

# Crystal structure and Hirshfeld surface analysis of (Z)-2-amino-4-(2,6-dichlorophenyl)-5-(1-hydroxyethylidene)-6-oxo-1-phenyl-1,4,5,6-tetrahydropyridine-3-carbonitrile

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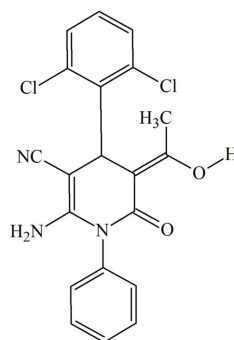
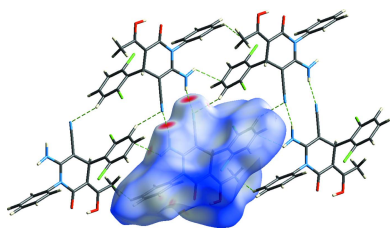
**Supporting information:** this article has supporting information at journals.iucr.org/e

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The molecular conformation of the title compound, C<sub>20</sub>H<sub>15</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>2</sub>, is stabilized by an intramolecular O—H···O hydrogen bond, forming an *S*(6) ring motif. The central pyridine ring is almost planar [maximum deviation = 0.074 (3) Å]. It subtends dihedral angles of 86.10 (15) and 87.17 (14)°, respectively, with the phenyl and dichlorophenyl rings, which are at an angle of 21.28 (15)° to each other. The =C(—OH)CH<sub>3</sub> group is coplanar. In the crystal, molecules are linked by intermolecular N—H···N and C—H···N hydrogen bonds, and N—H···π and C—H···π interactions, forming a three-dimensional network. The most important contributions to the crystal packing are from H···H (33.1%), C···H/H···C (22.5%), Cl···H/H···Cl (14.1%), O···H/H···O (11.9%) and N···H/H···N (9.7%) interactions.

## 1. Chemical context

The development of effective methods for the construction of small-sized molecules bearing a nitrogen heterocycle is a very important proposition in organic synthesis and catalysis (Abdel-Hafiz *et al.*, 2012; Gurbanov *et al.*, 2018; Zubkov *et al.*, 2018). As members of this family, pyridine derivatives play a key role in flavor chemistry, crystal engineering, and the development of biologically active compounds (Adams & De Kimpe, 2006; Mahmoudi *et al.*, 2019; Mamedov *et al.*, 2020). The pyridine core is a key bioactive fragment of diverse natural products (niacin, pyridoxine, nicotine, NADP<sup>+</sup>) and series of derivatives constitute promising drugs in medicinal chemistry (Mohsin & Ahmad, 2018).



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

Cg2 is the centroid of the C7–C12 phenyl ring.

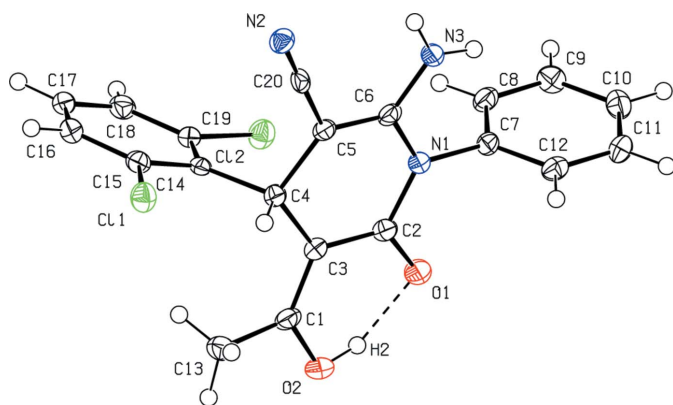
<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O2–H2...O1	0.86 (4)	1.72 (4)	2.514 (3)	153 (4)
N3–H3A...N2 <sup>i</sup>	0.86 (4)	2.22 (4)	3.032 (4)	159 (3)
C16–H16...N2 <sup>ii</sup>	0.95	2.62	3.308 (4)	129
N3–H3B...Cg2	0.88 (4)	2.88 (4)	3.581 (3)	138 (3)
C9–H9...Cg2 <sup>iii</sup>	0.95	2.70	3.564 (4)	151

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

In this study, in the framework of our ongoing structural studies (Naghiyev *et al.*, 2020, 2021*a,b*), we report the crystal structure and Hirshfeld surface analysis of the title compound, (*Z*)-2-amino-4-(2,6-dichlorophenyl)-5-(1-hydroxyethylidene)-6-oxo-1-phenyl-1,4,5,6-tetrahydropyridine-3-carbonitrile, previously mistakenly reported in the *E* isomeric form (Maharramov *et al.*, 2018). This compound was also previously mentioned as transient intermediate but neither isolated nor characterized (Naghiyeva *et al.*, 2019).

## 2. Structural commentary

The title compound crystallizes in the monoclinic space group  $P2_1/c$  with  $Z = 4$ , in which the asymmetric unit comprises one molecule. In the molecule (Fig. 1), the central pyridine ring (N1/C2–C6) is almost planar with a maximum deviation of 0.074 (3) Å for C4. The phenyl (C7–C12) and dichlorophenyl (C14–C19) rings are at an angle of 21.28 (15)°. They form dihedral angles of 86.10 (15) and 87.17 (14)°, respectively, with the central pyridine ring. The =C(–OH)CH<sub>3</sub> group is nearly coplanar with the pyridine ring with C2–C3–C1–O2 and C4–C3–C1–C13 torsion angles of only 5.5 (5) and 3.3 (5)°, respectively. A strong intramolecular O2–H2...O1 hydrogen bond (Fig. 1, Table 1) stabilizes the molecular conformation of the title molecule, creating an *S*(6) ring motif (Bernstein *et al.*, 1995).



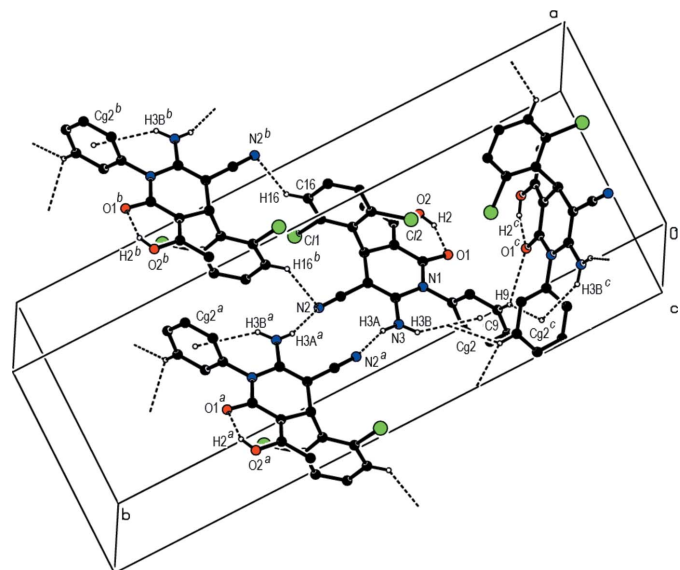
**Figure 1**  
The molecular structure of the title compound showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

**Table 2**  
Interatomic contacts of the title compound (Å).

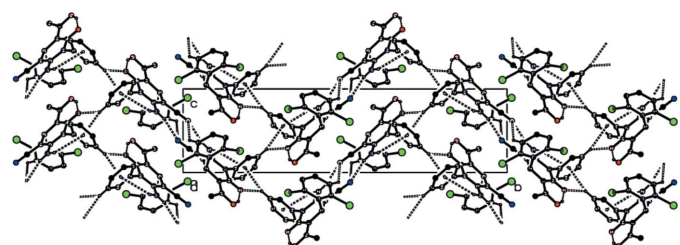
Contact	Distance	Symmetry operation
C11...C11	3.6744 (14)	$2 - x, 1 - y, 1 - z$
H4...C20	2.77	$1 - x, 1 - y, 1 - z$
O1...H9	2.54	$x, \frac{1}{2} - y, -\frac{1}{2} + z$
N2...H13C	2.81	$x, y, 1 + z$
H3A...N2	2.22 (4)	$1 - x, 1 - y, 2 - z$
H16...N2	2.62	$2 - x, 1 - y, 2 - z$
H11...H13B	2.54	$-1 + x, y, z$
H17...H3B	2.54	$1 + x, y, z$
H12...C18	2.93	$-1 + x, y, -1 + z$

## 3. Supramolecular features and Hirshfeld surface analysis

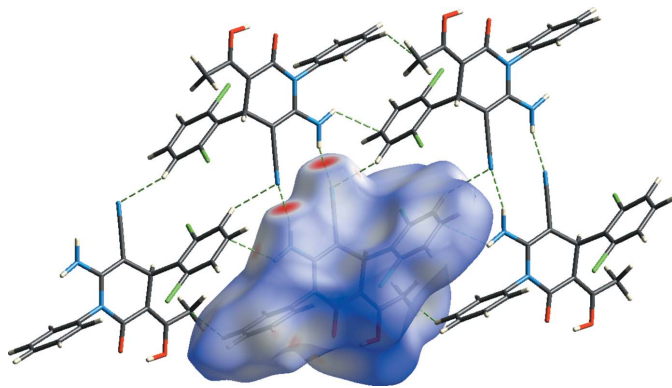
Intermolecular N3–H3A...N2 hydrogen bonds, which form an  $R_2^2(12)$  ring motif between pairs of molecules along the *b*-axis direction and an  $R_2^2(16)$  ring motif between pairs of molecules along the *a*-axis direction, together with N3–H3B...Cg2 and C9–H9...Cg2 interactions (Fig. 2, Tables 1 and 2; Cg2 is the centroid of the C7–C12 phenyl ring) create a three-dimensional network in the crystal (Figs. 2 and 3).



**Figure 2**  
A general view of the intra- and intermolecular O–H...O, N–H...N hydrogen bonding and N–H... $\pi$  and C–H... $\pi$  interactions in the title compound. Symmetry codes: (a)  $1 - x, 1 - y, 2 - z$ ; (b)  $2 - x, 1 - y, 2 - z$ ; (c)  $x, \frac{1}{2} - y, \frac{1}{2} + z$ .

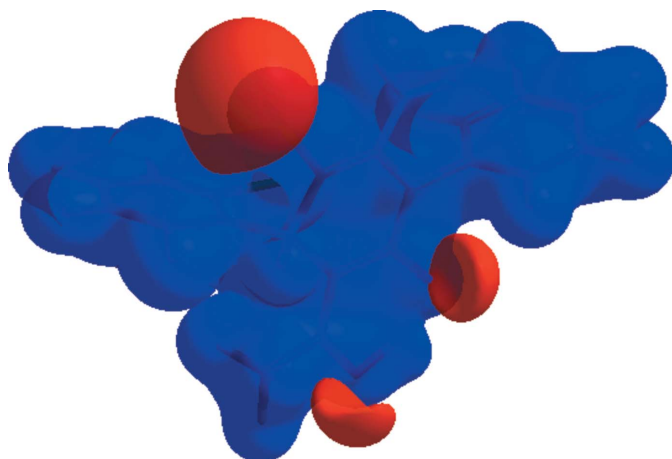


**Figure 3**  
A view down the *a* axis of the crystal packing of the title compound based on the intermolecular interactions shown in Fig. 2.



**Figure 4**  
Hirshfeld surface of the title compound mapped with  $d_{\text{norm}}$ .

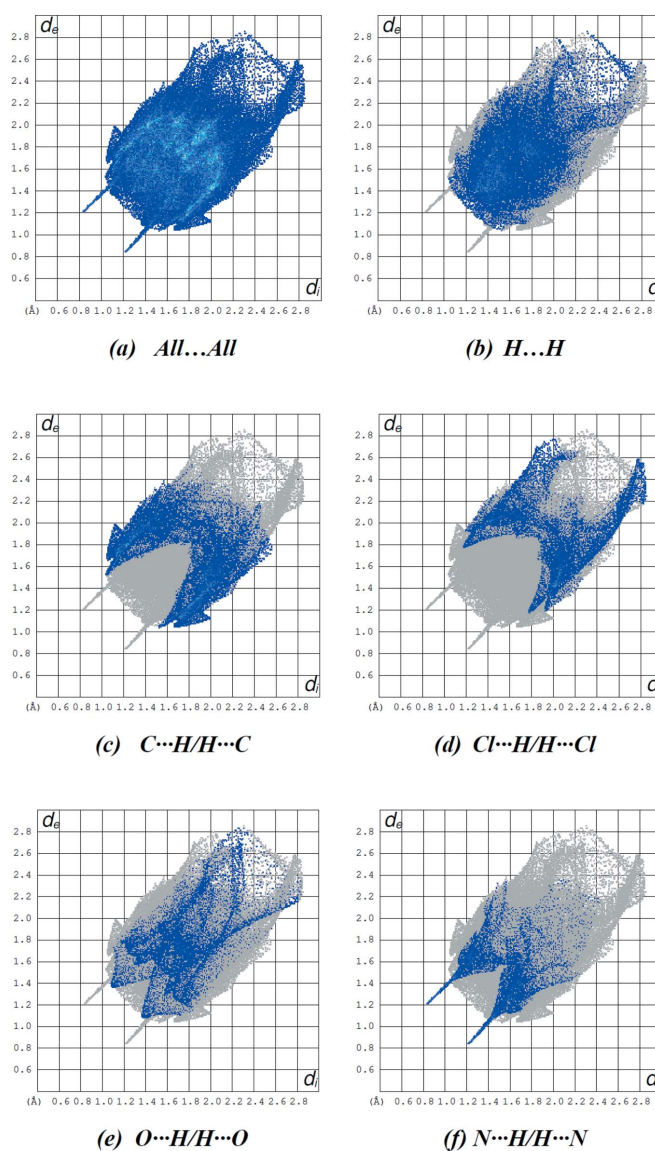
The Hirshfeld surfaces were calculated and the two-dimensional fingerprint plots generated using *Crystal Explorer 17.5* (Turner *et al.*, 2017). The use of various hues and intensities to represent short and long contacts, as well as the relative intensity of the connections, allows Hirshfeld surfaces to depict intermolecular interactions. Fig. 4 shows the three-dimensional Hirshfeld surfaces of the title compound plotted over  $d_{\text{norm}}$  (normalized contact distance) in the range of  $-0.4290$  to  $1.5192$  a.u. The red patches that appear around N2 are caused by the intermolecular N3—H3A $\cdots$ N2 and C16—H16 $\cdots$ N2 interactions, which are important in the packing of the title molecule. Bright red dots near N2 and amine hydrogen atoms H3A and H3B highlight their functions as hydrogen-bonding acceptors and donors, respectively; these also appear as blue and red areas on the Hirshfeld surface mapped over electrostatic potential (Spackman *et al.*, 2008) in Fig. 5, corresponding to positive and negative potentials. Positive electrostatic potential (hydrogen-bond donors) is



**Figure 5**  
View of the three-dimensional Hirshfeld surface of the title compound plotted over electrostatic potential 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, respectively, around the atoms, corresponding to positive and negative potentials.

shown in blue, whereas negative electrostatic potential is indicated in red (hydrogen-bond acceptors).

In Fig. 6, the overall two-dimensional fingerprint plot for the title compound and those delineated into H $\cdots$ H, C $\cdots$ H/H $\cdots$ C, Cl $\cdots$ H/H $\cdots$ Cl, O $\cdots$ H/H $\cdots$ O and N $\cdots$ H/H $\cdots$ N contacts, as well as their relative contributions to the Hirshfeld surface, are presented, while details of the various contacts are given in Table 2. The percentage contributions to the Hirshfeld surfaces from the various interatomic contacts are as follows: H $\cdots$ H (33.1%; Fig. 6*b*), C $\cdots$ H/H $\cdots$ C (22.5%; Fig. 6*c*), Cl $\cdots$ H/H $\cdots$ Cl (14.1%; Fig. 6*d*), O $\cdots$ H/H $\cdots$ O (11.9%; Fig. 6*e*) and N $\cdots$ H/H $\cdots$ N (9.7%; Fig. 6*f*). Other Cl $\cdots$ C/C $\cdots$ Cl, C $\cdots$ C, Cl $\cdots$ O/O $\cdots$ Cl, Cl $\cdots$ N/N $\cdots$ Cl, N $\cdots$ C/C $\cdots$ N, O $\cdots$ N/N $\cdots$ O,



**Figure 6**  
The two-dimensional fingerprint plots of the title compound, showing (a) all interactions, and delineated into (b) H $\cdots$ H, (c) C $\cdots$ H/H $\cdots$ C, (d) Cl $\cdots$ H/H $\cdots$ Cl, (e) O $\cdots$ H/H $\cdots$ O and (f) N $\cdots$ H/H $\cdots$ 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].

**Table 3**

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

Contact	Percentage contribution
H...H	33.1
C...H/H...C	22.5
Cl...H/H...Cl	14.1
O...H/H...O	11.9
N...H/H...N	9.7
Cl...C/C...Cl	2.1
C...C	1.4
Cl...O/O...Cl	1.2
Cl...N/N...Cl	1.1
N...C/C...N	1.0
O...N/N...O	0.6
Cl...Cl	0.6
O...C/C...O	0.5
N...N	0.1

Cl...Cl, O...C/C...O and N...N contacts contribute less than 2.1% to Hirshfeld surface mapping and have little directional influence on molecular packing (Table 3).

#### 4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.39, update of August 2018; Groom *et al.*, 2016) using *Conquest* (Bruno *et al.*, 2002) for the tetrahydropyridine unit revealed 1339 hits. Some interesting structures related to the title compound based on their tetrahydropyridine moieties include: ethyl 4-hydroxy-2,6-diphenyl-5-(phenylsulfanyl)pyridine-3-carboxylate (refcode SETWOE: Suresh *et al.*, 2007), ethyl 2,6-bis(4-fluorophenyl)-4-hydroxy-5-(4-methylphenylsulfanyl)pyridine-3-carboxylate (SETWUK: Suresh *et al.*, 2007), 2,6-diamino-4-chloropyrimidin-1-ium 2-carboxy-3-nitrobenzoate (JEBRAM: Mohana *et al.*, 2017) and 2,6-diamino-4-chloropyrimidin-1-ium 4-methylbenzene-1-sulfonate monohydrate (JEBREQ: Mohana *et al.*, 2017).

The polysubstituted pyridines, SETWOE (space group:  $P2_1/c$ ) and SETWUK (space group:  $P2_1/n$ ), adopt nearly planar structures. The crystal structure of SETWOE is stabilized by intermolecular C—H...O and C—H... $\pi$  interactions. The C—H...O hydrogen bonds generate rings with  $R_2^2(14)$  and  $R_2^2(20)$  motifs. The crystal structure of SETWUK is stabilized by intermolecular C—H...F and C—H... $\pi$  interactions. The C—H...F bond generates a linear chain with a  $C(14)$  motif. In addition, in SETWOE and SETWUK, intramolecular O—H...O interactions are found, which generate an  $S(6)$  graph-set motif. No significant aryl–aryl or  $\pi$ – $\pi$  interactions exist in these structures. All this bears some resemblance to the title compound.

In both the related salts, JEBRAM (space group:  $P\bar{1}$ ) and JEBREQ (space group:  $P\bar{1}$ ), the N atom in the 1-position of the pyrimidine ring is protonated. In JEBRAM, the protonated N atom and the amino group of the pyrimidinium cation interact with the carboxylate group of the anion through N—H...O hydrogen bonds, forming a heterosynthon with an  $R_2^2(8)$  ring motif. In the hydrated salt JEBREQ, the presence of the water molecule prevents the formation of the familiar

**Table 4**

Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{15}Cl_2N_3O_2$
$M_r$	400.25
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
$a, b, c$ (Å)	9.662 (1), 27.010 (3), 7.4782 (8)
$\beta$ (°)	111.571 (2)
$V$ (Å <sup>3</sup> )	1814.9 (3)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.38
Crystal size (mm)	0.24 × 0.21 × 0.02
Data collection	
Diffractometer	Bruker D8 QUEST PHOTON-III CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
$T_{min}, T_{max}$	0.864, 0.986
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	27440, 4180, 2631
$R_{int}$	0.099
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.053, 0.126, 1.01
No. of reflections	4180
No. of parameters	255
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.50, -0.37

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

$R_2^2(8)$  ring motif. Instead, an expanded ring [*i.e.*  $R_2^3(8)$ ] is formed involving the sulfonate group, the pyrimidinium cation and the water molecule. Both salts form a supramolecular homosynthon [ $R_2^2(8)$  ring motif] through N—H...N hydrogen bonds. The molecular structures are further stabilized by  $\pi$ – $\pi$  stacking, and C=O... $\pi$ , C—H...O and C—H...Cl interactions. None of these are found in the crystal packing of the title compound. It appears that the protonation state of the pyrimidine ring influences the intermolecular interactions within the crystal lattices to a substantial extent.

#### 5. Synthesis and crystallization

The title compound was synthesized using our previously reported procedure (Maharramov *et al.*, 2018), and colorless prisms were obtained upon recrystallization from its methanol solution.

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The positional parameters of the H atoms of the hydroxy and amine groups were determined from difference electron-density maps and were refined freely [ $O2-H2 = 0.86$  (4) Å,  $N3-H3A = 0.86$  (4) Å and  $N3-H3B = 0.88$  (4) Å]. Their isotropic displacement parameters were



refined using a riding model with  $U_{\text{iso}}(\text{H})$  set to either  $1.2U_{\text{eq}}(\text{N})$  for the  $\text{NH}_2$  group or  $1.5U_{\text{eq}}(\text{O})$  for the OH group. The C-bound H atoms were positioned geometrically ( $\text{C}-\text{H} = 0.95\text{--}1.00 \text{ \AA}$ ) and allowed to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for the methyl group and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for aromatic and methine H atoms.

### Acknowledgements

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

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### References

- Abdel-Hafiz, I. S., Ramiz, M. M. M. & Elian, M. A. (2012). *J. Chem. Sci.* **124**, 647–655.
- Adams, A. & De Kimpe, N. (2006). *Chem. Rev.* **106**, 2299–2319.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bruker (2013). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2018). *APEX3*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* **B58**, 389–397.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Gurbanov, A. V., Mahmoudi, G., Guedes da Silva, M. F. C., Zubkov, F. I., Mahmudov, K. T. & Pombeiro, A. J. L. (2018). *Inorg. Chim. Acta*, **471**, 130–136.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
- Maharramov, A. M., Naghiyev, F. N., Asgerova, A. R., Guseynov, E. Z. & Mamedov, I. G. (2018). *Azerbaijan Chem. J.* **4**, 33–38.
- Mahmoudi, G., Khandar, A. A., Afkhami, F. A., Miroslaw, B., Gurbanov, A. V., Zubkov, F. I., Kennedy, A., Franconetti, A. & Frontera, A. (2019). *CrystEngComm*, **21**, 108–117.
- Mamedov, I., Naghiyev, F., Maharramov, A., Uwangue, O., Farewell, A., Sunnerhagen, P. & Erdelyi, M. (2020). *Mendeleev Commun.* **30**, 498–499.
- Mohana, M., Thomas Muthiah, P. & Butcher, R. J. (2017). *Acta Cryst.* **C73**, 536–540.
- Mohsin, N. & Ahmad, M. (2018). *Turk. J. Chem.* **42**, 1191–1216.
- Naghiyev, F. N., Cisterna, J., Khalilov, A. N., Maharramov, A. M., Askerov, R. K., Asadov, K. A., Mamedov, I. G., Salmanli, K. S., Cárdenas, A. & Brito, I. (2020). *Molecules*, **25**, 2235–2248.
- Naghiyev, F. N., Grishina, M. M., Khrustalev, V. N., Khalilov, A. N., Akkurt, M., Akobirshoeva, A. A. & Mamedov, I. G. (2021a). *Acta Cryst.* **E77**, 195–199.
- Naghiyev, F. N., Maharramov, A. M., Asadov, K. A. & Mamedov, I. G. (2019). *Russ. J. Org. Chem.* **55**, 388–391.
- Naghiyev, F. N., Tereshina, T. A., Khrustalev, V. N., Akkurt, M., Khalilov, A. N., Akobirshoeva, A. A. & Mamedov, I. G. (2021b). *Acta Cryst.* **E77**, 512–515.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Spackman, M. A., McKinnon, J. J. & Jayatilaka, D. (2008). *CrystEngComm*, **10**, 377–388.
- Spek, A. L. (2020). *Acta Cryst.* **E76**, 1–11.
- Suresh, J., Suresh Kumar, R., Perumal, S., Mostad, A. & Natarajan, S. (2007). *Acta Cryst.* **C63**, o141–o144.
- Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. University of Western Australia. <http://hirshfeldsurface.net>.
- Zubkov, F. I., Mertsalov, D. F., Zaytsev, V. P., Varlamov, A. V., Gurbanov, A. V., Dorovatovskii, P. V., Timofeeva, T. V., Khrustalev, V. N. & Mahmudov, K. T. (2018). *J. Mol. Liq.* **249**, 949–952.

## supporting information

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## Crystal structure and Hirshfeld surface analysis of (Z)-2-amino-4-(2,6-dichlorophenyl)-5-(1-hydroxyethylidene)-6-oxo-1-phenyl-1,4,5,6-tetrahydropyridine-3-carbonitrile

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### 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).

### (Z)-2-Amino-4-(2,6-dichlorophenyl)-5-(1-hydroxyethylidene)-6-oxo-1-phenyl-1,4,5,6-tetrahydropyridine-3-carbonitrile

#### Crystal data

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 $M_r = 400.25$   
 Monoclinic,  $P2_1/c$   
 $a = 9.662$  (1) Å  
 $b = 27.010$  (3) Å  
 $c = 7.4782$  (8) Å  
 $\beta = 111.571$  (2)°  
 $V = 1814.9$  (3) Å<sup>3</sup>  
 $Z = 4$

$F(000) = 824$   
 $D_x = 1.465$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 2887 reflections  
 $\theta = 2.3$ – $25.6$ °  
 $\mu = 0.38$  mm<sup>-1</sup>  
 $T = 100$  K  
 Plate, colourless  
 $0.24 \times 0.21 \times 0.02$  mm

#### Data collection

Bruker D8 QUEST PHOTON-III CCD  
 diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Krause *et al.*, 2015)  
 $T_{\min} = 0.864$ ,  $T_{\max} = 0.986$   
 27440 measured reflections

4180 independent reflections  
 2631 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.099$   
 $\theta_{\max} = 27.5$ °,  $\theta_{\min} = 2.3$ °  
 $h = -12 \rightarrow 12$   
 $k = -35 \rightarrow 35$   
 $l = -9 \rightarrow 9$

#### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.053$   
 $wR(F^2) = 0.126$   
 $S = 1.01$   
 4180 reflections

255 parameters  
 0 restraints  
 Primary atom site location: dual  
 Secondary atom site location: dual  
 Hydrogen site location: mixed

H atoms treated by a mixture of independent

and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 2.0157P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.50 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL,

$$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.0024 (2)

*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 ( $\text{\AA}^2$ )*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.86090 (9)	0.51416 (3)	0.60657 (12)	0.0256 (2)
Cl2	0.73128 (9)	0.32459 (3)	0.75788 (12)	0.0262 (2)
O1	0.3936 (2)	0.32320 (9)	0.2910 (3)	0.0280 (5)
O2	0.5668 (3)	0.34472 (9)	0.1210 (3)	0.0286 (6)
H2	0.502 (4)	0.3295 (15)	0.155 (6)	0.043*
N1	0.3832 (3)	0.36887 (10)	0.5389 (4)	0.0190 (6)
N2	0.6028 (3)	0.51570 (10)	0.8819 (4)	0.0213 (6)
N3	0.3468 (3)	0.41829 (11)	0.7719 (4)	0.0216 (6)
H3A	0.376 (4)	0.4411 (13)	0.857 (5)	0.026*
H3B	0.275 (4)	0.3976 (13)	0.763 (5)	0.026*
C1	0.6193 (3)	0.38087 (12)	0.2516 (4)	0.0222 (7)
C2	0.4484 (3)	0.35814 (12)	0.4048 (4)	0.0215 (7)
C3	0.5700 (3)	0.38792 (12)	0.3994 (4)	0.0190 (7)
C4	0.6393 (3)	0.42841 (12)	0.5454 (4)	0.0185 (7)
H4	0.6402	0.4592	0.4717	0.022*
C5	0.5438 (3)	0.43903 (11)	0.6633 (4)	0.0178 (6)
C6	0.4288 (3)	0.40975 (12)	0.6622 (4)	0.0190 (6)
C7	0.2636 (3)	0.33754 (11)	0.5457 (4)	0.0182 (6)
C8	0.2954 (3)	0.29874 (12)	0.6757 (4)	0.0225 (7)
H8	0.3954	0.2923	0.7572	0.027*
C9	0.1808 (4)	0.26931 (12)	0.6866 (5)	0.0247 (7)
H9	0.2018	0.2428	0.7762	0.030*
C10	0.0355 (4)	0.27893 (12)	0.5655 (5)	0.0254 (7)
H10	-0.0431	0.2588	0.5722	0.030*
C11	0.0039 (3)	0.31762 (12)	0.4351 (5)	0.0233 (7)
H11	-0.0959	0.3239	0.3526	0.028*
C12	0.1182 (3)	0.34720 (12)	0.4251 (4)	0.0219 (7)
H12	0.0970	0.3739	0.3362	0.026*
C13	0.7339 (4)	0.41270 (13)	0.2175 (5)	0.0262 (7)
H13A	0.7588	0.3988	0.1121	0.039*
H13B	0.8235	0.4139	0.3346	0.039*
H13C	0.6943	0.4462	0.1834	0.039*
C14	0.8003 (3)	0.41904 (12)	0.6829 (4)	0.0168 (6)
C15	0.9070 (3)	0.45717 (12)	0.7254 (4)	0.0206 (7)

C16	1.0502 (3)	0.45270 (13)	0.8591 (5)	0.0237 (7)
H16	1.1177	0.4797	0.8851	0.028*
C17	1.0934 (3)	0.40785 (13)	0.9546 (4)	0.0252 (7)
H17	1.1915	0.4041	1.0469	0.030*
C18	0.9949 (3)	0.36865 (13)	0.9164 (5)	0.0238 (7)
H18	1.0255	0.3378	0.9793	0.029*
C19	0.8510 (3)	0.37491 (12)	0.7852 (4)	0.0194 (7)
C20	0.5773 (3)	0.48144 (12)	0.7841 (4)	0.0190 (7)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.0223 (4)	0.0243 (4)	0.0291 (4)	−0.0013 (3)	0.0083 (3)	0.0025 (4)
C12	0.0236 (4)	0.0258 (4)	0.0260 (4)	−0.0006 (3)	0.0056 (3)	0.0049 (4)
O1	0.0271 (12)	0.0342 (14)	0.0240 (12)	−0.0085 (11)	0.0108 (10)	−0.0124 (11)
O2	0.0296 (13)	0.0394 (15)	0.0171 (12)	−0.0043 (11)	0.0091 (10)	−0.0072 (11)
N1	0.0169 (13)	0.0243 (15)	0.0161 (13)	−0.0028 (11)	0.0063 (10)	−0.0035 (11)
N2	0.0213 (14)	0.0210 (14)	0.0200 (14)	−0.0026 (11)	0.0058 (11)	−0.0030 (12)
N3	0.0199 (14)	0.0270 (15)	0.0196 (14)	−0.0071 (12)	0.0095 (11)	−0.0081 (12)
C1	0.0210 (16)	0.0286 (18)	0.0135 (15)	0.0038 (13)	0.0022 (12)	−0.0012 (14)
C2	0.0200 (15)	0.0275 (18)	0.0160 (15)	0.0009 (13)	0.0053 (12)	−0.0023 (14)
C3	0.0174 (15)	0.0225 (17)	0.0152 (15)	−0.0002 (12)	0.0038 (12)	−0.0001 (13)
C4	0.0157 (15)	0.0228 (17)	0.0166 (15)	0.0014 (12)	0.0055 (12)	−0.0020 (13)
C5	0.0172 (15)	0.0207 (16)	0.0139 (15)	0.0005 (12)	0.0037 (12)	−0.0014 (13)
C6	0.0162 (14)	0.0237 (17)	0.0135 (15)	0.0036 (12)	0.0012 (12)	−0.0002 (13)
C7	0.0175 (15)	0.0185 (16)	0.0184 (15)	−0.0037 (12)	0.0062 (12)	−0.0048 (13)
C8	0.0201 (16)	0.0264 (18)	0.0174 (16)	0.0015 (13)	0.0026 (13)	−0.0003 (14)
C9	0.0275 (17)	0.0219 (17)	0.0254 (18)	0.0030 (14)	0.0106 (14)	0.0049 (14)
C10	0.0228 (16)	0.0245 (18)	0.0310 (19)	−0.0028 (14)	0.0124 (14)	−0.0042 (15)
C11	0.0177 (15)	0.0259 (18)	0.0223 (17)	0.0019 (13)	0.0024 (13)	0.0013 (14)
C12	0.0230 (16)	0.0224 (17)	0.0177 (16)	0.0031 (13)	0.0044 (13)	0.0001 (13)
C13	0.0264 (17)	0.033 (2)	0.0206 (17)	0.0037 (15)	0.0107 (14)	0.0041 (15)
C14	0.0152 (14)	0.0241 (16)	0.0126 (14)	0.0025 (12)	0.0070 (11)	−0.0011 (12)
C15	0.0200 (15)	0.0254 (17)	0.0179 (16)	0.0040 (13)	0.0088 (13)	0.0024 (14)
C16	0.0185 (15)	0.0315 (19)	0.0222 (17)	−0.0020 (13)	0.0089 (13)	−0.0035 (14)
C17	0.0162 (15)	0.042 (2)	0.0173 (16)	0.0027 (14)	0.0063 (13)	−0.0010 (15)
C18	0.0219 (16)	0.0307 (19)	0.0196 (16)	0.0047 (14)	0.0087 (13)	0.0047 (14)
C19	0.0174 (15)	0.0266 (17)	0.0150 (15)	−0.0009 (13)	0.0066 (12)	−0.0022 (13)
C20	0.0110 (14)	0.0270 (18)	0.0193 (16)	0.0044 (12)	0.0058 (12)	0.0062 (14)

*Geometric parameters (Å, °)*

C11—C15	1.751 (3)	C7—C12	1.387 (4)
C12—C19	1.747 (3)	C8—C9	1.390 (4)
O1—C2	1.250 (4)	C8—H8	0.9500
O2—C1	1.342 (4)	C9—C10	1.387 (4)
O2—H2	0.86 (4)	C9—H9	0.9500
N1—C2	1.397 (4)	C10—C11	1.385 (5)



N1—C6	1.401 (4)	C10—H10	0.9500
N1—C7	1.448 (4)	C11—C12	1.387 (4)
N2—C20	1.149 (4)	C11—H11	0.9500
N3—C6	1.354 (4)	C12—H12	0.9500
N3—H3A	0.86 (4)	C13—H13A	0.9800
N3—H3B	0.88 (4)	C13—H13B	0.9800
C1—C3	1.368 (4)	C13—H13C	0.9800
C1—C13	1.496 (4)	C14—C19	1.404 (4)
C2—C3	1.437 (4)	C14—C15	1.408 (4)
C3—C4	1.516 (4)	C15—C16	1.382 (4)
C4—C5	1.519 (4)	C16—C17	1.390 (5)
C4—C14	1.538 (4)	C16—H16	0.9500
C4—H4	1.0000	C17—C18	1.382 (5)
C5—C6	1.361 (4)	C17—H17	0.9500
C5—C20	1.421 (4)	C18—C19	1.386 (4)
C7—C8	1.385 (4)	C18—H18	0.9500
C1—O2—H2	105 (3)	C8—C9—H9	120.3
C2—N1—C6	121.3 (3)	C11—C10—C9	120.6 (3)
C2—N1—C7	118.7 (2)	C11—C10—H10	119.7
C6—N1—C7	120.0 (2)	C9—C10—H10	119.7
C6—N3—H3A	118 (2)	C10—C11—C12	120.0 (3)
C6—N3—H3B	118 (2)	C10—C11—H11	120.0
H3A—N3—H3B	123 (3)	C12—C11—H11	120.0
O2—C1—C3	122.6 (3)	C11—C12—C7	119.5 (3)
O2—C1—C13	113.5 (3)	C11—C12—H12	120.2
C3—C1—C13	123.8 (3)	C7—C12—H12	120.2
O1—C2—N1	117.1 (3)	C1—C13—H13A	109.5
O1—C2—C3	123.3 (3)	C1—C13—H13B	109.5
N1—C2—C3	119.6 (3)	H13A—C13—H13B	109.5
C1—C3—C2	118.4 (3)	C1—C13—H13C	109.5
C1—C3—C4	119.4 (3)	H13A—C13—H13C	109.5
C2—C3—C4	122.1 (3)	H13B—C13—H13C	109.5
C3—C4—C5	110.7 (2)	C19—C14—C15	114.7 (3)
C3—C4—C14	115.6 (2)	C19—C14—C4	124.6 (3)
C5—C4—C14	108.9 (2)	C15—C14—C4	120.5 (3)
C3—C4—H4	107.1	C16—C15—C14	123.7 (3)
C5—C4—H4	107.1	C16—C15—C11	116.4 (3)
C14—C4—H4	107.1	C14—C15—C11	120.0 (2)
C6—C5—C20	117.8 (3)	C15—C16—C17	118.7 (3)
C6—C5—C4	123.7 (3)	C15—C16—H16	120.7
C20—C5—C4	118.4 (3)	C17—C16—H16	120.7
N3—C6—C5	123.7 (3)	C18—C17—C16	120.5 (3)
N3—C6—N1	114.8 (3)	C18—C17—H17	119.8
C5—C6—N1	121.4 (3)	C16—C17—H17	119.8
C8—C7—C12	120.6 (3)	C17—C18—C19	119.2 (3)
C8—C7—N1	119.5 (3)	C17—C18—H18	120.4
C12—C7—N1	119.9 (3)	C19—C18—H18	120.4

C7—C8—C9	119.9 (3)	C18—C19—C14	123.2 (3)
C7—C8—H8	120.1	C18—C19—C12	115.9 (3)
C9—C8—H8	120.1	C14—C19—C12	120.9 (2)
C10—C9—C8	119.5 (3)	N2—C20—C5	179.2 (3)
C10—C9—H9	120.3		
C6—N1—C2—O1	-174.8 (3)	C6—N1—C7—C8	-86.5 (4)
C7—N1—C2—O1	3.5 (4)	C2—N1—C7—C12	-86.2 (4)
C6—N1—C2—C3	3.4 (4)	C6—N1—C7—C12	92.2 (3)
C7—N1—C2—C3	-178.2 (3)	C12—C7—C8—C9	-0.4 (5)
O2—C1—C3—C2	-5.5 (5)	N1—C7—C8—C9	178.3 (3)
C13—C1—C3—C2	173.5 (3)	C7—C8—C9—C10	0.5 (5)
O2—C1—C3—C4	177.7 (3)	C8—C9—C10—C11	-0.3 (5)
C13—C1—C3—C4	-3.3 (5)	C9—C10—C11—C12	-0.1 (5)
O1—C2—C3—C1	6.4 (5)	C10—C11—C12—C7	0.3 (5)
N1—C2—C3—C1	-171.7 (3)	C8—C7—C12—C11	0.0 (5)
O1—C2—C3—C4	-176.9 (3)	N1—C7—C12—C11	-178.7 (3)
N1—C2—C3—C4	5.0 (4)	C3—C4—C14—C19	-48.4 (4)
C1—C3—C4—C5	165.1 (3)	C5—C4—C14—C19	76.9 (4)
C2—C3—C4—C5	-11.6 (4)	C3—C4—C14—C15	136.5 (3)
C1—C3—C4—C14	-70.5 (4)	C5—C4—C14—C15	-98.2 (3)
C2—C3—C4—C14	112.8 (3)	C19—C14—C15—C16	-1.0 (4)
C3—C4—C5—C6	11.6 (4)	C4—C14—C15—C16	174.6 (3)
C14—C4—C5—C6	-116.5 (3)	C19—C14—C15—C11	179.1 (2)
C3—C4—C5—C20	-169.4 (3)	C4—C14—C15—C11	-5.3 (4)
C14—C4—C5—C20	62.5 (4)	C14—C15—C16—C17	1.4 (5)
C20—C5—C6—N3	-1.3 (5)	C11—C15—C16—C17	-178.7 (2)
C4—C5—C6—N3	177.7 (3)	C15—C16—C17—C18	0.0 (5)
C20—C5—C6—N1	176.3 (3)	C16—C17—C18—C19	-1.7 (5)
C4—C5—C6—N1	-4.7 (5)	C17—C18—C19—C14	2.2 (5)
C2—N1—C6—N3	174.1 (3)	C17—C18—C19—C12	-176.1 (2)
C7—N1—C6—N3	-4.2 (4)	C15—C14—C19—C18	-0.8 (4)
C2—N1—C6—C5	-3.6 (4)	C4—C14—C19—C18	-176.2 (3)
C7—N1—C6—C5	178.0 (3)	C15—C14—C19—C12	177.3 (2)
C2—N1—C7—C8	95.1 (3)	C4—C14—C19—C12	1.9 (4)

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

$Cg2$  is the centroid of the C7–C12 phenyl ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 $\cdots$ O1	0.86 (4)	1.72 (4)	2.514 (3)	153 (4)
N3—H3A $\cdots$ N2 <sup>i</sup>	0.86 (4)	2.22 (4)	3.032 (4)	159 (3)
C16—H16 $\cdots$ N2 <sup>ii</sup>	0.95	2.62	3.308 (4)	129
N3—H3B $\cdots$ $Cg2$	0.88 (4)	2.88 (4)	3.581 (3)	138 (3)
C9—H9 $\cdots$ $Cg2$ <sup>iii</sup>	0.95	2.70	3.564 (4)	151

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