



# Crystal structure of 4-carbamoylpyridinium chloride

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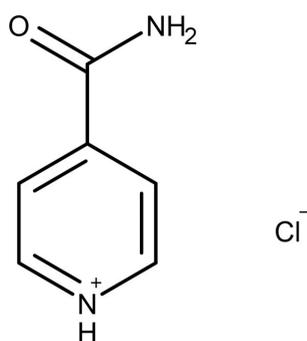
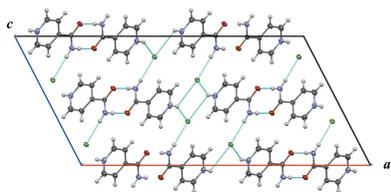
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The hydrochloride salt of isonicotinamide,  $C_6H_7N_2O^+ \cdot Cl^-$ , has been synthesized from a dilute solution of hydrochloric acid in acetonitrile. The compound displays monoclinic symmetry (space group  $C2/c$ ) at 150 K, similar to the related hydrochloride salt of nicotinamide. The asymmetric unit contains one protonated isonicotinamide molecule and a chloride anion. An array of hydrogen-bonding interactions, including a peculiar bifurcated pyridinium–chloride interaction, results in linear chains running almost perpendicularly in the  $[150]$  and  $[1\bar{5}0]$  directions within the structure. A description of the hydrogen-bonding network and comparison with similar compounds are presented.

## 1. Chemical context

Often compounds which exhibit a desirable biological function may not possess the correct physical properties for practical usage. The ability to manipulate the properties of a compound in a controlled manner, while maintaining the biological activity, is one of the ultimate goals of crystal engineering (Desiraju *et al.*, 2011). Converting a biologically active compound into its hydrochloride salt has proven a successful technique in this regard (Byrn *et al.*, 1999). The structural determination and analysis of neutral, co-crystalline, and salt forms of various molecules is necessary in order to expand the library of reliable tools that can be used in the design of new materials.



Isonicotinamide is a useful compound in crystal engineering as it possesses amide and pyridyl groups which have the capability to form a plethora of well established and predictable hydrogen-bonding arrangements (Bhogala *et al.*, 2004). It also displays polymorphism in the solid state on account of its flexible hydrogen-bonding capacity (Aakeröy *et al.*, 2003; Li *et al.*, 2011). As a result, the molecule has been heavily investigated by many groups as a co-crystal former in lots of different

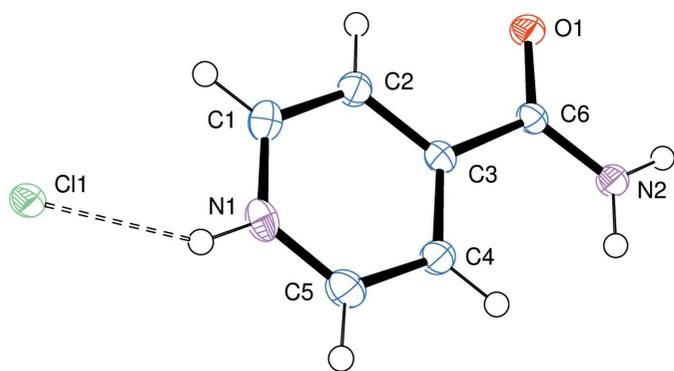


Figure 1

The asymmetric unit of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The dashed line represents a hydrogen bond.

scenarios (Vishweshwar *et al.*, 2003; Bhogala *et al.*, 2005; Aakeröy *et al.*, 2007; Thompson *et al.*, 2011; Tothadi & Desiraju, 2012; Dubey & Desiraju, 2014; Kerr *et al.*, 2015). The compound is also of mild pharmaceutical interest given its similarity to nicotinamide, the amide of Vitamin B<sub>3</sub>. The hydrochloride salt of this molecule has been synthesized and the structure determined, the results of which are discussed herein.

## 2. Structural commentary

The asymmetric unit of the title compound, shown in Fig. 1, consists of one chloride anion and a protonated isonicotinamide cation, confirmed by the identification of a proton 0.9 Å from the pyridine N atom in a difference Fourier map. The isonicotinamide cation is planar: the root-mean-square deviation of the pyridinium ring is 0.0062 Å, with an angle of 1.3 (2)° between the planes of the pyridinium and amide

Table 1

Hydrogen-bond geometry (Å, °).

<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>
C1—H1···O1 <sup>i</sup>	0.95	2.74	3.295 (2)	118
C2—H2···O1 <sup>i</sup>	0.92	2.61	3.2205 (18)	124
C4—H4···Cl1 <sup>iii</sup>	0.95	2.59	3.5377 (15)	172
C5—H5···Cl1 <sup>iii</sup>	0.93	2.62	3.3284 (15)	133
N1—H1A···Cl1	0.89	2.24	3.0416 (12)	149
N1—H1A···Cl1 <sup>iii</sup>	0.89	2.95	3.4882 (13)	121
N2—H2A···O1 <sup>iv</sup>	0.88 (2)	2.02 (2)	2.8892 (15)	174 (2)
N2—H2B···Cl1 <sup>ii</sup>	0.87 (2)	2.33 (2)	3.1907 (13)	169 (2)

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

moieties. Analysis of structures in the Cambridge Structural Database (CSD, Version 5.37, update November 2015; Groom & Allen, 2014) containing the 4-carbamoylpyridinium cation show that the angle between the amide and pyridinium planes can take any value between 0 and 50° with no distinct configurational preference.

## 3. Supramolecular features

The most interesting feature of the crystal structure is the intermolecular interaction between the pyridinium groups and chloride ions. Two pyridinium protons form bifurcated hydrogen bonds to two chloride ions, forming an  $R_2^2(4)$  ring motif which is positioned on a centre of inversion, as shown in Fig. 2 (A). The interaction is similar to those found in many tetrahalometallate  $[MX_4]^{2-}$  compounds, though primarily when the  $[MX_4]^{2-}$  unit is planar (Adams *et al.*, 2006). It is also encountered in some hydrochloride salts of molecules incorporating a pyridinium group (Nattinen & Rissanen, 2003; Zhao *et al.*, 2008). The two unique N—H···Cl hydrogen bonds formed by each proton in this arrangement are usually of

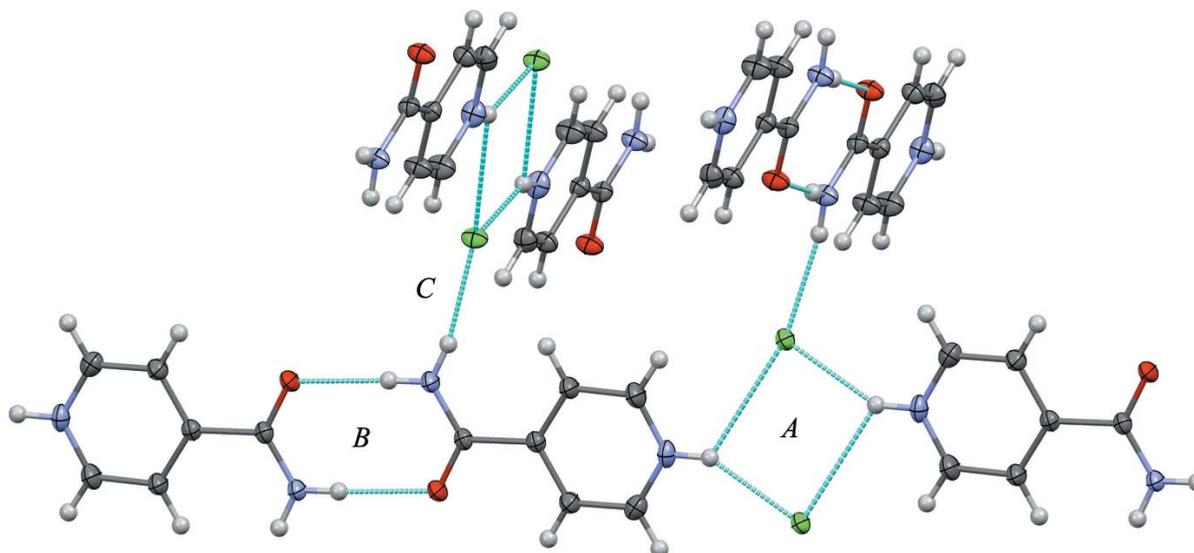
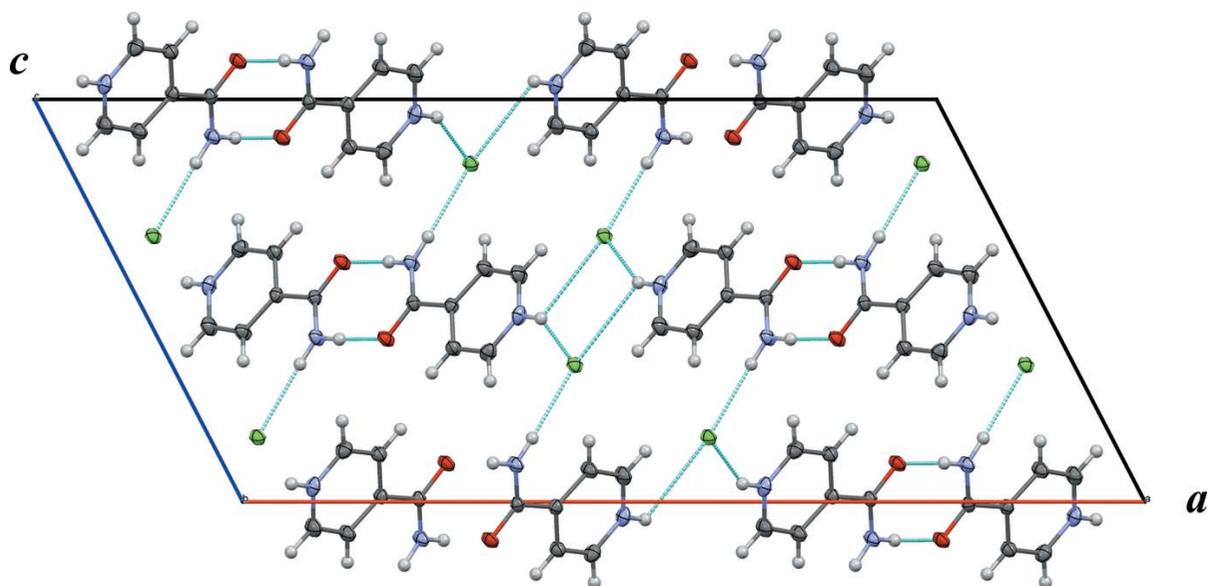


Figure 2

A view of the hydrogen bonding arrangements within 4-carbamoylpyridinium chloride, showing the pyridinium–chloride (A) amide–amide (B) and amine–chloride (C) interactions. Hydrogen bonds are drawn as light-blue dashed lines. Possible C—H···X interactions have been omitted.



**Figure 3**  
Crystal packing diagram of 4-carbamoylpyridinium chloride viewed along the  $b$  axis. Hydrogen bonds are drawn as light-blue dashed lines.

similar length, though one is distinctly longer than the other in this compound [ $N \cdots Cl = 3.0416(12) \text{ \AA}$  and  $3.4882(13) \text{ \AA}$ ]. The CSD (Version 5.37, update November 2015; Groom & Allen, 2014) reveals 426 structures of the hydrochloride salts of molecules incorporating a pyridinium group. 21 of these display bifurcated pyridinium–chloride hydrogen bonds, of which only 16 possess the  $R_2^2(4)$  ring motif. None of these simultaneously show the same asymmetry in the hydrogen-bond lengths (ratio of two  $N \cdots Cl$  lengths = 1.147; ratio of  $H \cdots Cl$  lengths = 1.317), and planarity (r.m.s.d. =  $0.0151 \text{ \AA}$ ) of the interaction as the title compound. Given the lack of examples of bifurcated hydrogen bonds in this type of material, it seems likely that it is a result of maximizing the other possible intermolecular interactions for a given system, where the bifurcation is a compromise. In other words, one short, linear  $N-H \cdots Cl$  bond is ideal, though bifurcation is energetically more favourable than a single, weaker interaction.

The amine group of the amide moiety is directed toward the carboxyl group of an adjacent molecule related by a centre of inversion; this shows the existence of a classic  $R_2^2(8)$  amide–amide interaction, seen in Fig. 2 (B). The combination of the two ring interactions form  $C_3^2(16)$  chains running in the  $[150]$  and  $[\bar{1}50]$  directions, and are related by a  $2_1$  screw axis. The two chain directions are almost perpendicular to each other ( $82^\circ$ ) and are held in this respective orientation by a  $C_4^3(10)$  interaction which incorporates the  $R_2^2(8)$  and  $R_2^2(4)$  motifs, and hydrogen bonds between the protons not involved in the amide–amide interactions and the chloride ions of neighbouring chains, as shown in Fig. 2 (C). For the overall packing arrangement, see Fig. 3. There is some evidence of  $C-H \cdots X$  hydrogen bonds (Table 1); however, these only seem to reinforce the stronger interactions discussed above and their role in determining the crystal packing in this compound is unclear.

The related salt of nicotinamide contains the same amide–amide interactions as in the title compound, though neither

3- or 4-carboxypyridinium chloride show the equivalent dicarboxylic acid interaction. (Gubin *et al.*, 1989; Slouf, 2001; Adams *et al.*, 2006). The chloride ions in these structures act only as hydrogen-bond acceptor atoms between donor atoms of molecules in the same chain, with no further interactions between the chains. It would be interesting to see how these almost classic co-crystal formers would behave when crystallized with the hydrochloride salts of other molecules, and whether the same hydrogen-bonding arrangements persist.

#### 4. Related structures

For the crystal structure of 4-carbamoylpyridinium dihydrogen phosphate, see Gholivand *et al.* (2007); for 4-carbamoylpyridinium perchlorate, see Chen (2009); for nicotinamide hydrochloride, see Gubin *et al.* (1989); for nicotinic acid hydrochloride, see Slouf (2001); and for isonicotinic acid hydrochloride and a comprehensive study on the tetrachloroplatinate and palladate salts of similar pyridinium compounds, see Adams *et al.* (2006).

#### 5. Synthesis and crystallization

Hydrochloric acid (0.08 ml, 12 M) in acetonitrile (3 ml) was added to isonicotinamide (0.244 g, 2 mmol) dissolved in acetonitrile (25 ml). The resultant white mixture was heated until the precipitate dissolved and the solution left to evaporate slowly over several days, resulting in the formation of large colourless block-shaped crystals of the title compound.

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms were readily identified in difference Fourier maps. The pyridinium

hydrogen atom was positioned in a geometrically optimized position; N1—H1A was constrained to a value of 0.88 Å with an su of 0.03 Å. C-bound H atoms were sited with a riding model and the C—H distance refined subject to the restraint that all C—H distances should be the same with an su of 0.03 Å. The amide hydrogen atoms were refined freely subject to restraint that the two N—H bond lengths were equal with an su of 0.03 Å and the H···H distance was  $\sqrt{3} \times l_{\text{N-H}}$  (su 0.03 Å) to set the H—N—H angle to 120°.

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**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>6</sub> H <sub>7</sub> N <sub>2</sub> O <sup>+</sup> ·Cl <sup>−</sup>
<i>M<sub>r</sub></i>	158.59
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	24.960 (2), 5.1055 (4), 12.4664 (9)
$\beta$ (°)	117.545 (5)
<i>V</i> (Å <sup>3</sup> )	1408.6 (2)
<i>Z</i>	8
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>−1</sup> )	0.47
Crystal size (mm)	0.34 × 0.28 × 0.26
Data collection	
Diffractometer	Stoe <i>IPDS 2</i>
Absorption correction	Analytical ( <i>X-RED</i> and <i>X-SHAPE</i> ; Stoe & Cie, 2012)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.861, 0.913
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	4768, 1865, 1520
<i>R<sub>int</sub></i>	0.047
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>−1</sup> )	0.685
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.034, 0.093, 1.01
No. of reflections	1865
No. of parameters	104
No. of restraints	8
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> )	0.45, −0.48

Computer programs: *X-AREA* (Stoe & Cie, 2012), *X-RED* (Stoe & Cie, 2012), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2008).

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## supporting information

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## Crystal structure of 4-carbamoylpyridinium chloride

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## Computing details

Data collection: *X-AREA* (Stoe & Cie, 2012); cell refinement: *X-AREA* (Stoe & Cie, 2012); data reduction: *X-RED* (Stoe & Cie, 2012); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b).

## 4-Carbamoylpyridinium chloride

## Crystal data

$C_6H_7N_2O^+Cl^-$

$M_r = 158.59$

Monoclinic, *C2/c*

$a = 24.960$  (2) Å

$b = 5.1055$  (4) Å

$c = 12.4664$  (9) Å

$\beta = 117.545$  (5)°

$V = 1408.6$  (2) Å<sup>3</sup>

$Z = 8$

$F(000) = 656$

$D_x = 1.496$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 5016 reflections

$\theta = 3.7$ – $59.1$ °

$\mu = 0.47$  mm<sup>-1</sup>

$T = 150$  K

Block, colourless

$0.34 \times 0.28 \times 0.26$  mm

## Data collection

Stoe IPDS 2

diffractometer

Radiation source: fine-focus sealed X-ray tube

Detector resolution: 6.67 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: analytical

(*X-RED* and *X-SHAPE*; Stoe & Cie, 2012)

$T_{\min} = 0.861$ ,  $T_{\max} = 0.913$

4768 measured reflections

1865 independent reflections

1520 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.047$

$\theta_{\max} = 29.2$ °,  $\theta_{\min} = 1.8$ °

$h = -34 \rightarrow 34$

$k = -6 \rightarrow 6$

$l = -17 \rightarrow 17$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.093$

$S = 1.01$

1865 reflections

104 parameters

8 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent

and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0636P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.45$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.48$  e Å<sup>-3</sup>

*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.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.05337 (2)	1.08640 (7)	0.66004 (3)	0.02094 (12)
C1	0.14210 (7)	0.6050 (3)	0.62858 (14)	0.0235 (3)
H1	0.1565 (2)	0.7082 (17)	0.7004 (12)	0.028*
C2	0.17821 (6)	0.4124 (3)	0.61830 (13)	0.0206 (3)
H2	0.2164 (7)	0.3837 (6)	0.6800 (11)	0.025*
C3	0.15607 (5)	0.2616 (3)	0.51318 (11)	0.0175 (3)
C4	0.09760 (6)	0.3065 (3)	0.42116 (13)	0.0236 (3)
H4	0.0814 (3)	0.2027 (17)	0.3497 (12)	0.028*
C5	0.06356 (7)	0.5048 (3)	0.43560 (14)	0.0270 (3)
H5	0.0247 (7)	0.5390 (7)	0.3747 (12)	0.032*
C6	0.19697 (6)	0.0497 (3)	0.50687 (12)	0.0173 (3)
N1	0.08665 (6)	0.6468 (2)	0.53714 (12)	0.0228 (3)
H1A	0.0642 (4)	0.775 (2)	0.54449 (16)	0.027*
N2	0.17626 (5)	-0.0961 (2)	0.40762 (11)	0.0209 (3)
O1	0.24768 (4)	0.0199 (2)	0.59516 (9)	0.0228 (2)
H2A	0.2004 (8)	-0.216 (4)	0.4039 (16)	0.027*
H2B	0.1426 (8)	-0.069 (4)	0.3420 (17)	0.027*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.01780 (17)	0.0231 (2)	0.01907 (18)	0.00607 (12)	0.00610 (13)	-0.00009 (13)
C1	0.0261 (7)	0.0220 (7)	0.0249 (7)	-0.0003 (5)	0.0138 (6)	-0.0034 (6)
C2	0.0179 (6)	0.0215 (7)	0.0208 (6)	0.0012 (5)	0.0075 (5)	-0.0015 (5)
C3	0.0171 (6)	0.0167 (6)	0.0190 (6)	0.0021 (5)	0.0087 (5)	0.0014 (5)
C4	0.0195 (6)	0.0255 (8)	0.0212 (6)	0.0065 (5)	0.0056 (5)	-0.0034 (6)
C5	0.0207 (7)	0.0294 (8)	0.0277 (7)	0.0091 (6)	0.0086 (6)	0.0003 (6)
C6	0.0155 (6)	0.0170 (7)	0.0190 (6)	0.0022 (5)	0.0075 (5)	0.0013 (5)
N1	0.0236 (6)	0.0195 (6)	0.0303 (7)	0.0055 (5)	0.0166 (5)	0.0003 (5)
N2	0.0173 (5)	0.0217 (6)	0.0198 (6)	0.0061 (4)	0.0052 (5)	-0.0024 (5)
O1	0.0170 (4)	0.0250 (6)	0.0202 (5)	0.0067 (4)	0.0034 (4)	-0.0015 (4)

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

C1—N1	1.342 (2)	C4—H4	0.951 (16)
C1—C2	1.3795 (19)	C5—N1	1.336 (2)

C1—H1	0.955 (16)	C5—H5	0.931 (18)
C2—C3	1.3948 (19)	C6—O1	1.2443 (17)
C2—H2	0.918 (16)	C6—N2	1.3271 (18)
C3—C4	1.3964 (18)	N1—H1A	0.894 (14)
C3—C6	1.5141 (18)	N2—H2A	0.876 (16)
C4—C5	1.3858 (19)	N2—H2B	0.871 (18)
N1—C1—C2	119.73 (14)	N1—C5—C4	119.84 (14)
N1—C1—H1	120.1	N1—C5—H5	120.1
C2—C1—H1	120.1	C4—C5—H5	120.1
C1—C2—C3	119.26 (13)	O1—C6—N2	123.66 (12)
C1—C2—H2	120.4	O1—C6—C3	118.43 (12)
C3—C2—H2	120.4	N2—C6—C3	117.91 (12)
C2—C3—C4	119.39 (12)	C5—N1—C1	122.81 (12)
C2—C3—C6	117.34 (11)	C5—N1—H1A	118.6
C4—C3—C6	123.25 (12)	C1—N1—H1A	118.6
C5—C4—C3	118.94 (14)	C6—N2—H2A	117.5 (12)
C5—C4—H4	120.5	C6—N2—H2B	125.3 (12)
C3—C4—H4	120.5	H2A—N2—H2B	116.7 (16)

*Hydrogen-bond geometry (Å, °)*

<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>
C1—H1...O1 <sup>i</sup>	0.95	2.74	3.295 (2)	118
C2—H2...O1 <sup>i</sup>	0.92	2.61	3.2205 (18)	124
C4—H4...Cl1 <sup>ii</sup>	0.95	2.59	3.5377 (15)	172
C5—H5...Cl1 <sup>iii</sup>	0.93	2.62	3.3284 (15)	133
N1—H1A...Cl1	0.89	2.24	3.0416 (12)	149
N1—H1A...Cl1 <sup>iii</sup>	0.89	2.95	3.4882 (13)	121
N2—H2A...O1 <sup>iv</sup>	0.88 (2)	2.02 (2)	2.8892 (15)	174 (2)
N2—H2B...Cl1 <sup>ii</sup>	0.87 (2)	2.33 (2)	3.1907 (13)	169 (2)

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