



# Unusual formation of (*E*)-11-(aminomethylene)-8,9,10,11-tetrahydropyrido[2',3':4,5]pyrimido-[1,2-*a*]azepin-5(7*H*)-one and its crystal structure

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Received 29 August 2017

Accepted 13 September 2017

Edited by D.-J. Xu, Zhejiang University (Yuquan Campus), China

**Keywords:** fused pyrimidines; formylation; Vilsmeier–Haack reagent; X-ray structure analysis; crystal structure.

**CCDC reference:** 1530092

**Supporting information:** this article has supporting information at [journals.iucr.org/e](https://journals.iucr.org/e)

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Selective C-formylation of 8,9,10,11-tetrahydropyrido[2',3':4,5]pyrimido[1,2-*a*]azepin-5(7*H*)-one has been studied for the first time. It was revealed that formylation proceeds by the formation of an intermediate salt, which due to the re-amination process on treatment with aqueous ammonia transformed into the corresponding (*E*)-11-(aminomethylene)-8,9,10,11-tetrahydropyrido[2',3':4,5]pyrimido[1,2-*a*]azepin-5(7*H*)-one, C<sub>13</sub>H<sub>14</sub>N<sub>4</sub>O, as an *E*-isomer. Formylation was carried out by Vilsmeier–Haack reagent and the structure of the synthesized compound was confirmed by X-ray structural analysis, spectroscopic and LC–MS methods. In the molecule, the seven-membered pentamethylene ring adopts a twist-boat conformation.

## 1. Chemical context

Pyrimidine-containing heterocyclic compounds are widely distributed in nature (Lagoja, 2005) and among synthetic compounds (Joshi *et al.*, 2016; Roopan & Sompalle, 2016). These compounds are of theoretical and practical interest, having plural reactivity and with many prospective biologically active compounds among the synthesized derivatives.

In previous reports we have described several syntheses, *viz.* the reaction of 2,3-trimethylenepyrido[2,3-*d*]pyrimidin-4-one with aromatic aldehydes (Khodjaniyazov, 2015*a,b*; Khodjaniyazov & Ashurov, 2016), selective reduction with sodium borohydride (Khodjaniyazov *et al.*, 2016*b*), and the formation of (*E*)-9-(*N,N*-dimethylaminomethylidene)-8,9-dihydropyrido[2,3-*d*]pyrrolo[1,2-*a*]pyrimidin-5(7*H*)-one (Khodjaniyazov *et al.*, 2016*a*). In this current report we present the results of reaction of 8,9,10,11-tetrahydropyrido[2',3':4,5]pyrimido[1,2-*a*]azepin-5(7*H*)-one (**1**) with the Vilsmeier–Haack reagent, decomposition by water and subsequent treatment with aqueous ammonia. We carried out the interaction of **1** with a formylating agent and, at the end of the reaction, the unusual final product (*E*)-11-(aminomethylene)-8,9,10,11-tetrahydropyrido[2',3':4,5]pyrimido-[1,2-*a*]azepin-5(7*H*)-one (**3**) was isolated after treatment (re-amination) of 11-dimethylaminomethylidene derivative (**2**) with aqueous ammonia. The reaction proceeds as shown in Fig. 1. The

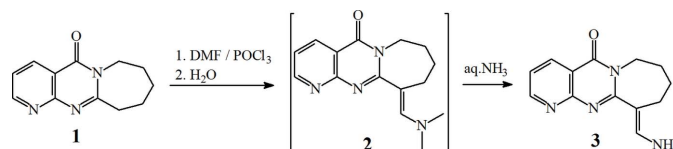
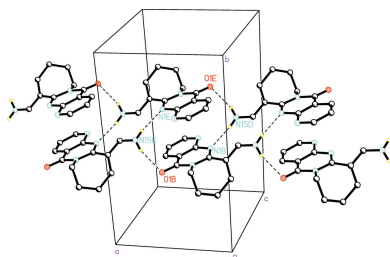
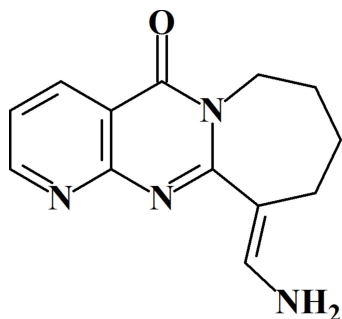


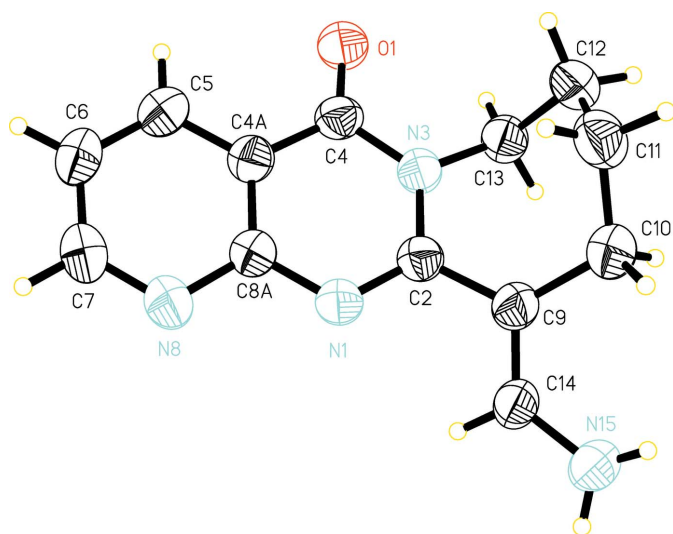
Figure 1  
Reaction scheme.

reaction product was different from that obtained in the case of formylation of 2,3-trimethylenepyrido[2,3-*d*]pyrimidin-4-one [pyrido[2,3-*d*]pyrrolo[1,2-*a*]pyrimidin-5(7*H*)-one; Khodjaniyazov *et al.*, 2016*a*]. This fact was explained by re-amination of the initially formed dimethylaminomethylidene derivative **2** under action of aqueous ammonia to give (*E*)-11-(aminomethylene)-8,9,10,11-tetrahydropyrido[2',3':4,5]-pyrimido[1,2-*a*]azepin-5(7*H*)-one (**3**) as the final product



## 2. Structural commentary

The title compound crystallizes in the centrosymmetric monoclinic  $P2_1/c$  (No. 14) space group. The asymmetric unit contains one crystallographically independent molecule. A displacement ellipsoid plot showing the atom-numbering scheme is presented in Fig. 2. In the molecule, the seven-membered pentamethylene ring exhibits a twist-boat conformation and has an approximate twofold symmetry with a  $C_2$  axis passing through atom C12 and midpoint of the C2—C9 bond. The amino group is *E*-oriented and hybridization of the N atom in this group lies between  $sp^3$  and  $sp^2$ . The C—N bond makes an angle of  $155^\circ$  with the bisector of the H—N—H angle. The equivalent angle in methylamine with a pyramidal  $sp^3$ -hybridized N atom is  $\sim 123^\circ$  (Klingebiel *et al.*, 2002) and it



**Figure 2**  
The molecular structure of compound **3**, with the atom labelling and 50% probability displacement ellipsoids.

**Table 1**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N15-H1\cdots O1^i$	0.85 (3)	2.21 (3)	3.017 (3)	159 (3)
$N15-H2\cdots N1^{ii}$	0.85 (5)	2.31 (5)	3.146 (3)	168 (4)
$N15-H2\cdots N8^{ii}$	0.85 (5)	2.79 (5)	3.401 (4)	131 (4)

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

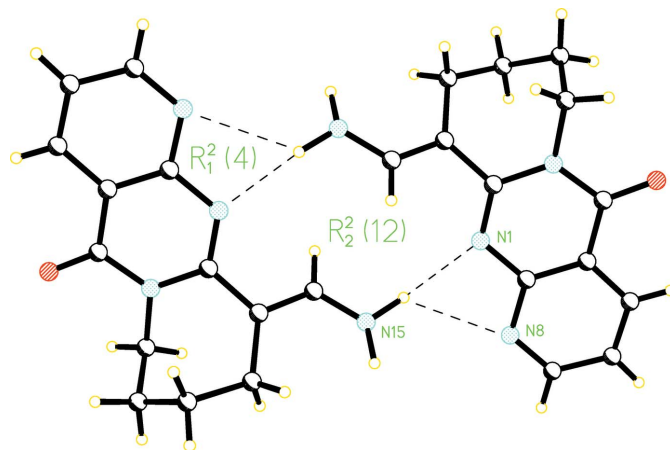
is nearly  $180^\circ$  in formamide with a planar  $sp^2$ -hybridized N atom (Gajda & Katrusiak, 2011). The pyrimidine ring is twisted slightly, which may be because of the influence of the twisted seven-membered azepane ring. The N1—C8A—N4A—C4 torsion angle of is  $8.7 (4)^\circ$ .

## 3. Supramolecular features

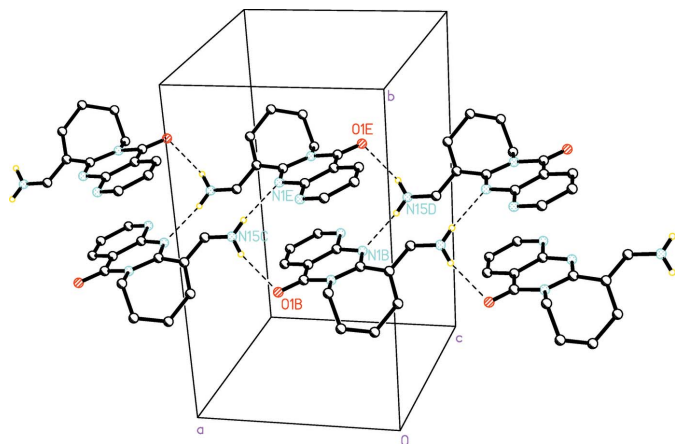
In the crystal, hydrogen bonds with 16 ring and three chain motifs are generated by  $N-H\cdots N$  and  $N-H\cdots O$  contacts (Table 1). The amino group is located close to the nitrogen atoms N1 and N8 of an inversion-related molecule, forming hydrogen bonds with  $R_1^2(4)$  and  $R_2^2(12)$  graph-set motifs (Fig. 3). This amino group also forms a hydrogen bond with the C=O oxygen atom of a molecule translated along the *a* axis, which links the molecules into  $R_4^4(16)$  rings. Hydrogen-bonded chains are formed along [100] by alternating  $R_2^2(12)$  and  $R_4^4(16)$  rings (Fig. 4). These chains are stabilized by intermolecular  $\pi$ - $\pi$ -stacking interactions observed between the pyridine and pyrimidine rings [centroid-centroid distance =  $3.669 (2) \text{ \AA}$ ; symmetry operation  $1-x, 1-y, 1-z$ ].

## 4. Database survey

A search of the Cambridge Structural Database (Version 5.38, last update November 2016; Groom *et al.*, 2016) for the 4-azaquinazoline moiety gave eight hits. Only one of these is a related structure, a tricyclic 4-azaquinazolin-4-one with a



**Figure 3**  
Hydrogen bonding in the title compound showing the  $R_1^2(4)$  and  $R_2^2(12)$  graph-set motifs.



**Figure 4**  
Hydrogen-bonded chain formation in **3**.

substituent on the third ring (VAMBET; Khodjaniyazov & Ashurov, 2016).

## 5. Synthesis and crystallization

**Materials and methods.** The results of electro spray ionization mass spectrometry (ESI-MS) were recorded using a 6420 TripleQuadLC/MC (Agilent Technologies, US) LC-MS spectrometer. The measurements were carried out in positive-ion mode.  $^1\text{H}$  NMR spectra were recorded in  $\text{CD}_3\text{OD}$  on a Varian 400-MR spectrometer operating accordingly at 400 MHz. Hexamethyldisiloxane (HMDSO) was used as internal standard and the chemical shift of  $^1\text{H}$  was recorded in ppm. Melting points were measured on a Boetius and MEL-TEMP apparatus manufactured by Branstead international (USA) and are uncorrected. IR spectra were recorded on an IR Fourier System 2000 (Perkin-Elmer) as KBr pellets.

The reaction process was monitored by TLC on Silufol UV-254 plates using a  $\text{CHCl}_3/\text{CH}_3\text{OH}$  (12:1) solvent system and the developed plates were visualized under a UV lamp. Solvents were purified by standard procedures. Organic solutions were dried over anhydrous  $\text{Na}_2\text{SO}_4$  or with dried  $\text{CaCl}_2$ .

**Synthesis of (E)-11-(aminomethylene)-8,9,10,11-tetrahydropyrido[2',3':4,5]-pyrimido[1,2-a]azepin-5(7H)-one (**3**).** A round-bottom flask with freshly distilled DMF (3 ml, 39 mmol) was cooled by an ice-water bath and  $\text{POCl}_3$  (1 ml, 10.7 mmol) was added dropwise. The mixture was stirred (30 min), then 8,9,10,11-tetrahydropyrido[2',3':4,5]pyrimido[1,2-a]azepin-5(7H)-one (**1**) (0.51 g, 2.4 mmol) was added into the reaction mixture. The reaction mixture was heated in a water bath for 1.5 h at 343 K and left for another day. Water (4 ml) was poured into the flask. TLC monitoring showed that the initial compound had fully transformed. The reaction mixture was treated by aqueous ammonia solution up to pH 9. The obtained solution was extracted by chloroform (30 mL) three times. The chloroform part was dried over  $\text{Na}_2\text{SO}_4$  and the solvent was removed. Yield 0.34 g (60%), m.p. 458–460 K,

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$
$M_r$	242.28
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
$a, b, c$ (Å)	8.7260 (7), 15.236 (3), 8.6642 (7)
$\beta$ (°)	98.046 (8)
$V$ (Å <sup>3</sup> )	1140.6 (3)
$Z$	4
Radiation type	Cu $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.76
Crystal size (mm)	0.40 × 0.35 × 0.15
Data collection	
Diffractometer	Oxford Diffraction Xcalibur, Ruby
Absorption correction	Multi-scan (CrysAlis PRO; Oxford Diffraction, 2007)
$T_{\min}, T_{\max}$	0.965, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	7589, 2328, 1478
$R_{\text{int}}$	0.059
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.631
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.050, 0.141, 1.04
No. of reflections	2328
No. of parameters	171
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.18, -0.20

Computer programs: CrysAlis PRO (Oxford Diffraction, 2007), SHELXS7 and XP in SHELXTL (Sheldrick, 2008) and SHELXL2014/7 (Sheldrick, 2015).

$R_f$  0.63. Single crystals of **3** were grown from acetone solution by slow evaporation of the solvent at room temperature.

UV spectrum (ethanol,  $\lambda_{\text{max}}$ , nm) neutral medium: 279.58, 348.97; acidic medium (HCl): 280.24, 362.37, 420.80; neutralization (HCl+NaOH): 279.12, 318.11, 362.29; basic medium (NaOH): 275.83, 347.71. IR spectrum (KBr,  $\nu$ , cm<sup>-1</sup>): 3382 (NH<sub>2</sub>), 3325, 3203, 3064, 2924, 2869, 2824, 1642, 1613 (NH), 1591, 1562, 1523, 1470, 1433, 1389, 1353, 1319, 1267, 1249, 1227, 1184, 1126, 1107, 1077, 1045, 976, 934, 864, 825, 783, 735, 688, 663, 601, 548, 420. LC-MS (+ESI): 243  $[M+H]^+$ , 216.1, 201.1, 174, 160.9, 148.0, 121.0, 93.0, 79.0, 55.1, 39.1.  $^1\text{H}$  NMR spectrum [400 MHz,  $\text{CD}_3\text{OD}$ ,  $\delta$ , ppm,  $J$  (Hz)]: 1.77 (2H,  $m$ ,  $\gamma\text{-CH}_2$ ), 1.92 (2H,  $m$ ,  $\delta\text{-CH}_2$ ), 2.385 (2H,  $m$ ,  $\beta\text{-CH}_2$ ), 4.195 (2H,  $t$ ,  $J = 6.1$ ,  $\varepsilon\text{-CH}_2$ ), 7.454 (1H,  $br s$ ,  $=\text{CH}$ ), 7.28 (1H,  $dd$ ,  $J = 4.6, 7.9$ , H-6), 8.45 (1H,  $dd$ ,  $J = 7.9, 2.1$ , H-5), 8.735 (1H,  $dd$ ,  $J = 4.6, 2.1$ , H-7).

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H-bound N atoms were freely refined. C-bound H atoms were refined as riding with C–H = 0.93 or 0.97 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

## Funding information

The work was supported by fundamental grant FA-F7-T207 ‘Theoretical aspects of formation of the asymmetric centers in

biologically active heterocyclic molecules' from the Academy of Sciences of the Republic of Uzbekistan.

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## supporting information

*Acta Cryst.* (2017). E73, 1497-1500 [https://doi.org/10.1107/S2056989017013093]

## Unusual formation of (*E*)-11-(aminomethylene)-8,9,10,11-tetrahydropyrido[2',3':4,5]pyrimido[1,2-*a*]azepin-5(7*H*)-one and its crystal structure

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### Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2007); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2007); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2007); program(s) used to solve structure: *SHELXS7* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2014/7* (Sheldrick, 2015).

### (*E*)-11-(Aminomethylene)-8,9,10,11-tetrahydropyrido[2',3':4,5]pyrimido[1,2-*a*]azepin-5(7*H*)-one

#### Crystal data

$C_{13}H_{14}N_4O$

$M_r = 242.28$

Monoclinic,  $P2_1/c$

$a = 8.7260$  (7) Å

$b = 15.236$  (3) Å

$c = 8.6642$  (7) Å

$\beta = 98.046$  (8)°

$V = 1140.6$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 512$

$D_x = 1.411$  Mg m<sup>-3</sup>

Melting point: 458(2) K

Cu  $K\alpha$  radiation,  $\lambda = 1.54184$  Å

Cell parameters from 911 reflections

$\theta = 5.9\text{--}75.7^\circ$

$\mu = 0.76$  mm<sup>-1</sup>

$T = 293$  K

Plate, colourless

$0.40 \times 0.35 \times 0.15$  mm

#### Data collection

Oxford Diffraction Xcalibur, Ruby  
diffractometer

Radiation source: Enhance (Cu) X-ray Source

Graphite monochromator

Detector resolution: 10.2576 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan

(*CrysAlis Pro*; Oxford Diffraction, 2007)

$T_{\min} = 0.965$ ,  $T_{\max} = 1.000$

7589 measured reflections

2328 independent reflections

1478 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.059$

$\theta_{\max} = 76.7^\circ$ ,  $\theta_{\min} = 5.1^\circ$

$h = -9 \rightarrow 10$

$k = -19 \rightarrow 18$

$l = -10 \rightarrow 8$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.050$

$wR(F^2) = 0.141$

$S = 1.04$

2328 reflections

171 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 0.003P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.18 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$$

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.6098 (2)	0.35990 (15)	0.1710 (2)	0.0621 (5)
N3	0.3638 (2)	0.39263 (13)	0.2102 (2)	0.0449 (4)
N1	0.2921 (2)	0.40925 (14)	0.4621 (2)	0.0472 (5)
N8	0.4731 (3)	0.39670 (16)	0.6821 (2)	0.0569 (5)
N15	−0.1422 (3)	0.49351 (19)	0.2758 (3)	0.0606 (6)
C2	0.2547 (3)	0.40679 (15)	0.3099 (3)	0.0438 (5)
C9	0.0935 (3)	0.41797 (17)	0.2412 (3)	0.0478 (5)
C4A	0.5549 (3)	0.36809 (16)	0.4323 (3)	0.0468 (5)
C8A	0.4417 (3)	0.39271 (15)	0.5243 (3)	0.0459 (5)
C4	0.5167 (3)	0.37221 (16)	0.2626 (3)	0.0476 (5)
C14	0.0100 (3)	0.47631 (17)	0.3123 (3)	0.0491 (5)
H14A	0.0630	0.5078	0.3950	0.059*
C13	0.3195 (3)	0.40613 (17)	0.0415 (3)	0.0502 (6)
H13A	0.4110	0.4200	−0.0056	0.060*
H13B	0.2492	0.4556	0.0247	0.060*
C5	0.7016 (3)	0.34430 (18)	0.5046 (3)	0.0557 (6)
H5A	0.7782	0.3280	0.4457	0.067*
C12	0.2420 (3)	0.32550 (18)	−0.0367 (3)	0.0560 (6)
H12A	0.1995	0.3400	−0.1432	0.067*
H12B	0.3189	0.2798	−0.0403	0.067*
C6	0.7310 (3)	0.34538 (19)	0.6636 (3)	0.0576 (6)
H6A	0.8268	0.3281	0.7154	0.069*
C10	0.0156 (3)	0.3637 (2)	0.1043 (3)	0.0607 (7)
H10A	−0.0772	0.3374	0.1341	0.073*
H10B	−0.0163	0.4030	0.0177	0.073*
C7	0.6134 (3)	0.3731 (2)	0.7466 (3)	0.0603 (6)
H7A	0.6354	0.3750	0.8547	0.072*
C11	0.1136 (3)	0.2911 (2)	0.0480 (3)	0.0617 (7)
H11A	0.1589	0.2566	0.1368	0.074*
H11B	0.0474	0.2527	−0.0214	0.074*
H1	−0.201 (4)	0.456 (2)	0.224 (4)	0.112 (16)*
H2	−0.181 (6)	0.527 (3)	0.338 (5)	0.16 (2)*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0464 (10)	0.0880 (14)	0.0538 (10)	0.0053 (9)	0.0141 (8)	−0.0095 (9)
N3	0.0398 (10)	0.0537 (11)	0.0415 (10)	−0.0006 (8)	0.0065 (8)	−0.0030 (8)
N1	0.0420 (10)	0.0574 (12)	0.0430 (10)	0.0022 (9)	0.0082 (8)	−0.0032 (8)
N8	0.0562 (13)	0.0707 (14)	0.0428 (11)	0.0026 (10)	0.0039 (9)	−0.0027 (9)
N15	0.0465 (13)	0.0786 (17)	0.0566 (13)	0.0100 (11)	0.0072 (10)	0.0016 (11)
C2	0.0416 (12)	0.0462 (12)	0.0440 (12)	−0.0003 (9)	0.0070 (9)	−0.0030 (9)
C9	0.0400 (12)	0.0593 (14)	0.0443 (12)	0.0014 (10)	0.0071 (9)	−0.0003 (10)
C4A	0.0424 (12)	0.0492 (13)	0.0484 (12)	−0.0002 (10)	0.0047 (10)	−0.0026 (9)
C8A	0.0430 (12)	0.0494 (13)	0.0450 (12)	0.0015 (9)	0.0049 (9)	−0.0019 (9)
C4	0.0404 (12)	0.0500 (12)	0.0533 (13)	0.0002 (10)	0.0097 (10)	−0.0076 (10)
C14	0.0393 (12)	0.0630 (15)	0.0446 (12)	0.0021 (11)	0.0042 (9)	0.0033 (10)
C13	0.0478 (13)	0.0601 (15)	0.0436 (12)	0.0002 (11)	0.0088 (10)	0.0018 (10)
C5	0.0450 (14)	0.0610 (16)	0.0611 (15)	0.0061 (11)	0.0074 (11)	−0.0003 (11)
C12	0.0616 (16)	0.0598 (16)	0.0457 (13)	0.0034 (12)	0.0044 (11)	−0.0082 (10)
C6	0.0467 (13)	0.0625 (16)	0.0600 (15)	0.0042 (11)	−0.0053 (11)	0.0051 (12)
C10	0.0461 (14)	0.0748 (18)	0.0598 (16)	−0.0004 (13)	0.0023 (11)	−0.0098 (13)
C7	0.0628 (16)	0.0693 (17)	0.0455 (13)	−0.0001 (13)	−0.0036 (11)	0.0008 (11)
C11	0.0616 (17)	0.0634 (17)	0.0589 (16)	−0.0091 (13)	0.0046 (12)	−0.0110 (12)

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

O1—C4	1.227 (3)	C14—H14A	0.9300
N3—C4	1.383 (3)	C13—C12	1.516 (4)
N3—C2	1.389 (3)	C13—H13A	0.9700
N3—C13	1.473 (3)	C13—H13B	0.9700
N1—C2	1.314 (3)	C5—C6	1.365 (4)
N1—C8A	1.364 (3)	C5—H5A	0.9300
N8—C7	1.323 (4)	C12—C11	1.516 (4)
N8—C8A	1.357 (3)	C12—H12A	0.9700
N15—C14	1.347 (3)	C12—H12B	0.9700
N15—H1	0.852 (19)	C6—C7	1.398 (4)
N15—H2	0.849 (19)	C6—H6A	0.9300
C2—C9	1.458 (3)	C10—C11	1.519 (4)
C9—C14	1.352 (3)	C10—H10A	0.9700
C9—C10	1.525 (4)	C10—H10B	0.9700
C4A—C5	1.392 (3)	C7—H7A	0.9300
C4A—C8A	1.405 (3)	C11—H11A	0.9700
C4A—C4	1.463 (3)	C11—H11B	0.9700
C4—N3—C2	122.98 (19)	C12—C13—H13B	109.3
C4—N3—C13	117.70 (18)	H13A—C13—H13B	107.9
C2—N3—C13	119.16 (19)	C6—C5—C4A	118.8 (2)
C2—N1—C8A	118.76 (19)	C6—C5—H5A	120.6
C7—N8—C8A	117.3 (2)	C4A—C5—H5A	120.6
C14—N15—H1	120 (3)	C11—C12—C13	112.1 (2)

C14—N15—H2	116 (4)	C11—C12—H12A	109.2
H1—N15—H2	118 (4)	C13—C12—H12A	109.2
N1—C2—N3	122.2 (2)	C11—C12—H12B	109.2
N1—C2—C9	119.8 (2)	C13—C12—H12B	109.2
N3—C2—C9	118.0 (2)	H12A—C12—H12B	107.9
C14—C9—C2	116.2 (2)	C5—C6—C7	118.4 (2)
C14—C9—C10	120.1 (2)	C5—C6—H6A	120.8
C2—C9—C10	123.6 (2)	C7—C6—H6A	120.8
C5—C4A—C8A	119.3 (2)	C11—C10—C9	115.8 (2)
C5—C4A—C4	121.9 (2)	C11—C10—H10A	108.3
C8A—C4A—C4	118.7 (2)	C9—C10—H10A	108.3
N8—C8A—N1	115.9 (2)	C11—C10—H10B	108.3
N8—C8A—C4A	121.6 (2)	C9—C10—H10B	108.3
N1—C8A—C4A	122.3 (2)	H10A—C10—H10B	107.4
O1—C4—N3	121.1 (2)	N8—C7—C6	124.6 (2)
O1—C4—C4A	124.5 (2)	N8—C7—H7A	117.7
N3—C4—C4A	114.40 (19)	C6—C7—H7A	117.7
N15—C14—C9	126.7 (2)	C12—C11—C10	113.0 (2)
N15—C14—H14A	116.6	C12—C11—H11A	109.0
C9—C14—H14A	116.6	C10—C11—H11A	109.0
N3—C13—C12	111.7 (2)	C12—C11—H11B	109.0
N3—C13—H13A	109.3	C10—C11—H11B	109.0
C12—C13—H13A	109.3	H11A—C11—H11B	107.8
N3—C13—H13B	109.3		

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N15—H1 $\cdots$ O1 <sup>i</sup>	0.85 (3)	2.21 (3)	3.017 (3)	159 (3)
N15—H2 $\cdots$ N1 <sup>ii</sup>	0.85 (5)	2.31 (5)	3.146 (3)	168 (4)
N15—H2 $\cdots$ N8 <sup>ii</sup>	0.85 (5)	2.79 (5)	3.401 (4)	131 (4)

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