     | C15—C16 1.389 (6) |
| C5—C14 | 1.429 (6)    | C16—C17 1.420 (6) |
| C5—C6 | 1.433 (7)      | C16—H16 0.9500  |
| C6—C15 | 1.520 (6)     | C17—C18 1.329 (6) |
| C7—C8 | 1.353 (6)      | C17—H17 0.9500  |
| Bond          | Distance (Å) | Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|---------------|--------------|
| C7—C12        | 1.360 (6)    | C18—C19       | 1.380 (6)    | C19—C20       | 1.417 (6)    |
| C8—C9         | 1.437 (7)    | C19—H19       | 0.9500       |               |              |
| C8—H8         | 0.9500       | C20—H20       | 0.9500       |               |              |
| C9—C10        | 1.371 (7)    |               |              |               |              |
| C6—N1—C2      | 121.0 (4)    | C10—C11—H11   | 119.1        |               |              |
| C6—N1—C7      | 120.1 (4)    | C12—C11—H11   | 119.1        |               |              |
| C2—N1—C7      | 118.6 (3)    | C7—C12—C11    | 121.1 (4)    |               |              |
| O1—C2—N1      | 116.5 (4)    | C7—C12—H12    | 119.5        |               |              |
| O1—C2—C3      | 126.0 (4)    | C11—C12—H12   | 119.5        |               |              |
| N1—C2—C3      | 117.5 (4)    | C4—C13—H13A   | 109.5        |               |              |
| C4—C3—C2      | 123.2 (4)    | C4—C13—H13B   | 109.5        |               |              |
| C4—C3—H3      | 118.4        | H13A—C13—H13B | 109.5        |               |              |
| C2—C3—H3      | 118.4        | C4—C13—H13C   | 109.5        |               |              |
| C3—C4—C5      | 115.7 (4)    | H13A—C13—H13C | 109.5        |               |              |
| C3—C4—C13     | 121.7 (4)    | H13B—C13—H13C | 109.5        |               |              |
| C5—C4—C13     | 122.6 (4)    | N2—C14—C5     | 176.7 (5)    |               |              |
| C14—C5—C6     | 119.2 (4)    | C20—C15—C16   | 116.6 (4)    |               |              |
| C14—C5—C4     | 117.1 (4)    | C20—C15—C6    | 121.9 (4)    |               |              |
| C6—C5—C4      | 123.6 (4)    | C16—C15—C6    | 121.4 (4)    |               |              |
| N1—C6—C5      | 118.9 (4)    | C15—C16—C17   | 123.4 (4)    |               |              |
| N1—C6—C15     | 116.8 (4)    | C15—C16—H16   | 118.3        |               |              |
| C5—C6—C15     | 124.0 (4)    | C17—C16—H16   | 118.3        |               |              |
| C8—C7—C12     | 118.1 (4)    | C18—C17—C16   | 118.8 (4)    |               |              |
| C8—C7—N1      | 118.7 (4)    | C18—C17—H17   | 120.6        |               |              |
| C12—C7—N1     | 123.1 (4)    | C16—C17—H17   | 120.6        |               |              |
| C7—C8—C9      | 120.4 (4)    | C17—C18—C19   | 119.0 (4)    |               |              |
| C7—C8—H8      | 119.8        | C17—C18—Br1   | 118.9 (3)    |               |              |
| C9—C8—H8      | 119.8        | C19—C18—Br1   | 122.1 (3)    |               |              |
| C10—C9—C8     | 122.2 (4)    | C18—C19—C20   | 121.8 (4)    |               |              |
| C10—C9—H9     | 118.9        | C18—C19—H19   | 119.1        |               |              |
| C8—C9—H9      | 118.9        | C20—C19—H19   | 119.1        |               |              |
| C11—C10—C9    | 116.4 (4)    | C15—C20—C19   | 120.4 (4)    |               |              |
| C11—C10—H10   | 121.8        | C15—C20—H20   | 119.8        |               |              |
| C9—C10—H10    | 121.8        | C19—C20—H20   | 119.8        |               |              |
| C10—C11—C12   | 121.8 (5)    |               |              |               |              |

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sup-4
C13—C4—C5—C6 $\quad$ -179.8 (4)  
C2—N1—C6—C5 $\quad$ 3.4 (6)  
C7—N1—C6—C5 $\quad$ -169.9 (4)  
C2—N1—C6—C15 $\quad$ -171.3 (4)  
C7—N1—C6—C15 $\quad$ 15.4 (6)  
C14—C5—C6—N1 $\quad$ -179.1 (4)  
C4—C5—C6—N1 $\quad$ -0.2 (7)  
C14—C5—C6—C15 $\quad$ -4.8 (7)  
C4—C5—C6—C15 $\quad$ 174.1 (4)  
C6—N1—C7—C8 $\quad$ 71.1 (5)  
C2—N1—C7—C8 $\quad$ -102.3 (5)  
C6—N1—C7—C12 $\quad$ -111.3 (5)  
N1—C6—C15—C16 $\quad$ 65.0 (6)  
C5—C6—C15—C16 $\quad$ -109.5 (5)  
C20—C15—C16—C17 $\quad$ -0.8 (6)  
C6—C15—C16—C17 $\quad$ 176.8 (4)  
C5—C6—C15—C16 $\quad$ -109.5 (5)  
C2—N1—C6—C15 $\quad$ -171.3 (4)  
C7—N1—C6—C15 $\quad$ 15.4 (6)  
C14—C5—C6—C15 $\quad$ -4.8 (7)  
C4—C5—C6—C15 $\quad$ 174.1 (4)  
C6—N1—C15—C16 $\quad$ -177.6 (4)  
C16—C15—C16—C17 $\quad$ 1.3 (7)  
C15—C16—C17—C18 $\quad$ 176.8 (4)  
C16—C15—C20—C19 $\quad$ 0.4 (7)  
C17—C16—C17—C18 $\quad$ 179.7 (3)  
C16—C17—C18—Br1 $\quad$ 179.5 (3)  
C14—C5—C6—N1 $\quad$ -179.1 (4)  
C4—C5—C6—N1 $\quad$ -0.2 (7)  
C14—C5—C6—C15 $\quad$ -4.8 (7)  
C4—C5—C6—C15 $\quad$ 174.1 (4)  
C6—N1—C7—C8 $\quad$ 71.1 (5)  
C2—N1—C7—C8 $\quad$ -102.3 (5)  
C6—N1—C7—C12 $\quad$ -111.3 (5)  
C16—C15—C16—C17 $\quad$ 1.3 (7)  
C15—C16—C17—C18 $\quad$ 176.8 (4)  
C16—C15—C20—C19 $\quad$ 0.4 (7)  
C17—C16—C17—C18 $\quad$ 179.7 (3)  
C16—C17—C18—Br1 $\quad$ 179.5 (3)  
C14—C5—C6—C15 $\quad$ -4.8 (7)  
C4—C5—C6—C15 $\quad$ 174.1 (4)  
C6—N1—C15—C16 $\quad$ -177.6 (4)  
C18—C19—C20—C15 $\quad$ 0.4 (7)  
C16—C15—C20—C19 $\quad$ -0.1 (7)  
C6—C15—C20—C19 $\quad$ -177.6 (4)  
C18—C19—C20—C15 $\quad$ 0.4 (7)  

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| C16—H16···N2i | 0.95 | 2.55 | 3.234 (6) | 129 |
| C17—H17···O1ii | 0.95 | 2.56 | 3.342 (6) | 140 |
| C20—H20···O1iii | 0.95 | 2.40 | 3.256 (6) | 150 |

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