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Crystal structure and Hirshfeld surface analysis of ethyl 6′-amino-2′-(chloromethyl)-5′-cyano-2-oxo-1,2-dihydrospiro[indoline-3,4′-pyran]-3′-carboxylate

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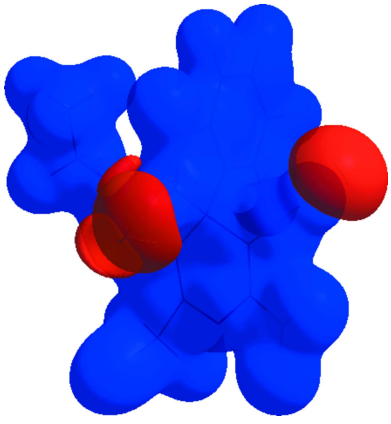
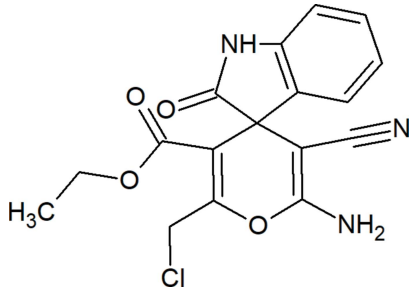
The molecular conformation of the title compound, $C_{17}H_{14}ClN_3O_4$, is stabilized by an intramolecular C—H···O contact, forming an $S(6)$ ring motif. In the crystal, the molecules are connected by N—H···O hydrogen-bond pairs along the b-axis direction as dimers with $R_2^2(8)$ and $R_2^2(14)$ ring motifs and as ribbons formed by intermolecular C—H···N hydrogen bonds. There are weak van der Waals interactions between the ribbons. The most important contributions to the surface contacts are from H···H (34.9%), O···H/H···O (19.2%), C···H/H···C (11.9%), Cl···H/H···Cl (10.7%) and N···H/H···N (10.4%) interactions, as concluded from a Hirshfeld surface analysis.



1. Chemical context

Being the most significant tools in organic synthesis, carbon–carbon and carbon–heteroatom coupling reactions are important for the construction of fine chemicals such as pharmaceuticals, fragrances, antioxidants, *etc*. (Yadigarov *et al.*, 2009; Khalilov *et al.*, 2018*a*,*b*; Zubkov *et al.*, 2018). These methods have found widespread application in the design of diverse heterocyclic ring systems, as well as spiro-heterocyclic compounds (Gurbanov *et al.*, 2018; Maharramov *et al.*, 2019; Mahmoudi *et al.*, 2019; Mamedov *et al.*, 2019; Yin *et al.*, 2020). The spirooxindole moiety is a key bioactive fragment of various natural products (Fig. 1), series of derivatives already being used in medicinal practice (Zhou *et al.*, 2020).



In this work, in the framework of our ongoing structural studies (Akkurt *et al.*, 2018; Naghiyev *et al.*, 2020, 2021), we report the crystal structure and Hirshfeld surface analysis of

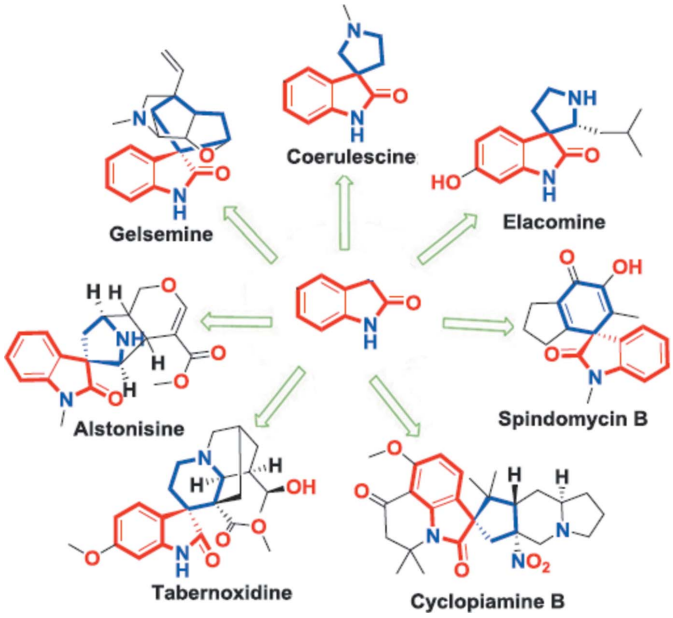


Figure 1
Natural products containing the spirooxindole motif.

the title compound, ethyl 6′-amino-2′-(chloromethyl)-5′-cyano-2-oxo-1,2-dihydrospiro[indoline-3,4′-pyran]-3′-carboxylate.

2. Structural commentary

In the title compound (Fig. 2), the 2,3-dihydro-1*H*-indole ring system (N1/C1/C4/C12–C17) is nearly planar [maximum deviation = 0.039 (1) Å for C1], while the 4*H*-pyran ring (O1/C2–C6) adopts a flattened-boat conformation [puckering parameters (Cremer & Pople, 1975): Q_T = 0.1091 (13) Å, θ = 77.0 (6) ° and φ = 139.6 (7) °]. The planes of the 2,3-dihydro-1*H*-indole ring system and the 4*H*-pyran ring are approximately perpendicular to each other, subtending a dihedral angle of 84.52 (5)°. The C5—C6—C11—Cl1, C6—C5—C8—O2, C6—C5—C8—O3, C5—C8—O3—C9 and C8—O3—C9—C10 torsion angles are −103.28 (13), −29.78 (18), 150.69 (11), 178.03 (10) and −169.29 (12)°, respectively. An intramolecular C11—H11*B*···O2 contact stabilizes the molecular conformation of the title compound (Fig. 2, Table 1), generating an *S*(6) ring motif (Bernstein *et al.*, 1995).

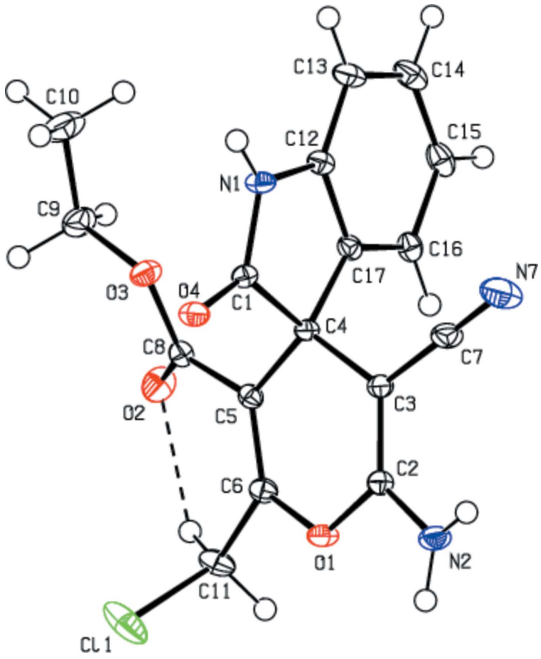


Figure 2
The molecular structure of the title compound, showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4^{i}	0.853 (17)	1.981 (17)	2.8292 (14)	173.0 (17)
N2—H2*B*···O4^{ii}	0.887 (18)	2.095 (18)	2.9636 (15)	166.0 (17)
C11—H11*B*···O2	0.99	2.15	2.9039 (17)	131
C13—H13···N7^{iii}	0.95	2.56	3.333 (2)	138

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

3. Supramolecular features

In the crystal, the molecules are joined by N—H···O hydrogen-bond pairs along the *b*-axis direction as dimers with $R_2^2(8)$ and $R_2^2(14)$ ring motifs and by intermolecular C—H···N hydrogen bonds as ribbons (Table 1; Figs. 3 and 4). Between the ribbons are only weak van der Waals contacts (Table 2). There are no C—H···π or π–π interactions in the crystal structure.

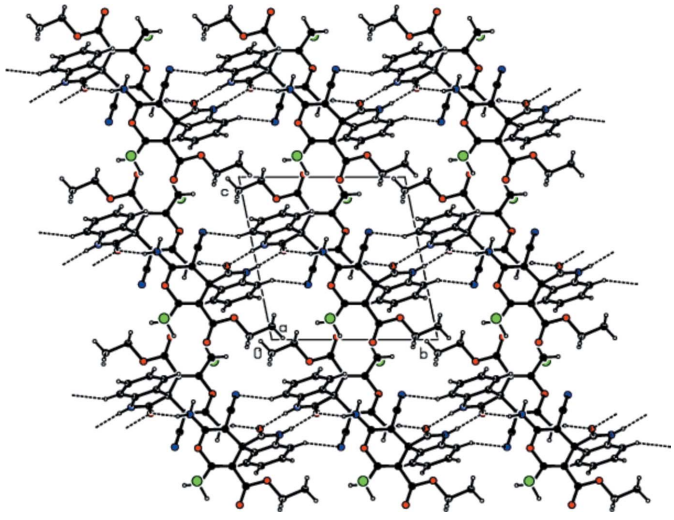


Figure 3
A view of the intermolecular N—H···O and C—H···N hydrogen bonds in the crystal packing of the title compound down the *a* axis.

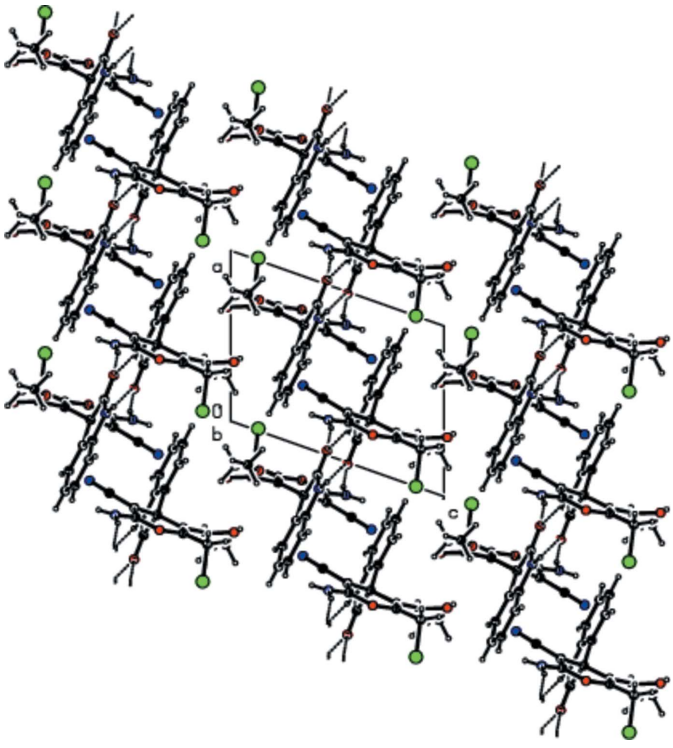


Figure 4
A view of the intermolecular N—H···O and C—H···N hydrogen bonds in the crystal packing of the title compound down the *b* axis.

4. Hirshfeld surface analysis

A Hirshfeld surface analysis was performed to investigate the intermolecular interactions (Tables 1 and 2) quantitatively and the associated two-dimensional fingerprint plots (McKinnon *et al.*, 2007) were generated with *CrystalExplorer17* (Turner *et al.*, 2017). The Hirshfeld surface plotted over d_{norm} in the range −0.6053 to 1.4079 a.u. is shown in Fig. 5. The red spots on the Hirshfeld surface represent N—H···O contacts. The Hirshfeld surface mapped over electrostatic potential (Spackman *et al.*, 2008) is shown in Fig. 6. The positive electrostatic potential (blue region) over the surface indicates hydrogen-donor potential, whereas the hydrogen-bond acceptors are represented by negative electrostatic potential (red region).

Fig. 7 shows the full two-dimensional fingerprint plot and those delineated into the major contacts: the H···H (34.9%; Fig. 7*b*) interactions are the major factor in the crystal packing

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

Contact	Distance	Symmetry operation
O3···H15	2.88	−1 + *x*, *y*, *z*
H9*A*···Cl1	3.06	−*x*, 1 − *y*, 2 − *z*
H2*B*···O4	2.095	−*x*, 1 − *y*, 1 − *z*
H16···H11*B*	2.37	1 − *x*, 1 − *y*, 2 − *z*
H1···O4	1.981	−*x*, −*y*, 1 − *z*
H16···H2*A*	2.49	1 − *x*, 1 − *y*, 1 − *z*
H13···N7	2.56	1 − *x*, −*y*, 1 − *z*
H10*A*···H11*A*	2.49	*x*, − 1 + *y*, *z*
H10*A*···C14	2.93	1 − *x*, −*y*, 2 − *z*

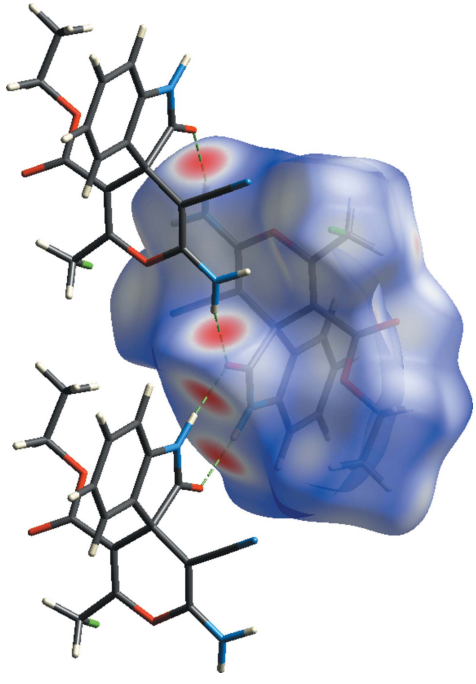


Figure 5
Hirshfeld surface of the title compound mapped with d_{norm} in the range −0.6053 to 1.4079 a.u.

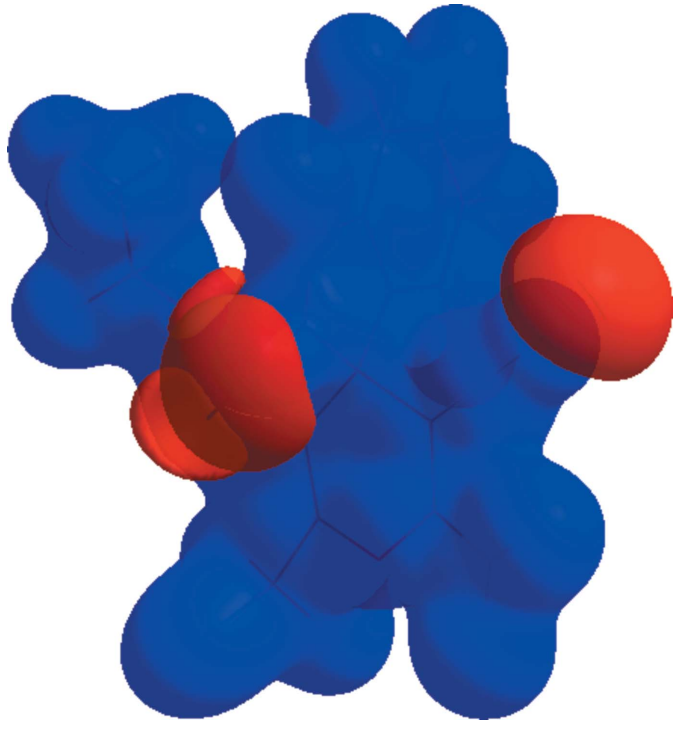


Figure 6
View of the three-dimensional Hirshfeld surface of the title compound plotted over electrostatic potential energy in the range −0.0500 to 0.0500 a.u. using the STO-3 G basis set at the Hartree–Fock level of theory. Hydrogen-bond donors and acceptors are shown as blue and red regions around the atoms, corresponding to positive and negative potentials, respectively.

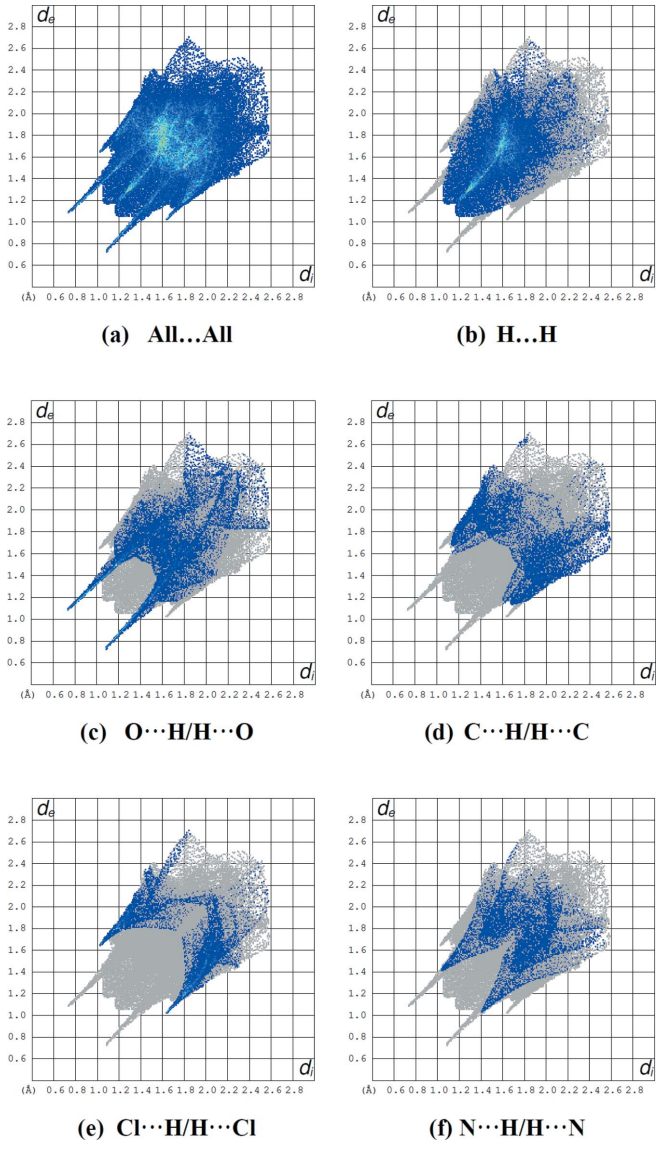


Figure 7
The two-dimensional fingerprint plots of the title compound, showing (*a*) all interactions, and those delineated into (*b*) H···H, (*c*) O···H/H···O, (*d*) C···H/H···C, (*e*) Cl···H/H···Cl and (*f*) N···H/H···N interactions [d_e and d_i represent the distances from a point on the Hirshfeld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

with O···H/H···O (19.2%; Fig. 7*c*), C···H/H···C (11.9%; Fig. 7*d*), Cl···H/H···Cl (10.7%; Fig. 7*e*) and N···H/H···N (10.4%; Fig. 7*f*) interactions representing the next highest contributions. Other weak interactions (contribution percentages) are O···N/N···O (2.3%), O···C/C···O (2.1%), N···C/C···N (2.1%), Cl···N/N···Cl (1.7%), Cl···O/O···Cl (1.4%), C···C (1.0%), N···N (0.7%), O···O (0.6%), Cl···C/C···Cl (0.6%) and Cl···Cl (0.3%).

5. Database survey

A survey of the Cambridge Structural Database (CSD version 5.41, update of March 2020; Groom *et al.*, 2016) using 2-amino-6-(chloromethyl)-4*H*-pyran-3-carbonitrile as the main skeleton revealed the presence of three structures, ethyl 6-amino-2-(chloromethyl)-5-cyano-4-(*o*-tolyl)-4*H*-pyran-3-carboxylate (CSD refcode HIRNUS; Athimoolam *et al.*, 2007), 2-amino-6-chloromethyl-3-cyano-5-ethoxycarbonyl-4-(2-furyl)-4*H*-pyran (JEGWEX; Lokaj *et al.*, 1990) and ethyl 6′-amino-2′-(chloromethyl)-5′-cyano-2-oxo-1,2-dihydrospiro[indole-3,4′-pyran]-3′-carboxylate (WIMBEC; Magerramov *et al.*, 2018).

In the crystal of HIRNUS, the six-membered pyran ring adopts a near-boat conformation. The crystal structure features two intramolecular C—H···O interactions and the crystal packing is stabilized by intermolecular N—H···O hydrogen bonds. These lead to two primary motifs, *viz.* $R_2^2(12)$ and $C(8)$. Combination of these primary motifs leads to a secondary $R_2^2(20)$ ring motif.

In the crystal of JEGWEX, a potential precursor for fluoroquinoline synthesis, the pyran ring is nearly planar, with the most outlying atoms displaced from the best-plane fit through all non-H atoms by 0.163 (2) and 0.118 (2) Å. The molecules are arranged in layers oriented parallel to the (011) plane. In addition, the molecules are linked by a weak C—H···O hydrogen bond, which gives rise to chains with base vector [111].

In WIMBEC, the pyran ring exhibits a near-boat conformation with puckering parameters Q_T = 0.085 (7) Å, θ = 84 (5)° and φ = 154 (5)°. In the crystal, molecules are linked as dimers by pairs of N—H···O hydrogen bonds, forming ribbons along the *b*-axis direction. These ribbons are connected by weak van der Waals interactions, stabilizing the molecular packing.

6. Synthesis and crystallization

The title compound was synthesized using previously reported procedures (Luo *et al.*, 2015; Magerramov *et al.*, 2018), and colourless needles were obtained upon recrystallization from methanol solution.

7. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. 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 = 0.853 (17), N2—H2*A* = 0.843 (19) and N2—H2*B* = 0.889 (18) 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 the others. Four reflections, 0 0 1, 0 1 0, 1 0 0 and 1 2 0, affected by the incident beam-stop and owing to poor agreement between observed and calculated intensities, and five outliers, $\bar{1}$ $\bar{3}$ 3, 3 1 1, $\bar{1}$ 1 4, $\bar{1}$ $\bar{6}$ 9 and 4 $\bar{11}$ 2, were omitted in the final cycles of refinement.

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{14}ClN_3O_4$
M_r	359.76
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, b, c (Å)	8.0218 (2), 10.2278 (3), 10.6714 (3)
α, β, γ (°)	98.8503 (7), 108.0048 (7), 96.3852 (6)
V (Å^3)	810.92 (4)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.26
Crystal size (mm)	0.25 × 0.20 × 0.15
Data collection	
Diffractometer	Bruker D8 QUEST PHOTON-III CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.903, 0.949
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18865, 5899, 4685
R_{int}	0.039
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.758
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.106, 1.03
No. of reflections	5899
No. of parameters	236
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.44, −0.63

Computer programs: *APEX3* (Bruker, 2018), *SAINT* (Bruker, 2013), *SHELXT2014/5* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

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The authors' contributions are as follows. Conceptualization, FNN and IGM; methodology, FNN and IGM; investigation, VNK, FNN, MMG and AAA; writing (original draft), MA and IGM; writing (review and editing of the manuscript), MA and IGM; visualization, MA, FNN and IGM; funding acquisition, VNK and FNN; resources, ATH, AAA and FNN; supervision, IGM and MA.;

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supporting information

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Crystal structure and Hirshfeld surface analysis of ethyl 6′-amino-2′-(chloromethyl)-5′-cyano-2-oxo-1,2-dihydrospiro[indoline-3,4′-pyran]-3′-carboxylate

Farid N. Naghiyev, Maria M. Grishina, Victor N. Khrustalev, Mehmet Akkurt, Afet T. Huseynova, Anzurat A. Akobirshoeva and İbrahim G. Mamedov

Computing details

Data collection: *APEX3* (Bruker, 2018); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

Ethyl 6′-amino-2′-(chloromethyl)-5′-cyano-2-oxo-1,2-dihydrospiro[indoline-3,4′-pyran]-3′-carboxylate

Crystal data

$C_{17}H_{14}ClN_3O_4$
M_r = 359.76
Triclinic, $P\overline{1}$
a = 8.0218 (2) Å
b = 10.2278 (3) Å
c = 10.6714 (3) Å
α = 98.8503 (7)°
β = 108.0048 (7)°
γ = 96.3852 (6)°
V = 810.92 (4) Å^3

Z = 2
$F(000)$ = 372
D_x = 1.473 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6340 reflections
θ = 2.6–32.5°
μ = 0.26 mm^{-1}
T = 100 K
Prism, colourless
0.25 × 0.20 × 0.15 mm

Data collection

Bruker D8 QUEST PHOTON-III CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.903, T_{max} = 0.949
18865 measured reflections

5899 independent reflections
4685 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 32.6°, θ_{min} = 2.6°
h = −12→12
k = −15→15
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.106
S = 1.03
5899 reflections
236 parameters
0 restraints

Primary atom site location: difference Fourier map
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2 + 0.4187P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.63$ e Å^{-3}

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	−0.00786 (5)	0.62296 (4)	0.86942 (4)	0.03426 (11)
O1	0.20564 (12)	0.57639 (8)	0.66693 (9)	0.01580 (17)
O2	0.34827 (14)	0.39501 (10)	1.01602 (9)	0.0221 (2)
O3	0.24269 (13)	0.20082 (9)	0.86649 (9)	0.01705 (17)
O4	−0.01410 (11)	0.18103 (8)	0.54781 (9)	0.01560 (17)
N1	0.22730 (14)	0.07160 (10)	0.58525 (11)	0.01426 (19)
H1	0.171 (2)	−0.0075 (17)	0.5472 (17)	0.017*
N2	0.20156 (16)	0.58493 (11)	0.45919 (12)	0.0189 (2)
H2A	0.198 (2)	0.5484 (18)	0.3819 (19)	0.023*
H2B	0.158 (2)	0.6601 (18)	0.4714 (18)	0.023*
C1	0.14677 (15)	0.18025 (11)	0.59191 (11)	0.0124 (2)
C2	0.23180 (15)	0.51172 (11)	0.55510 (12)	0.0137 (2)
C3	0.28549 (15)	0.38996 (11)	0.54920 (12)	0.0131 (2)
C4	0.29313 (15)	0.30748 (11)	0.65670 (11)	0.01141 (19)
C5	0.27019 (15)	0.39250 (11)	0.77759 (11)	0.01218 (19)
C6	0.23527 (15)	0.51749 (12)	0.77729 (12)	0.0138 (2)
C7	0.32238 (18)	0.33266 (13)	0.43295 (13)	0.0182 (2)
N7	0.3547 (2)	0.28501 (14)	0.33968 (13)	0.0300 (3)
C8	0.29278 (15)	0.33459 (12)	0.90096 (12)	0.0139 (2)
C9	0.2632 (2)	0.12998 (14)	0.97758 (14)	0.0231 (3)
H9A	0.1751	0.1491	1.0225	0.028*
H9B	0.3840	0.1588	1.0446	0.028*
C10	0.2340 (3)	−0.01675 (15)	0.91875 (16)	0.0317 (3)
H10A	0.2419	−0.0684	0.9899	0.048*
H10B	0.3251	−0.0348	0.8779	0.048*
H10C	0.1160	−0.0431	0.8500	0.048*
C11	0.21988 (17)	0.61386 (13)	0.89102 (13)	0.0187 (2)
H11A	0.2843	0.7039	0.8960	0.022*
H11B	0.2752	0.5848	0.9765	0.022*
C12	0.41277 (15)	0.10561 (12)	0.64735 (12)	0.0137 (2)
C13	0.53735 (17)	0.02074 (13)	0.66518 (13)	0.0181 (2)
H13	0.5037	−0.0737	0.6349	0.022*
C14	0.71502 (17)	0.08061 (14)	0.72987 (13)	0.0201 (2)
H14	0.8044	0.0255	0.7431	0.024*
C15	0.76464 (16)	0.21894 (14)	0.77546 (13)	0.0188 (2)
H15	0.8866	0.2568	0.8189	0.023*

C16	0.63576 (16)	0.30242 (12)	0.75758 (12)	0.0150 (2)
H16	0.6684	0.3968	0.7893	0.018*
C17	0.45955 (15)	0.24390 (12)	0.69254 (11)	0.0126 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.01877 (16)	0.0398 (2)	0.0354 (2)	0.00475 (13)	0.00875 (14)	−0.01772 (16)
O1	0.0210 (4)	0.0116 (4)	0.0157 (4)	0.0066 (3)	0.0060 (3)	0.0028 (3)
O2	0.0293 (5)	0.0206 (4)	0.0140 (4)	−0.0004 (4)	0.0064 (4)	0.0013 (3)
O3	0.0244 (4)	0.0127 (4)	0.0150 (4)	0.0044 (3)	0.0067 (3)	0.0042 (3)
O4	0.0128 (4)	0.0121 (4)	0.0196 (4)	0.0027 (3)	0.0029 (3)	0.0014 (3)
N1	0.0146 (4)	0.0092 (4)	0.0171 (5)	0.0030 (3)	0.0032 (4)	0.0006 (3)
N2	0.0264 (6)	0.0154 (5)	0.0196 (5)	0.0099 (4)	0.0099 (4)	0.0080 (4)
C1	0.0139 (5)	0.0103 (5)	0.0128 (5)	0.0022 (4)	0.0041 (4)	0.0020 (4)
C2	0.0137 (5)	0.0124 (5)	0.0157 (5)	0.0032 (4)	0.0052 (4)	0.0033 (4)
C3	0.0152 (5)	0.0114 (5)	0.0137 (5)	0.0037 (4)	0.0055 (4)	0.0030 (4)
C4	0.0125 (5)	0.0091 (4)	0.0129 (5)	0.0029 (4)	0.0044 (4)	0.0021 (4)
C5	0.0114 (5)	0.0124 (5)	0.0121 (5)	0.0021 (4)	0.0037 (4)	0.0009 (4)
C6	0.0136 (5)	0.0130 (5)	0.0135 (5)	0.0029 (4)	0.0032 (4)	0.0010 (4)
C7	0.0233 (6)	0.0174 (5)	0.0178 (6)	0.0101 (5)	0.0079 (5)	0.0079 (4)
N7	0.0461 (8)	0.0317 (6)	0.0223 (6)	0.0239 (6)	0.0170 (6)	0.0113 (5)
C8	0.0127 (5)	0.0144 (5)	0.0156 (5)	0.0028 (4)	0.0059 (4)	0.0029 (4)
C9	0.0362 (7)	0.0196 (6)	0.0195 (6)	0.0091 (5)	0.0134 (5)	0.0097 (5)
C10	0.0528 (10)	0.0182 (6)	0.0293 (7)	0.0106 (6)	0.0163 (7)	0.0111 (6)
C11	0.0182 (5)	0.0175 (5)	0.0169 (5)	0.0065 (4)	0.0029 (4)	−0.0032 (4)
C12	0.0142 (5)	0.0137 (5)	0.0136 (5)	0.0047 (4)	0.0045 (4)	0.0027 (4)
C13	0.0220 (6)	0.0171 (5)	0.0173 (6)	0.0106 (4)	0.0071 (5)	0.0035 (4)
C14	0.0194 (6)	0.0270 (6)	0.0171 (6)	0.0131 (5)	0.0066 (5)	0.0056 (5)
C15	0.0130 (5)	0.0288 (6)	0.0157 (5)	0.0065 (4)	0.0049 (4)	0.0049 (5)
C16	0.0145 (5)	0.0185 (5)	0.0128 (5)	0.0030 (4)	0.0056 (4)	0.0033 (4)
C17	0.0136 (5)	0.0144 (5)	0.0111 (5)	0.0041 (4)	0.0050 (4)	0.0027 (4)

Geometric parameters (Å, º)

Cl1—C11	1.7842 (13)	C6—C11	1.4871 (17)
O1—C2	1.3595 (15)	C7—N7	1.1550 (18)
O1—C6	1.3725 (14)	C9—C10	1.497 (2)
O2—C8	1.2063 (15)	C9—H9A	0.9900
O3—C8	1.3417 (14)	C9—H9B	0.9900
O3—C9	1.4586 (15)	C10—H10A	0.9800
O4—C1	1.2308 (14)	C10—H10B	0.9800
N1—C1	1.3495 (14)	C10—H10C	0.9800
N1—C12	1.4064 (15)	C11—H11A	0.9900
N1—H1	0.853 (17)	C11—H11B	0.9900
N2—C2	1.3379 (15)	C12—C13	1.3837 (16)
N2—H2A	0.843 (19)	C12—C17	1.3907 (16)
N2—H2B	0.889 (18)	C13—C14	1.3966 (19)

C1—C4	1.5592 (16)	C13—H13	0.9500
C2—C3	1.3610 (15)	C14—C15	1.393 (2)
C3—C7	1.4183 (17)	C14—H14	0.9500
C3—C4	1.5156 (16)	C15—C16	1.3995 (17)
C4—C5	1.5138 (16)	C15—H15	0.9500
C4—C17	1.5183 (16)	C16—C17	1.3840 (16)
C5—C6	1.3390 (16)	C16—H16	0.9500
C5—C8	1.4944 (16)		

C2—O1—C6	119.01 (9)	C10—C9—H9A	110.3
C8—O3—C9	115.95 (10)	O3—C9—H9B	110.3
C1—N1—C12	111.77 (10)	C10—C9—H9B	110.3
C1—N1—H1	123.4 (11)	H9A—C9—H9B	108.6
C12—N1—H1	124.8 (11)	C9—C10—H10A	109.5
C2—N2—H2A	118.0 (12)	C9—C10—H10B	109.5
C2—N2—H2B	119.3 (11)	H10A—C10—H10B	109.5
H2A—N2—H2B	120.6 (16)	C9—C10—H10C	109.5
O4—C1—N1	126.32 (11)	H10A—C10—H10C	109.5
O4—C1—C4	125.13 (10)	H10B—C10—H10C	109.5
N1—C1—C4	108.42 (9)	C6—C11—Cl1	110.59 (9)
N2—C2—O1	110.94 (10)	C6—C11—H11A	109.5
N2—C2—C3	127.13 (11)	Cl1—C11—H11A	109.5
O1—C2—C3	121.91 (10)	C6—C11—H11B	109.5
C2—C3—C7	118.87 (11)	Cl1—C11—H11B	109.5
C2—C3—C4	122.67 (10)	H11A—C11—H11B	108.1
C7—C3—C4	118.26 (10)	C13—C12—C17	122.36 (11)
C5—C4—C3	109.52 (9)	C13—C12—N1	128.15 (11)
C5—C4—C17	112.86 (9)	C17—C12—N1	109.49 (10)
C3—C4—C17	112.55 (9)	C12—C13—C14	116.79 (12)
C5—C4—C1	113.49 (9)	C12—C13—H13	121.6
C3—C4—C1	107.25 (9)	C14—C13—H13	121.6
C17—C4—C1	100.85 (9)	C15—C14—C13	121.72 (11)
C6—C5—C8	120.03 (10)	C15—C14—H14	119.1
C6—C5—C4	121.88 (10)	C13—C14—H14	119.1
C8—C5—C4	118.07 (9)	C14—C15—C16	120.36 (12)
C5—C6—O1	123.81 (11)	C14—C15—H15	119.8
C5—C6—C11	127.27 (11)	C16—C15—H15	119.8
O1—C6—C11	108.91 (10)	C17—C16—C15	118.24 (11)
N7—C7—C3	178.80 (14)	C17—C16—H16	120.9
O2—C8—O3	123.11 (11)	C15—C16—H16	120.9
O2—C8—C5	127.00 (11)	C16—C17—C12	120.53 (11)
O3—C8—C5	109.89 (10)	C16—C17—C4	130.24 (11)
O3—C9—C10	106.89 (11)	C12—C17—C4	109.23 (10)
O3—C9—H9A	110.3		

C12—N1—C1—O4	−179.07 (12)	C2—O1—C6—C5	−7.59 (17)
C12—N1—C1—C4	4.71 (13)	C2—O1—C6—C11	173.03 (10)
C6—O1—C2—N2	−178.30 (10)	C9—O3—C8—O2	−1.51 (17)

C6—O1—C2—C3	0.39 (17)	C9—O3—C8—C5	178.03 (10)
N2—C2—C3—C7	2.90 (19)	C6—C5—C8—O2	−29.78 (18)
O1—C2—C3—C7	−175.56 (11)	C4—C5—C8—O2	148.52 (12)
N2—C2—C3—C4	−171.94 (12)	C6—C5—C8—O3	150.69 (11)
O1—C2—C3—C4	9.61 (18)	C4—C5—C8—O3	−31.00 (14)
C2—C3—C4—C5	−11.44 (15)	C8—O3—C9—C10	−169.29 (12)
C7—C3—C4—C5	173.69 (10)	C5—C6—C11—Cl1	−103.28 (13)
C2—C3—C4—C17	−137.85 (12)	O1—C6—C11—Cl1	76.07 (11)
C7—C3—C4—C17	47.28 (14)	C1—N1—C12—C13	176.98 (12)
C2—C3—C4—C1	112.13 (12)	C1—N1—C12—C17	−2.67 (14)
C7—C3—C4—C1	−62.74 (13)	C17—C12—C13—C14	−0.81 (18)
O4—C1—C4—C5	58.07 (15)	N1—C12—C13—C14	179.59 (12)
N1—C1—C4—C5	−125.66 (10)	C12—C13—C14—C15	0.58 (19)
O4—C1—C4—C3	−63.02 (15)	C13—C14—C15—C16	0.2 (2)
N1—C1—C4—C3	113.24 (10)	C14—C15—C16—C17	−0.69 (18)
O4—C1—C4—C17	179.05 (11)	C15—C16—C17—C12	0.48 (17)
N1—C1—C4—C17	−4.69 (12)	C15—C16—C17—C4	−178.77 (11)
C3—C4—C5—C6	4.62 (15)	C13—C12—C17—C16	0.29 (18)
C17—C4—C5—C6	130.85 (11)	N1—C12—C17—C16	179.96 (10)
C1—C4—C5—C6	−115.19 (12)	C13—C12—C17—C4	179.68 (11)
C3—C4—C5—C8	−173.65 (9)	N1—C12—C17—C4	−0.65 (13)
C17—C4—C5—C8	−47.42 (13)	C5—C4—C17—C16	−56.14 (16)
C1—C4—C5—C8	66.54 (13)	C3—C4—C17—C16	68.46 (15)
C8—C5—C6—O1	−177.31 (10)	C1—C4—C17—C16	−177.56 (12)
C4—C5—C6—O1	4.46 (18)	C5—C4—C17—C12	124.55 (10)
C8—C5—C6—C11	1.96 (18)	C3—C4—C17—C12	−110.86 (11)
C4—C5—C6—C11	−176.28 (11)	C1—C4—C17—C12	3.13 (12)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4^{i}	0.853 (17)	1.981 (17)	2.8292 (14)	173.0 (17)
N2—H2*B*···O4^{ii}	0.887 (18)	2.095 (18)	2.9636 (15)	166.0 (17)
C11—H11*B*···O2	0.99	2.15	2.9039 (17)	131
C13—H13···N7^{iii}	0.95	2.56	3.333 (2)	138

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