Crystal structure and Hirshfeld surface analysis of ethyl 2′-amino-5-bromo-3′-cyano-6′-methyl-2-oxo-spiro[indoline-3,4′-pyran]-5′-carboxylate

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The crystal used for structure determination contained, along with the title compound, C17H14BrN3O4, an admixture [0.0324 (11)] of its 7-bromo isomer. The 2,3-dihydro-1H-indole ring system is nearly planar, while the conformation of the 4H-pyran ring is close to a flattened boat. The mean planes of these fragments form a dihedral angle of 86.67 (9°). The carboxylate group lies near the plane of 4H-pyran, its orientation is stabilized by an intramolecular C—H···O contact. In the crystal, the molecules are connected into layers by N—H···O hydrogen bonds. The most important contributions to the crystal packing are from H···H (33.1%), O···H···O (16.3%), N···H···N (12.1%), Br···H···Br (11.5%) and C···H···C (10.6%) interactions.

1. Chemical context

The reactions that form C—C, C—N and C—O bonds play critical roles in various applications and in different fields of chemistry (Aliyeva et al., 2011; Zubkov et al., 2018; Viswanathan et al., 2019; Duruskari et al., 2020). Nitrogen heterocycles, especially those comprising indole fragments, are parts of various natural products and medicinal agents. This fragment constitutes the core of spiro-oxindole alkaloids, which exhibit a broad spectrum of biological activity (Edmondson et al., 1999; Ma & Hecht, 2004). The main synthetic pathway for the construction of spiro[4H-pyran-oxindole] compounds is based on three-component reactions (Fig. 1) of two 1,3-dicarbonyl (or other active methylene) compounds with isatin derivatives (Rad-Moghadam & Youseftabar-Miri, 2011).

Thus, in the framework of our ongoing structural studies (Naghiyev, Akkurt et al., 2020; Naghiyev, Cisterna et al., 2020;...
Naghiyev, Tereshina et al., 2021; Naghiyev et al., 2022; Khalilov et al., 2022; Mamedov et al., 2022), we report the crystal structure and Hirshfeld surface analysis of the title compound.

2. Structural commentary

The crystal used for structure determination contained, along with the title compound, an admixture of its 7-bromo isomer. That is why the Br1 atom is distributed over two positions, at C5 and C7, in a 0.9676 (11):0.0324 (11) ratio, whereas the positions of other atoms of these isomers coincide with each other (Fig. 2). The 2,3-dihydro-1\(H\)-indole ring system is nearly planar with the largest deviation from planarity being 0.048 (2) \(\AA\) for C3\(A\), while the conformation of the 4\(H\)-pyran ring is close to a flattened boat [puckering parameters (Cremer & Pople, 1975): \(Q_T = 0.105 (2) \ \AA\), \(\theta = 79.8 (11)°\) and \(\varphi = 196.9 (12)°\)], with the C8–C11 atoms forming the basal plane and O1 and C3 deviating from this plane by 0.063 (1) and 0.362 (2) \(\AA\), respectively. The mean planes of the 2,3-dihydro-1\(H\)-indole system and the 4\(H\)-pyran ring are approximately perpendicular to each other, forming a dihedral angle of 86.67 (5)°. The carboxylate group lies near the plane of 4\(H\)-pyran, with O3—C13—C10—C11 and O4—C13—C10—C3 torsion angles of −13.4 (3) and −8.8 (2)°, respectively. An intramolecular C16—H16\(A\)⋯O3 contact stabilizes the conformation of the molecule (Fig. 2, Table 1), generating an \(S(6)\) ring motif (Bernstein et al., 1995).

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, the molecules are linked by N—H⋯N and N—H⋯O hydrogen bonds, forming double layers parallel to (001) (Table 1; Figs. 3–6). In addition, C—H⋯\(\pi\) interactions involving the centroids of the 4\(H\)-pyran and benzene rings link adjacent molecules within these layers (Table 1; Fig. 7). The layers are joined by van der Waals interactions (Table 2).

![Figure 2](image1.png)

The molecular structure of the title compound with the atom labelling and displacement ellipsoids drawn at the 50% probability level. Only the major position of Br1 [0.9676 (11)] is shown.

![Figure 3](image2.png)

A general view of the packing of the title compound with N—H⋯N and N—H⋯O hydrogen bonds. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity. Symmetry codes: (i) \(-x + \frac{1}{2}, y + \frac{1}{2}, z\); (ii) \(-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}\); (iii) \(-x + \frac{1}{2}, y + \frac{1}{2}, z\); (iv) \(-x + \frac{1}{2}, y + \frac{1}{2}, z\); (v) \(-x + \frac{1}{2}, y + \frac{1}{2}, z\).

| \(D—H\)⋯\(A\) | \(D—H\) | \(H⋯A\) | \(D⋯A\) | \(D—H⋯A\) |
|---|---|---|---|---|
| N1—H1⋯N12\(^{ii}\) | 0.88 (3) | 2.00 (3) | 2.874 (3) | 170 (2) |
| N8—H8A⋯O2\(^{iii}\) | 0.88 (3) | 2.08 (3) | 2.940 (2) | 165 (3) |
| N8—H8B⋯O2\(^{iii}\) | 0.86 (3) | 2.15 (3) | 2.971 (2) | 158 (2) |
| C16—H16A⋯O3 | 0.98 | 2.30 | 2.865 (3) | 116 |
| C14—H14A⋯Cg2\(^{iv}\) | 0.99 | 2.92 | 3.773 (3) | 145 |
| C15—H15B⋯Cg3\(^{iv}\) | 0.98 | 2.99 | 3.729 (3) | 133 |

Symmetry codes: (i) \(-x + \frac{1}{2}, y + \frac{1}{2}, z\); (ii) \(-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}\); (iii) \(-x + \frac{1}{2}, y + \frac{1}{2}, z\); (iv) \(-x + \frac{1}{2}, y + \frac{1}{2}, z\).
A Hirshfeld surface analysis was performed to visualize the intermolecular interactions, and the accompanying two-dimensional fingerprint plots were generated with Crystal-Explorer17 (Turner et al., 2017). Fig. 8 depicts the Hirshfeld surface plotted over $d_{norm}$ in the range $-0.5859$ to $1.4054$ a.u. N–H···N and N–H···O contacts appear as red spots on the Hirshfeld surface.

The full two-dimensional fingerprint plot and those delineated into the major contributions are shown in Fig. 9: the H···H interactions (33.1%) are the major factor in the crystal packing, with O···H/·O (16.3%), N···H/·N (12.1%), Br···H/·Br (11.5%) and C···H/·C (10.6%) interactions representing the next highest contributions. Other contributions listed in Table 3 are less than 4.0%.

4. Database survey
A survey of the Cambridge Structural Database (CSD, Version 5.42, update of September 2021; Groom et al., 2016)
using 2-amino-6-methyl-4H-pyran-3-carbonitrile as the main skeleton revealed the presence of three structures, CSD refcodes WIMBEC02 (I; Naghiyev, Grishina et al., 2021), HIRNUS (II; Athimoolam et al., 2007) and JEGWEX (III; Lokaj et al., 1990).

In the crystal of I, the molecular conformation is maintained by intramolecular C—H···O interaction, generating a S(6) ring motif. The molecules are linked by pairs of N—H···O hydrogen bonds into dimers, those are linked by N—H···O contacts to form ribbons along the a-axis direction.

In the crystal of II, the six-membered pyran ring adopts a conformation close to a flattened boat, as in the title structure. The molecules are joined by pairs of N—H···N hydrogen bonds into dimers, those are linked by N—H···O contacts to form ribbons along the a-axis direction.

In the crystal of III, the pyran ring is nearly planar. The molecules are joined by pairs of N—H···N hydrogen bonds into centrosymmetric dimers, which are linked by N—H···O contacts into ribbons along the c-axis direction.

5. Synthesis and crystallization

The title compound was synthesized using the reported procedure (Rad-Moghadam & Youseftabar-Miri, 2011), and colourless crystals were obtained upon isothermal recrystallization from an ethanol/water (3:1) solution.
6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The Br1 and Br1’ atoms connected to the C5 and C7 atoms have occupancy ratios of 0.9676 (11):0.0324 (11). EXYZ and EADP instructions were used to refine the positional and displacement parameters of C5, C7 and their counterparts C5’, C7’. The H atoms of the NH and NH2 groups were located in a difference map, and their positional parameters were allowed to freely refine [N1—H1 = 0.88 (3), N8—H8A = 0.88 (3) and N8—H8B = 0.86 (3) Å], but their isotropic displacement parameters were constrained to take a value of 1.2Ueq(N). All H atoms bound to C atoms were positioned geometrically and refined as riding with C—H = 0.95 (aromatic), 0.99 (methylene) and 0.98 Å (methyl), with Ueq(C) for methyl H atoms and 1.2Ueq(C) for all others.

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Authors contributions are as follows. Conceptualization, ANK and IGM; methodology, ANK, FNN and IGM; investigation, ANK, MA and NUV; writing (original draft), MA and ANK; writing (review and editing of the manuscript), MA and ANK; visualization, MA, ANK and IGM; funding acquisition, VNK, AB and ANK; supervision, ANK and MA.

Table 4

| Crystall data | Chemical formula | C17H14BrN3O4 |
|--------------|-----------------|--------------|
| System group | M | Orthorhombic, Pbca |
| Temperature (K) | a, b, c (Å) | 100 |
| Space group | V (Å³) | 9.3880 (9), 12.2260 (12), 28.693 (3) |
| Z | 3293.3 (6) |
| Radiation type | Synchrotron, λ = 0.7450 Å |
| μ (mm⁻¹) | 2.84 |
| Crystal size (mm) | 0.15 × 0.12 × 0.10 |

Data collection

Diffractometer | Rayonix SX-165 CCD |
|---------------|-------------------|
| Absorption correction | Multi-scan (SCALA; Evans, 2006) |
| Tmin, Tmax | 0.626, 0.716 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 29648, 4526, 4225 |
| Rmin | 0.058 |
| (sinθ/λ)_{max} (Å⁻¹) | 0.692 |

Refinement

R[F² > 2σ(F²)], wR(F²), S | 0.045, 0.091, 1.13 |
| No. of reflections | 4526 |
| No. of parameters | 248 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |

Δρ_{max}, Δρ_{min} (e Å⁻³) | 0.79, −0.66 |

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Crystal structure and Hirshfeld surface analysis of ethyl 2′-amino-5-bromo-3′-cyano-6′-methyl-2-oxospiro[indoline-3,4′-pyran]-5′-carboxylate

Farid N. Naghiyev, Victor N. Khrustalev, Nikolai U. Venskovsky, Mehmet Akkurt, Ali N. Khalilov, Ajaya Bhattarai and İbrahim G. Mamedov

Computing details

Data collection: *Marcdd* (Doyle, 2011); cell refinement: *iMosflm* (Battye et al., 2011); data reduction: *iMosflm* (Battye et al., 2011); 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).

Ethyl 2′-amino-5-bromo-3′-cyano-6′-methyl-2-oxospiro[indoline-3,4′-pyran]-5′-carboxylate

Crystal data

\[ \text{C}_{17}\text{H}_{14}\text{BrN}_{3}\text{O}_{4} \]

Mr = 404.22

Orthorhombic, *Pbca*

\[ a = 9.3880 \text{ (9) Å} \]
\[ b = 12.2260 \text{ (12) Å} \]
\[ c = 28.693 \text{ (3) Å} \]

\[ V = 3293.3 \text{ (6) Å}^3 \]

\[ Z = 8 \]

\[ F(000) = 1632 \]

Synchrotron radiation, \( \lambda = 0.74500 \text{ Å} \)

Cell parameters from 1000 reflections

\[ \theta = 1.5–25.0^\circ \]

\[ \mu = 2.84 \text{ mm}^{-1} \]

\[ T = 100 \text{ K} \]

Prism, colourless

0.15 × 0.12 × 0.10 mm

Data collection

Rayonix SX-165 CCD diffractometer

\( \theta/2\theta \) scan

Absorption correction: multi-scan

(Scala; Evans, 2006)

\[ T_{\min } = 0.626, \ T_{\max } = 0.716 \]

29648 measured reflections

4526 independent reflections

4225 reflections with \( I > 2\sigma(I) \)

\[ R_{int} = 0.058 \]

\[ \theta_{\max } = 31.0^\circ, \ \theta_{\min } = 1.5^\circ \]

\[ h = -12\rightarrow12 \]

\[ k = -16\rightarrow14 \]

\[ l = -39\rightarrow39 \]

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\[ R[F^2 > 2\sigma(F^2)] = 0.045 \]

\[ wR(F^2) = 0.091 \]

\[ S = 1.13 \]

4526 reflections

248 parameters

0 restraints

H atoms treated by a mixture of independent and constrained refinement

\[ w = 1/[\sigma^2(F_c^2) + (0.017P)^2 + 5.6891P] \]

where \( P = (F_c^2 + 2F_s^2)/3 \)

\( \Delta \rho_{\max } = 0.79 \text{ e Å}^{-3} \)

\( \Delta \rho_{\min } = -0.66 \text{ e Å}^{-3} \)
Extinction correction: SHELXL-2018/3
(Sheldrick, 2015b),
Fc*=kFc[1+0.001xFc^2/λ^2]^{-1/4}
Extinction coefficient: 0.0033 (5)

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 (Å²)

|     | x       | y       | z       | Uiso* | Occ. (<1) |
|-----|---------|---------|---------|-------|-----------|
| Br1 | 0.62887 (3) | 0.85694 (2) | 0.50801 (2) | 0.02994 (10) | 0.9676 (11) |
| Br1' | 0.8404 (7) | 0.5117 (6) | 0.4176 (2) | 0.025 (2) | 0.0324 (11) |
| O1  | 0.18714 (16) | 0.81785 (13) | 0.30258 (5) | 0.0224 (3) |
| O2  | 0.46032 (16) | 0.57274 (12) | 0.27537 (5) | 0.0218 (3) |
| O3  | 0.12303 (17) | 0.54444 (14) | 0.39298 (6) | 0.0273 (3) |
| O4  | 0.35898 (17) | 0.51716 (13) | 0.38771 (6) | 0.0247 (3) |
| N1  | 0.62336 (19) | 0.57936 (15) | 0.33512 (6) | 0.0221 (4) |
| H1  | 0.678 (3) | 0.524 (2) | 0.3268 (10) | 0.026* |
| C2  | 0.5028 (2) | 0.60843 (16) | 0.31277 (7) | 0.0187 (4) |
| C3  | 0.4272 (2) | 0.69936 (16) | 0.34194 (7) | 0.0165 (3) |
| C3A | 0.5230 (2) | 0.70400 (16) | 0.38470 (7) | 0.0183 (4) |
| C4  | 0.5179 (2) | 0.77196 (17) | 0.42322 (7) | 0.0212 (4) |
| H4  | 0.442127 | 0.822416 | 0.427551 | 0.025* |
| C5  | 0.6285 (2) | 0.76336 (19) | 0.45537 (7) | 0.0248 (4) | 0.9676 (11) |
| C5' | 0.6285 (2) | 0.76336 (19) | 0.45537 (7) | 0.0248 (4) | 0.0324 (11) |
| H5' | 0.627663 | 0.809277 | 0.482082 | 0.030* | 0.0324 (11) |
| C6  | 0.7401 (2) | 0.6898 (2) | 0.44967 (8) | 0.0266 (4) |
| H6  | 0.812267 | 0.684771 | 0.472782 | 0.032* |
| C7  | 0.7467 (2) | 0.62349 (19) | 0.41036 (8) | 0.0254 (4) | 0.9676 (11) |
| H7  | 0.822784 | 0.573406 | 0.405830 | 0.031* | 0.9676 (11) |
| C7' | 0.7467 (2) | 0.62349 (19) | 0.41036 (8) | 0.0254 (4) | 0.0324 (11) |
| C7A | 0.6377 (2) | 0.63345 (17) | 0.37805 (7) | 0.0210 (4) |
| C8  | 0.3205 (2) | 0.86078 (17) | 0.29895 (7) | 0.0192 (4) |
| N8  | 0.3187 (2) | 0.95830 (15) | 0.27841 (7) | 0.0223 (4) |
| H8A | 0.396 (3) | 0.987 (2) | 0.2662 (10) | 0.027* |
| H8B | 0.240 (3) | 0.988 (2) | 0.2695 (9) | 0.027* |
| C9  | 0.4361 (2) | 0.80761 (16) | 0.31652 (7) | 0.0176 (4) |
| C10 | 0.2714 (2) | 0.66972 (16) | 0.34957 (7) | 0.0185 (4) |
| C11 | 0.1654 (2) | 0.72529 (17) | 0.32916 (7) | 0.0201 (4) |
| C12 | 0.5680 (2) | 0.86311 (16) | 0.31568 (7) | 0.0206 (4) |
| N12 | 0.6748 (2) | 0.90831 (17) | 0.31616 (7) | 0.0298 (4) |
| C13 | 0.2387 (2) | 0.57211 (17) | 0.37850 (7) | 0.0206 (4) |
| C14 | 0.3525 (3) | 0.42971 (18) | 0.42180 (8) | 0.0272 (5) |
| H14A | 0.319199 | 0.361186 | 0.407002 | 0.033* |
| H14B | 0.285916 | 0.449044 | 0.447248 | 0.033* |
### Geometric parameters (Å, °)

|                  | u^11          | u^22          | u^33          | u^12          | u^13          | u^23          |
|------------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Br1—C5           | 1.895 (2)     | C6—C7         | 1.390 (3)     |               |               |               |
| Br1’—C5’         | 1.639 (7)     | C6—H6         | 0.9500        |               |               |               |
| O1—C8            | 1.361 (2)     | C7—C7A        | 1.386 (3)     |               |               |               |
| O1—C11           | 1.380 (3)     | C7—H7         | 0.9500        |               |               |               |
| O2—C2            | 1.225 (3)     | C7’—C7A       | 1.386 (3)     |               |               |               |

### Atomic displacement parameters (Å²)

|                  | U₁₁          | U₂₂          | U₃₃          | U₁₂          | U₁₃          | U₂₃          |
|------------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Br1              | 0.02753 (14) | 0.03873 (16) | 0.02357 (13) | −0.00819 (10) | −0.00248 (9) | −0.00799 (9) |
| Br1’             | 0.021 (3)    | 0.028 (4)    | 0.025 (3)    | 0.008 (3)    | 0.001 (2)    | 0.008 (2)    |
| O1               | 0.0160 (7)   | 0.0240 (7)   | 0.0273 (7)   | −0.0005 (6)  | −0.0001 (6)  | 0.0033 (6)   |
| O2               | 0.0213 (7)   | 0.0214 (7)   | 0.0228 (7)   | −0.0018 (6)  | 0.0026 (5)   | −0.0041 (5)  |
| O3               | 0.0234 (8)   | 0.0299 (8)   | 0.0286 (8)   | −0.0064 (6)  | 0.0053 (6)   | 0.0022 (6)   |
| O4               | 0.0241 (8)   | 0.0206 (7)   | 0.0295 (8)   | −0.0008 (6)  | 0.0050 (6)   | 0.0057 (6)   |
| N1               | 0.0205 (8)   | 0.0208 (8)   | 0.0249 (8)   | 0.0054 (7)   | 0.0016 (7)   | −0.0008 (7)  |
| C2               | 0.0224 (9)   | 0.0223 (9)   | 0.0223 (9)   | −0.0009 (7)  | 0.0039 (7)   | 0.0017 (7)   |
| C3               | 0.0226 (9)   | 0.0155 (8)   | 0.0199 (8)   | 0.0001 (7)   | 0.0014 (7)   | 0.0004 (7)   |
| C3A              | 0.0167 (8)   | 0.0203 (9)   | −0.0020 (7)  | 0.0005 (7)   | 0.0020 (7)   |               |
| C4               | 0.0195 (9)   | 0.0222 (9)   | 0.0220 (9)   | −0.0029 (8)  | 0.0010 (7)   | −0.0007 (7)  |
| C5               | 0.0231 (10)  | 0.0312 (11)  | 0.0200 (9)   | −0.0065 (9)  | −0.0006 (8)  | −0.0013 (8)  |
| C5’              | 0.0231 (10)  | 0.0312 (11)  | 0.0200 (9)   | −0.0065 (9)  | −0.0006 (8)  | −0.0013 (8)  |
| C6               | 0.0221 (10)  | 0.0331 (11)  | 0.0247 (10)  | −0.0037 (9)  | −0.0041 (8)  | 0.0053 (9)   |
| C7               | 0.0241 (8)   | 0.0286 (10)  | 0.0287 (10)  | 0.0027 (8)   | −0.0010 (8)  | 0.0054 (8)   |
| C7’              | 0.0190 (9)   | 0.0286 (10)  | 0.0287 (10)  | 0.0027 (8)   | −0.0010 (8)  | 0.0054 (8)   |
| C7A              | 0.0196 (9)   | 0.0232 (9)   | 0.0232 (9)   | −0.0005 (8)  | 0.0010 (7)   | 0.0028 (7)   |
| C8               | 0.0202 (11)  | 0.0204 (9)   | 0.0189 (9)   | −0.0007 (7)  | 0.0010 (7)   | −0.0017 (7)  |
| N8               | 0.0191 (8)   | 0.0221 (8)   | 0.0257 (9)   | 0.0020 (7)   | −0.0005 (7)  | 0.0049 (7)   |
| C9               | 0.0156 (8)   | 0.0164 (8)   | 0.0210 (9)   | −0.0018 (7)  | 0.0003 (7)   | −0.0006 (7)  |
| C10              | 0.0174 (9)   | 0.0172 (8)   | 0.0208 (8)   | −0.0027 (7)  | 0.0031 (7)   | −0.0011 (7)  |
| C11              | 0.0168 (9)   | 0.0217 (9)   | 0.0219 (9)   | −0.0025 (7)  | 0.0024 (7)   | −0.0026 (7)  |
| C12              | 0.0233 (10)  | 0.0169 (8)   | 0.0216 (9)   | −0.0007 (8)  | −0.0019 (7)  | 0.0018 (7)   |
| N12              | 0.0260 (10)  | 0.0294 (10)  | 0.0339 (10)  | −0.0095 (8)  | −0.0049 (8)  | 0.0070 (8)   |
| C13              | 0.0225 (9)   | 0.0191 (9)   | 0.0200 (9)   | −0.0032 (8)  | 0.0024 (7)   | −0.0036 (7)  |
| C14              | 0.0331 (12)  | 0.0201 (9)   | 0.0284 (10)  | −0.0024 (9)  | 0.0039 (9)   | 0.0054 (8)   |
| C15              | 0.0414 (15)  | 0.0389 (14)  | 0.0483 (16)  | −0.0018 (12) | −0.0035 (12) | 0.0206 (12)  |
| C16              | 0.0160 (9)   | 0.0327 (11)  | 0.0350 (12)  | −0.0029 (9)  | 0.0024 (8)   | 0.0039 (9)   |
| Bond      | Distance (Å) | Bond       | Distance (Å) | Bond       | Distance (Å) |
|-----------|--------------|------------|--------------|------------|--------------|
| O3—C13    | 1.211 (3)    | C8—N8      | 1.330 (3)    |
| O4—C13    | 1.340 (3)    | C8—C9      | 1.362 (3)    |
| O4—C14    | 1.450 (3)    | N8—H8A     | 0.88 (3)     |
| N1—C2     | 1.349 (3)    | N8—H8B     | 0.86 (3)     |
| N1—C7A    | 1.404 (3)    | C9—C12     | 1.412 (3)    |
| N1—H1     | 0.88 (3)     | C10—C11    | 1.340 (3)    |
| C2—C3     | 1.562 (3)    | C10—C13    | 1.486 (3)    |
| C3—C9     | 1.513 (3)    | C11—C16    | 1.494 (3)    |
| C3—C3A    | 1.523 (3)    | C12—N12    | 1.146 (3)    |
| C3—C10    | 1.523 (3)    | C14—C15    | 1.505 (4)    |
| C3A—C4    | 1.383 (3)    | C14—H14A   | 0.9900       |
| C3A—C7A   | 1.393 (3)    | C14—H14B   | 0.9900       |
| C4—C5'    | 1.393 (3)    | C15—H15A   | 0.9800       |
| C4—H4     | 0.9500       | C15—H15C   | 0.9800       |
| C5—C6     | 1.390 (3)    | C16—H16A   | 0.9800       |
| C5'—C6    | 1.390 (3)    | C16—H16B   | 0.9800       |
| C5'—H5'   | 0.9500       | C16—H16C   | 0.9800       |
| C6—C7'    | 1.390 (3)    |             |              |
| C8—O1—C11 | 119.65 (16)  | C7—C7A—N1 | 128.0 (2)    |
| C13—O4—C14| 117.86 (17)  | C3A—C7A—N1| 109.74 (18)  |
| C2—N1—C7A| 111.92 (17)  | N8—C8—O1  | 111.60 (18)  |
| C2—N1—H1 | 124.4 (19)   | N8—C8—C9  | 127.0 (2)    |
| C7A—N1—H1| 122.7 (18)   | O1—C8—C9  | 121.37 (18)  |
| O2—C2—N1 | 126.56 (19)  | C8—N8—H8A | 122.0 (19)   |
| O2—C2—C3 | 125.12 (18)  | C8—N8—H8B | 121 (2)      |
| N1—C2—C3 | 108.30 (17)  | H8A—N8—H8B| 115 (3)      |
| C9—C3—C3A| 108.85 (16)  | C8—C9—C12 | 117.58 (18)  |
| C9—C3—C10 | 109.30 (16)  | C8—C9—C3  | 123.48 (18)  |
| C3A—C3—C10| 117.41 (16)  | C12—C9—C3 | 118.49 (17)  |
| C9—C3—C2 | 109.83 (15)  | C11—C10—C13| 119.88 (18) |
| C3A—C3—C2 | 100.96 (16)  | C11—C10—C3 | 122.01 (18) |
| C10—C3—C2| 110.12 (16)  | C13—C10—C3| 118.02 (17)  |
| C4—C3A—C7A| 120.55 (19)  | C10—C11—O1| 123.18 (18)  |
| C4—C3A—C3 | 130.23 (19)  | C10—C11—C16| 129.3 (2)   |
| C7A—C3A—C3| 108.85 (17)  | O1—C11—C16| 107.50 (18)  |
| C3A—C4—C5' | 117.3 (2)   | N12—C12—C9 | 178.3 (2)    |
| C3A—C4—C5 | 117.3 (2)    | O3—C13—O4 | 123.23 (19)  |
| C3A—C4—H4 | 121.4        | O3—C13—C10| 126.9 (2)    |
| C5—C4—H4 | 121.4        | O4—C13—C10| 109.82 (17)  |
| C6—C5—C4 | 122.2 (2)    | O4—C14—C15| 106.84 (19)  |
| C6—C5—Br1 | 118.89 (16)  | O4—C14—H14A| 110.4       |
| C4—C5—Br1 | 118.93 (17)  | C15—C14—H14A| 110.4       |
| C6—C5’—C4 | 122.2 (2)    | C15—C14—H14B| 110.4       |
| C6—C5’—H5’| 118.9        | H14A—C14—H14B| 108.6       |
| C4—C5’—H5’| 118.9        |             |              |
| C7—C6—C5 | 120.4 (2)    | C14—C15—H15A| 109.5       |
C7′—C6—C5′ 120.4 (2) C14—C15—H15B 109.5
C7—C6—H6 119.8 H15A—C15—H15B 109.5
C5—C6—H6 119.8 C14—C15—H15C 109.5
C7A—C7—C6 117.3 (2) H15A—C15—H15C 109.5
C7A—C7—H7 121.3 C11—C16—H16A 109.5
C6—C7—H7 121.3 C11—C16—H16B 109.5
C7A—C7′—C6 117.3 (2) C11—C16—H16C 109.5
C7A—C7′—Br1′ 123.7 (3) C14—O4—C13—O3 −8.9 (3)
C6—C7′—Br1′ 114.0 (3) C14—O4—C13—C10 170.02 (17)
C7′—C7A—C3A 122.2 (2) C11—O1—C8—N8 −170.14 (17)
C7—C7A—C3A 122.2 (2) C11—O1—C8—C9 7.7 (3)
C7′—C7A—N1 128.0 (2) C8—O1—C11—C10 −4.6 (3)

C7A—N1—C2—O2 −178.0 (2) C4—C3A—C7A—N1 −175.73 (18)
C7A—N1—C2—C3 3.9 (2) C3—C3A—C7A—N1 −2.1 (2)
O2—C2—C3—C9 −68.0 (2) C2—N1—C7A—C7′ 179.5 (2)
N1—C2—C3—C9 110.08 (18) C2—N1—C7A—C7 179.5 (2)
O2—C2—C3—C3A 177.15 (19) C2—N1—C7A—C3A −1.2 (2)
N1—C2—C3—C3A −4.7 (2) C11—O1—C8—N8 −170.14 (17)
O2—C2—C3—C10 52.4 (3) C11—O1—C8—C9 7.7 (3)
N1—C2—C3—C10 −129.51 (18) N8—C8—C9—C12 4.1 (3)
C9—C3—C3A—C4 61.3 (3) O1—C8—C9—C12 −173.39 (18)
C10—C3—C3A—C4 −63.5 (3) N8—C8—C9—C3 176.28 (19)
C2—C3—C3A—C4 176.8 (2) C11—O1—C8—C9 −1.2 (3)
C9—C3—C3A—C7A −111.51 (18) C3A—C3—C9—C8 −3.5 (2)
C10—C3—C3A—C7A 123.70 (19) C3A—C3—C9—C12 35.6 (2)
C2—C3—C3A—C7A 4.0 (2) C3A—C3—C9—C12 −173.50 (16)
C7A—C3A—C4—C5′ −2.4 (3) C3—C3A—C7A—N1 −2.1 (2)
C3—C3A—C4—C5′ −174.5 (2) C3—C3A—C7A—C7′ 179.5 (2)
C7A—C3A—C4—C5 −2.4 (3) C3—C3A—C7A—C7 179.5 (2)
C3—C3A—C4—C5 −174.5 (2) C3—C3A—C7A—C3A −1.2 (2)
C3A—C4—C5—C6 −0.2 (3) C3A—C3—C9—C8 35.6 (2)
C3A—C4—C5—Br1 178.57 (15) C3A—C3—C9—C12 −173.50 (16)
C3A—C4—C5′—Br1 −110.7 (2) C3—C10—C13—O3 −4.8 (2)
C3A—C4—C5′—C6 −0.2 (3) C3—C10—C13—O4 −8.8 (2)
C4—C5′—C6—C7 1.8 (3) C3—C10—C13—O4 170.1 (2)
Br1—C5—C6—C7 −176.99 (17) C3—C10—C13—O3 65.8 (2)
C4—C5′—C6—C7′ 1.8 (3) C3—C10—C13—O1 178.68 (18)
C5—C6—C7—C7A −0.7 (3) C3—C10—C13—O1 −4.9 (3)
C5′—C6—C7—C7′ −0.7 (3) C3—C10—C13—C10 −4.9 (3)
C5′—C6—C7—Br1′ −156.6 (3) C3—C10—C13—C16 174.8 (2)
C6—C7—C7A—C3A −2.0 (3) C3—C10—C13—C16 −1.6 (3)
Br1′—C7′—C7A—C3A 151.5 (3) C3—C10—C13—C16 174.8 (2)
C6—C7′—C7A—N1 177.2 (2) C3—C10—C13—C16 174.8 (2)
Br1′—C7′—C7A—N1 −29.3 (4) C3—C10—C13—C16 174.8 (2)
C6—C7′—C7A—C3A −2.0 (3) C3—C10—C13—C16 174.8 (2)
C6—C7′—C7A—N1 177.2 (2) C3—C10—C13—C16 −1.6 (3)
C4—C3A—C7A—C7′ 3.6 (3) C3—C10—C13—C16 174.8 (2)
C3—C3A—C7A—C7′ 177.22 (19) C3—C10—C13—C16 174.8 (2)
### Hydrogen-bond geometry (Å, °)

Cg2 and Cg3 are the centroids of the 4H-pyran ring (O1/C3/C8-C11) and the benzene ring (C3A/C4–C7/C7A) of the 2,3-dihydro-1H-indole ring system.

| D—H···A       | D—H | H···A | D···A | D—H···A |
|---------------|------|-------|-------|---------|
| N1—H1···N12i  | 0.88 (3) | 2.00 (3) | 2.874 (3) | 170 (2) |
| N8—H8A···O2ii | 0.88 (3) | 2.08 (3) | 2.940 (2) | 165 (3) |
| N8—H8B···O2iii| 0.86 (3) | 2.15 (3) | 2.971 (2) | 158 (3) |
| C16—H16A···O3 | 0.98 | 2.30 | 2.865 (3) | 116 |
| C14—H14A···Cg2iv | 0.99 | 2.92 | 3.773 (3) | 145 |
| C15—H15B···Cg3 | 0.98 | 2.99 | 3.729 (3) | 133 |
| C15—H15B···Cg4 | 0.98 | 2.99 | 3.729 (3) | 133 |

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