Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

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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Received 28 July 2022
Accepted 19 August 2022

Edited by A. V. Yatsenko, Moscow State University, Russia

Keywords: crystal structure; spiro-oxindoles; hydrogen bonds; van der Waals interactions; Hirshfeld surface analysis.

CCDC reference: 2202347

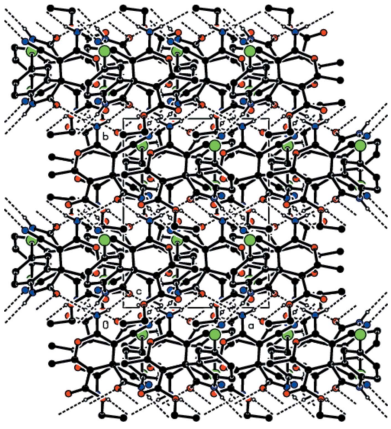
Supporting information: this article has supporting information at journals.iucr.org/e

The crystal used for structure determination contained, along with the title compound, $C_{17}H_{14}BrN_3O_4$, an admixture [0.0324 (11)] of its 7-bromo isomer. The 2,3-dihydro-1*H*-indole ring system is nearly planar, while the conformation of the 4*H*-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 4*H*-pyran, its orientation is stabilized by an intramolecular C—H···O contact. In the crystal, the molecules are connected into layers by N—H···N and N—H···O hydrogen bonds. The most important contributions to the crystal packing are from H···H (33.1%), O···H/H···O (16.3%), N···H/H···N (12.1%), Br···H/H···Br (11.5%) and C···H/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[4*H*-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;



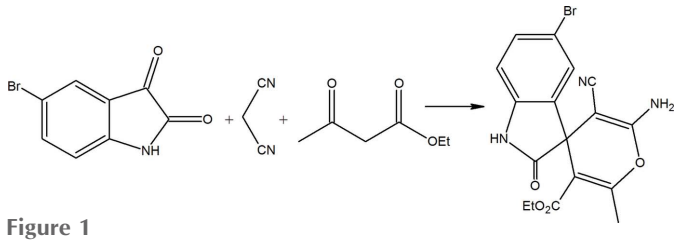
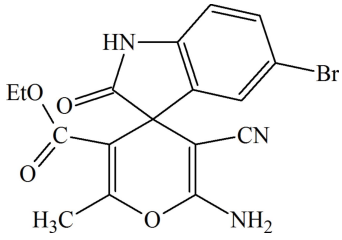


Figure 1
The three-component synthesis of the title compound.

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) Å 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) Å, θ = 79.8 (11)° and φ = 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) Å, 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 (9)°. 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).

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N12^{i}	0.88 (3)	2.00 (3)	2.874 (3)	170 (2)
N8—H8*A*···O2^{ii}	0.88 (3)	2.08 (3)	2.940 (2)	165 (3)
N8—H8*B*···O2^{iii}	0.86 (3)	2.15 (3)	2.971 (2)	158 (2)
C16—H16*A*···O3	0.98	2.30	2.865 (3)	116
C14—H14*A*···*Cg*2^{iv}	0.99	2.92	3.773 (3)	145
C15—H15*B*···*Cg*3	0.98	2.99	3.729 (3)	133

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

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···π 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).

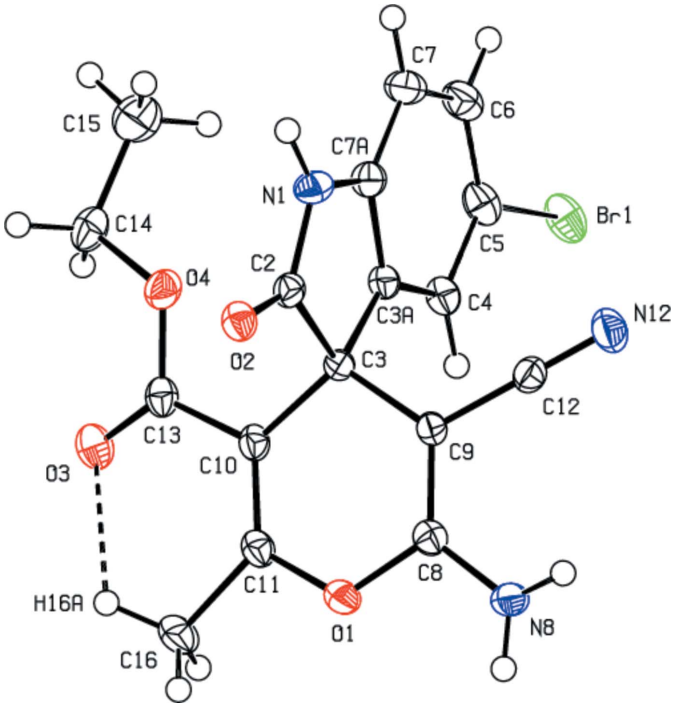


Figure 2
The molecular structure of the title compound with the atom labelling and displacement ellipsoids drawn at the 50% probability level. Only the major position of Br1 [0.9676 (11)] is shown.

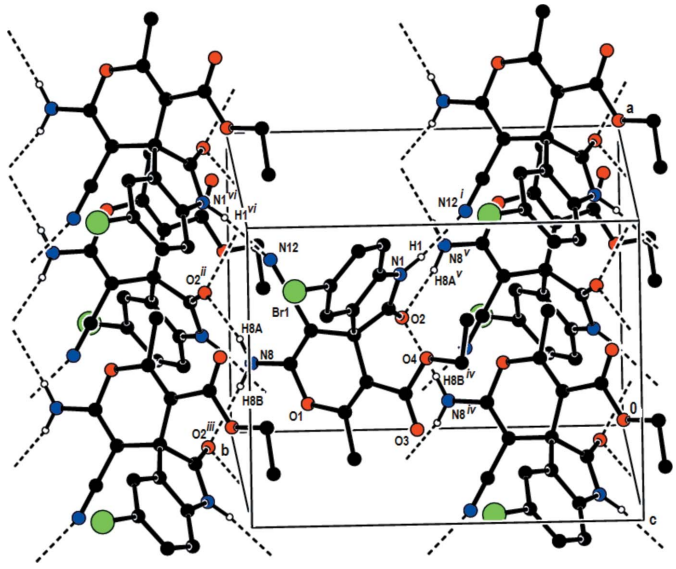


Figure 3
A general view of the packing of the title compound with N—H···N and N—H···O hydrogen bonds. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity. Symmetry codes: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, z$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y+\frac{1}{2}, z$; (iv) $-x+\frac{1}{2}, y-\frac{1}{2}, z$; (v) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (vi) $-x+\frac{3}{2}, y+\frac{1}{2}, z$.

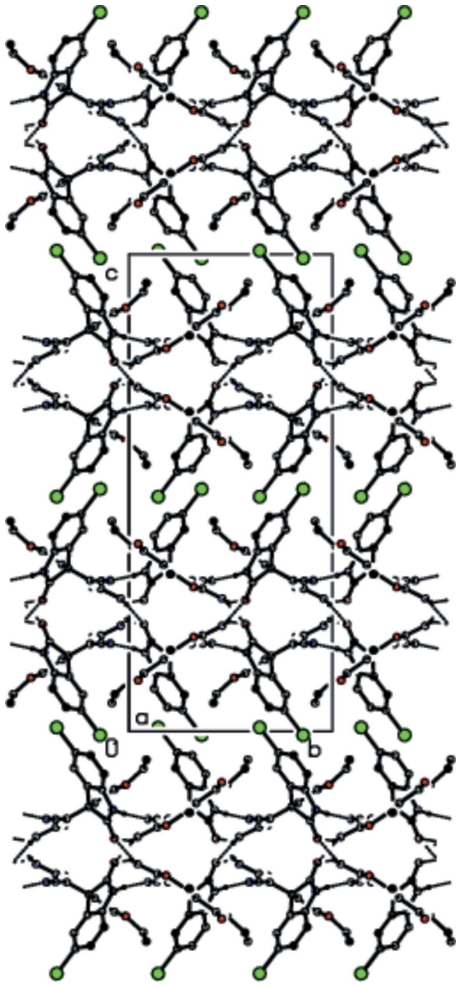


Figure 4
The packing of the title compound viewed along the *a* axis and showing the N—H···N and N—H···O hydrogen bonds. Only the hydrogen atoms involved in hydrogen bonding are shown.

A Hirshfeld surface analysis was performed to visualize the intermolecular interactions, and the accompanying two-dimensional fingerprint plots were generated with *CrystalExplorer17* (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.

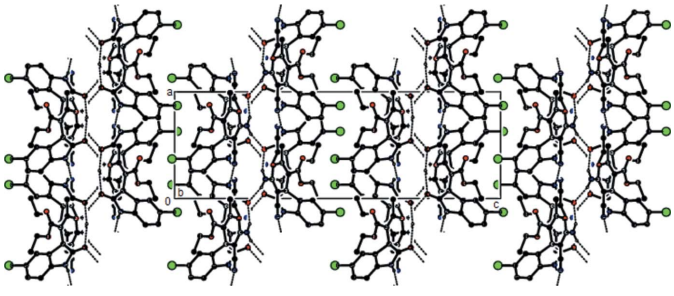


Figure 5
The packing of the title compound viewed along the *b* axis and showing N—H···N and N—H···O hydrogen bonds.

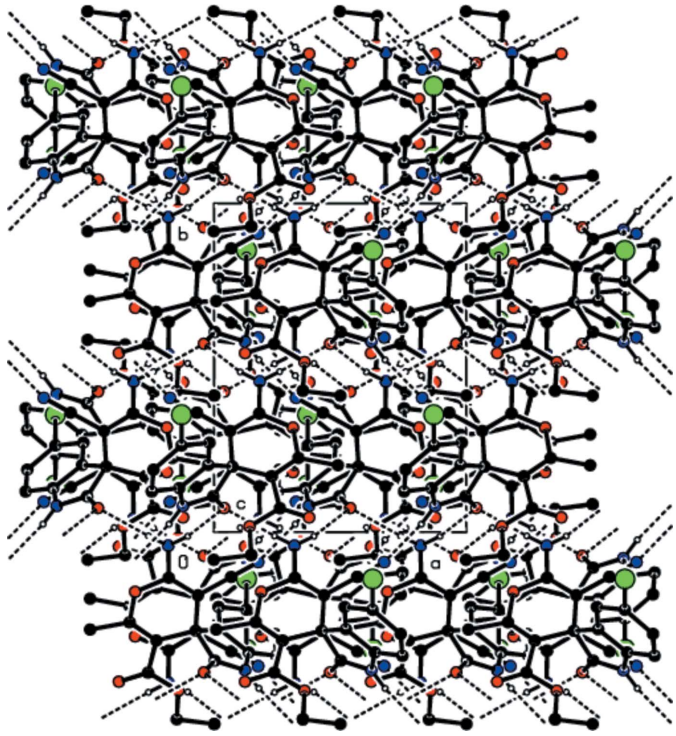


Figure 6
The packing of the title compound viewed along the *c* axis and showing N—H···N and N—H···O hydrogen bonds.

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/H···O (16.3%), N···H/H···N (12.1%), Br···H/H···Br (11.5%) and C···H/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)

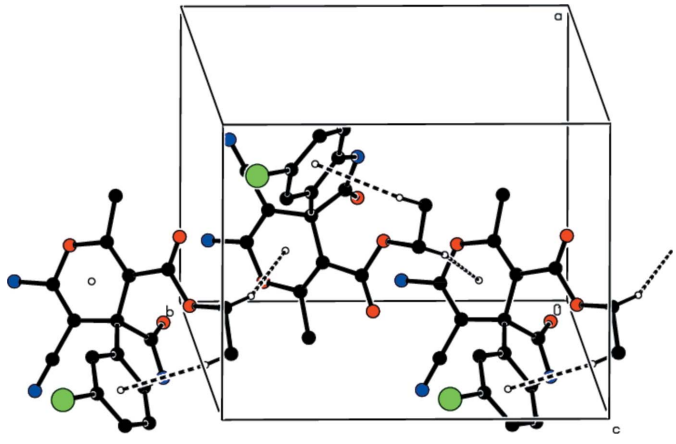


Figure 7
A general view of the packing in the unit cell of the title compound with C—H···π interactions shown as dashed lines.

Table 2
Summary of short interatomic contacts (Å) in the title compound.

Contact	Distance	Symmetry operation
H14*B*···Br1	3.07	$-\frac{1}{2}+x, \frac{3}{2}-y, 1-z$
H6···Br1	3.07	$\frac{1}{2}+x, \frac{3}{2}-y, 1-z$
H15*A*···Br1	2.99	$1-x, 1-y, 1-z$
N12···H1	2.00	$\frac{3}{2}-x, \frac{1}{2}+y, z$
Br1′···O3	2.775	$1+x, y, z$
O2···H8*A*	2.08	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$
N12···H8*B*	2.71	$\frac{1}{2}+x, y, \frac{1}{2}-z$
O2···H8*B*	2.15	$\frac{1}{2}-x, -\frac{1}{2}+y, z$

Table 3
Percentage contributions of interatomic contacts to the Hirshfeld surface for the title compound.

Contact	Percentage contribution
H···H	33.1
O···H/H···O	16.3
N···H/H···N	12.1
Br···H/H···Br	11.5
C···H/H···C	10.6
Br···O/O···Br	4.0
O···C/C···O	2.8
Br···Br	2.5
Br···C/C···Br	1.9
O···O	1.5
Br···N/N···Br	1.2
N···C/C···N	1.0
O···N/N···O	0.8
N···N	0.5
C···C	0.3

using 2-amino-6-methyl-4*H*-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 an intramolecular C—H···O interaction, generating a $S(6)$ ring motif. The molecules are linked by pairs of N—H···O hydrogen bonds into ribbons extending along the *b*-axis direction and consisting of $R_2^2(8)$ and $R_2^2(14)$ rings. Between the ribbons, there are weak van der Waals contacts.

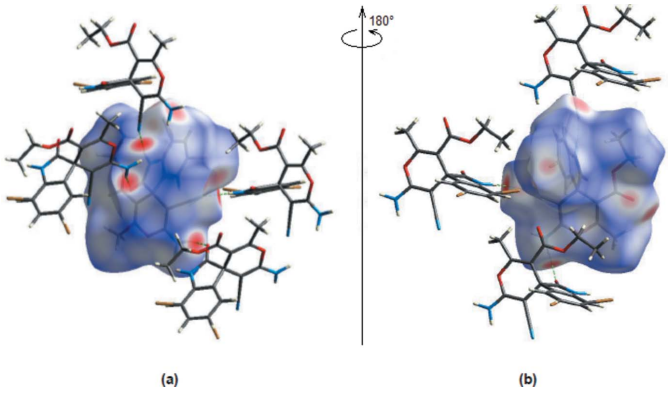


Figure 8
Front (*a*) and back (*b*) sides of the three-dimensional Hirshfeld surface of the title compound mapped over d_{norm}, with a fixed colour scale of −0.5859 to 1.4054 a.u.

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.

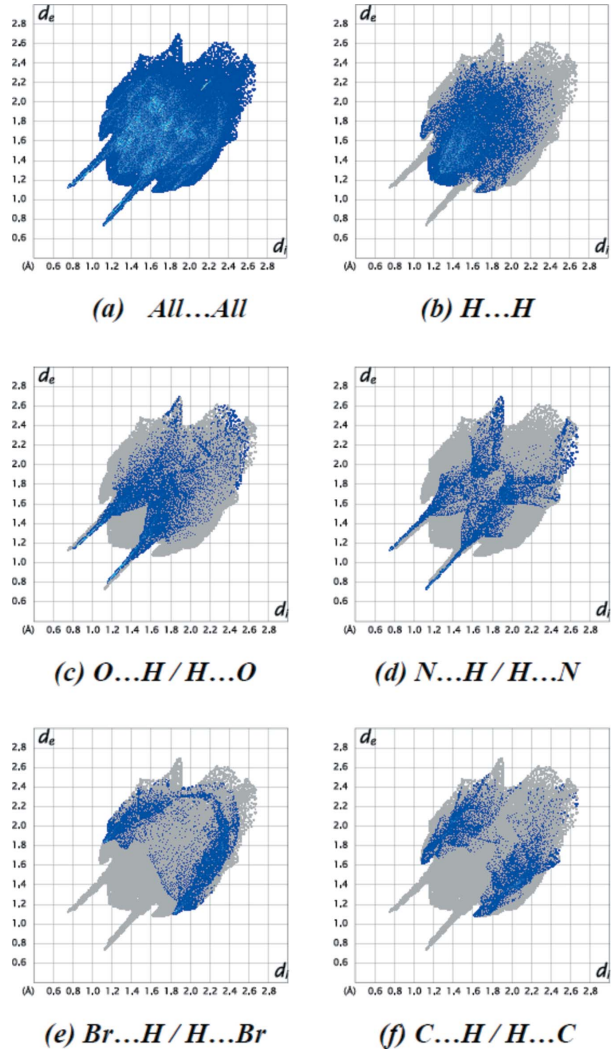


Figure 9
The two-dimensional fingerprint plots of the title compound, showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) O···H/H···O, (*d*) N···H/H···N, (*e*) Br···H/H···Br and (*f*) C···H/H···C interactions. [d_e and d_i represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

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 NH_2 groups were located in a difference map, and their positional parameters were allowed to freely refine [N1—H1 = 0.88 (3), N8—H8*A* = 0.88 (3) and N8—H8*B* = 0.86 (3) Å], but their isotropic displacement parameters were constrained to take a value of $1.2U_{eq}$(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 U_{iso}(H) = $1.5U_{eq}$(C) for methyl H atoms and $1.2U_{eq}$(C) for all others.

Table 4
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{14}BrN_3O_4$
M_r	404.22
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	100
a, *b*, *c* (Å)	9.3880 (9), 12.2260 (12), 28.693 (3)
V (Å^3)	3293.3 (6)
Z	8
Radiation type	Synchrotron, λ = 0.74500 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)
T_{min}, T_{max}	0.626, 0.716
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	29648, 4526, 4225
R_{int}	0.058
(sin θ/λ)$_{max}$ (Å^{-1})	0.692
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *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
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.79, −0.66

Computer programs: *Marccd* (Doyle, 2011), *iMosflm* (Battye *et al.*, 2011), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

Acknowledgements

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

Funding information

This paper was supported by Baku State University and the Ministry of Science and Higher Education of the Russian Federation [award No. 075–03–2020-223 (FSSF-2020–0017)].

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supporting information

Acta Cryst. (2022). E**78**, 942-946 [https://doi.org/10.1107/S2056989022008271]

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: *Marccd* (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

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Orthorhombic, *Pbca*
a = 9.3880 (9) Å
b = 12.2260 (12) Å
c = 28.693 (3) Å
V = 3293.3 (6) Å^3
Z = 8
$F(000)$ = 1632
D_x = 1.631 Mg m^{-3}
Synchrotron radiation, λ = 0.74500 Å
Cell parameters from 1000 reflections
θ = 1.5–25.0°
μ = 2.84 mm^{-1}
T = 100 K
Prism, colourless
0.15 × 0.12 × 0.10 mm

Data collection

Rayonix SX-165 CCD diffractometer
/f 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
θ_{max} = 31.0°, θ_{min} = 1.5°
h = −12→12
k = −16→14
l = −39→39

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
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.017P)^2 + 5.6891P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.79 e Å^{-3}
$\Delta\rho_{min}$ = −0.66 e Å^{-3}

Extinction correction: SHELXL-2018/3 (Sheldrick, 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
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*	U_{iso}*/U_{eq}	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*	

C15	0.5010 (3)	0.4153 (2)	0.44064 (11)	0.0428 (7)
H15A	0.501376	0.356587	0.463876	0.064*
H15B	0.532513	0.483667	0.455218	0.064*
H15C	0.565745	0.396395	0.415096	0.064*
C16	0.0088 (2)	0.7030 (2)	0.32966 (8)	0.0279 (5)
H16A	−0.007451	0.624599	0.334448	0.042*
H16B	−0.032855	0.725376	0.299839	0.042*
H16C	−0.035784	0.744306	0.355019	0.042*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
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	0.0174 (9)	0.0164 (8)	0.0223 (9)	−0.0009 (7)	0.0039 (7)	0.0017 (7)
C3	0.0143 (8)	0.0153 (8)	0.0199 (8)	0.0001 (7)	0.0014 (7)	0.0004 (7)
C3A	0.0167 (8)	0.0178 (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	0.0190 (9)	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)	0.0203 (9)	0.0232 (9)	−0.0005 (8)	0.0010 (7)	0.0028 (7)
C8	0.0182 (9)	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)

Geometric parameters (Å, º)

Br1—C5	1.895 (2)	C6—C7	1.390 (3)
Br1′—C7′	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)

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—C5	1.393 (3)	C15—H15B	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)	O4—C14—H14B	110.4
C6—C5′—H5′	118.9	C15—C14—H14B	110.4
C4—C5′—H5′	118.9	H14A—C14—H14B	108.6
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	H15B—C15—H15C	109.5
C6—C7—H7	121.3	C11—C16—H16A	109.5
C7A—C7′—C6	117.3 (2)	C11—C16—H16B	109.5
C7A—C7′—Br1′	123.7 (3)	H16A—C16—H16B	109.5
C6—C7′—Br1′	114.0 (3)	C11—C16—H16C	109.5
C7′—C7A—C3A	122.2 (2)	H16A—C16—H16C	109.5
C7—C7A—C3A	122.2 (2)	H16B—C16—H16C	109.5
C7′—C7A—N1	128.0 (2)		

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)	O1—C8—C9—C3	−1.2 (3)
C9—C3—C3A—C7A	−111.51 (18)	C3A—C3—C9—C8	−136.6 (2)
C10—C3—C3A—C7A	123.70 (19)	C10—C3—C9—C8	−7.1 (3)
C2—C3—C3A—C7A	4.0 (2)	C2—C3—C9—C8	113.8 (2)
C7A—C3A—C4—C5′	−2.4 (3)	C3A—C3—C9—C12	35.6 (2)
C3—C3A—C4—C5′	−174.5 (2)	C10—C3—C9—C12	165.02 (18)
C7A—C3A—C4—C5	−2.4 (3)	C2—C3—C9—C12	−74.1 (2)
C3—C3A—C4—C5	−174.5 (2)	C9—C3—C10—C11	10.0 (3)
C3A—C4—C5—C6	−0.2 (3)	C3A—C3—C10—C11	134.6 (2)
C3A—C4—C5—Br1	178.57 (15)	C2—C3—C10—C11	−110.7 (2)
C3A—C4—C5′—C6	−0.2 (3)	C9—C3—C10—C13	−173.50 (16)
C4—C5—C6—C7	1.8 (3)	C3A—C3—C10—C13	−48.9 (2)
Br1—C5—C6—C7	−176.99 (17)	C2—C3—C10—C13	65.8 (2)
C4—C5′—C6—C7′	1.8 (3)	C13—C10—C11—O1	178.68 (18)
C5—C6—C7—C7A	−0.7 (3)	C3—C10—C11—O1	−4.9 (3)
C5′—C6—C7′—C7A	−0.7 (3)	C13—C10—C11—C16	−1.6 (3)
C5′—C6—C7′—Br1′	−156.6 (3)	C3—C10—C11—C16	174.8 (2)
C6—C7′—C7A—C3A	−2.0 (3)	C8—O1—C11—C10	−4.6 (3)
Br1′—C7′—C7A—C3A	151.5 (3)	C8—O1—C11—C16	175.58 (18)
C6—C7′—C7A—N1	177.2 (2)	C14—O4—C13—O3	−8.9 (3)
Br1′—C7′—C7A—N1	−29.3 (4)	C14—O4—C13—C10	170.02 (17)
C6—C7—C7A—C3A	−2.0 (3)	C11—C10—C13—O3	−13.4 (3)
C6—C7—C7A—N1	177.2 (2)	C3—C10—C13—O3	170.1 (2)
C4—C3A—C7A—C7′	3.6 (3)	C11—C10—C13—O4	167.81 (18)
C3—C3A—C7A—C7′	177.22 (19)	C3—C10—C13—O4	−8.8 (2)

C4—C3A—C7A—C7	3.6 (3)	C13—O4—C14—C15	−156.2 (2)
C3—C3A—C7A—C7	177.22 (19)		

Hydrogen-bond geometry (Å, º)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N12^{i}	0.88 (3)	2.00 (3)	2.874 (3)	170 (2)
N8—H8*A*···O2^{ii}	0.88 (3)	2.08 (3)	2.940 (2)	165 (3)
N8—H8*B*···O2^{iii}	0.86 (3)	2.15 (3)	2.971 (2)	158 (2)
C16—H16*A*···O3	0.98	2.30	2.865 (3)	116
C14—H14*A*···*Cg*2^{iv}	0.99	2.92	3.773 (3)	145
C15—H15*B*···*Cg*3	0.98	2.99	3.729 (3)	133
C15—H15*B*···*Cg*4	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*.