



# Crystal structures of 4-chloropyridine-2-carbonitrile and 6-chloropyridine-2-carbonitrile exhibit different intermolecular $\pi$ -stacking, C—H $\cdots$ N<sub>nitrile</sub> and C—H $\cdots$ N<sub>pyridine</sub> interactions

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**Keywords:** crystal structure; chlorocyanopyridine;  $\pi$ -stacking; C—H $\cdots$ N interactions

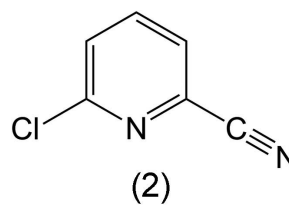
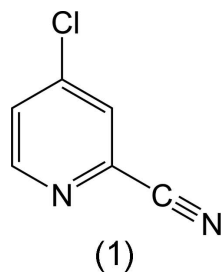
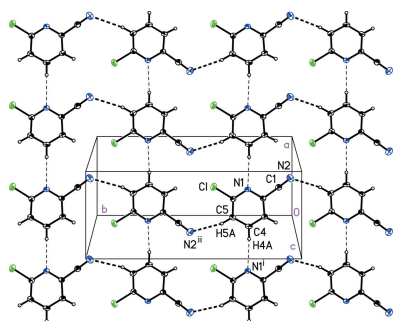
**CCDC references:** 1407613; 1407612

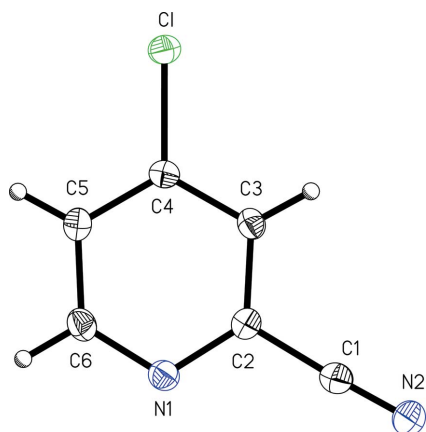
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The two title compounds are isomers of C<sub>6</sub>H<sub>3</sub>ClN<sub>2</sub> containing a pyridine ring, a nitrile group, and a chloro substituent. The molecules of each compound pack together in the solid state with offset face-to-face  $\pi$ -stacking, and intermolecular C—H $\cdots$ N<sub>nitrile</sub> and C—H $\cdots$ N<sub>pyridine</sub> interactions. 4-Chloropyridine-2-carbonitrile, (I), exhibits pairwise centrosymmetric head-to-head C—H $\cdots$ N<sub>nitrile</sub> and C—H $\cdots$ N<sub>pyridine</sub> interactions, forming one-dimensional chains, which are  $\pi$ -stacked in an offset face-to-face fashion. The intermolecular packing of the isomeric 6-chloropyridine-2-carbonitrile, (II), which differs only in the position of the chloro substituent on the pyridine ring, exhibits head-to-tail C—H $\cdots$ N<sub>nitrile</sub> and C—H $\cdots$ N<sub>pyridine</sub> interactions, forming two-dimensional sheets which are  $\pi$ -stacked in an offset face-to-face fashion. In contrast to (I), the offset face-to-face  $\pi$ -stacking in (II) is formed between molecules with alternating orientations of the chloro and nitrile substituents.

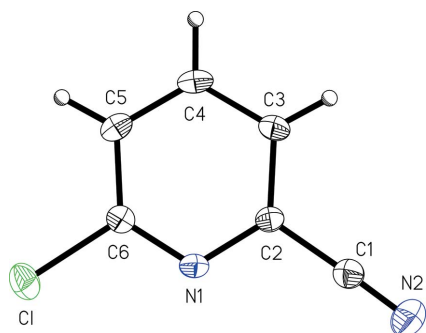
## 1. Chemical context

Chloropyridinecarbonitriles are members of a class of compounds containing the ubiquitous six-membered nitrogen-containing heterocycle pyridine. The pyridine heterocycle features prominently in many valuable synthetic compounds (Bull *et al.*, 2012). While several of the ten possible isomers of chloropyridinecarbonitrile are commercially available, none of their crystal structures have been reported in the literature, although the structure of 2-chloropyridine-4-carbonitrile has been deposited in the Cambridge Structural Database (Version 5.31, June 2015 with updates; Groom & Allen, 2014) as a private communication (refcode LOBVIJ). The title compounds represent two isomers of chloropyridine-2-carbonitrile, namely 4-chloropyridine-2-carbonitrile, (I), and 6-chloropyridine-2-carbonitrile, (II). In both cases, the intramolecular packing exhibits weak intermolecular C—H $\cdots$ N interactions, which are well documented (Desiraju & Steiner, 1999), as well as aromatic  $\pi$ -stacking interactions (Hunter & Saunders, 1990; Lueckheide *et al.*, 2013).





**Figure 1**  
A view of 4-chloropyridine-2-carbonitrile, (I), with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.



**Figure 2**  
A view of 6-chloropyridine-2-carbonitrile, (II), with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

4-Chloropyridine-2-carbonitrile, (I), may be synthesized by the cyanation of 4-chloropyridine *N*-oxide with trimethylsilylcarbonitrile (TMSCN) (Sakamoto *et al.*, 1985). More recently, it has been shown that (I) can be prepared in a one-step process from 4-nitropyridine *N*-oxide with ethyl chloroformate and TMSCN (Veerareddy *et al.*, 2011). (I) has found

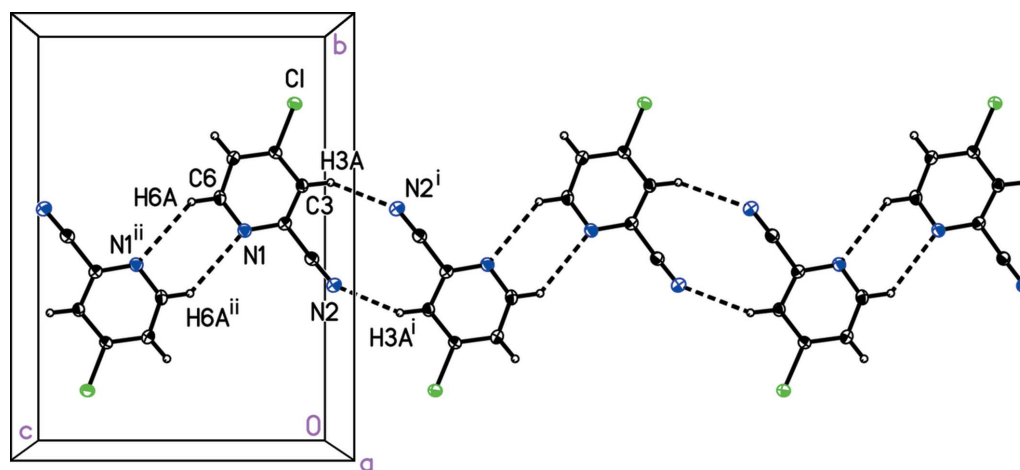
use as a building block for a family of chiral catalysts (Busto *et al.*, 2005).

6-Chloropyridine-2-carbonitrile, (II), may be synthesized by the vapor-phase chlorination of 2-cyanopyridine (Ruetman & Taplin, 1971), or by the cyanation of 2-chloropyridine *N*-oxide hydrochloride with sodium cyanide (Tsukamoto *et al.*, 2009). This compound has found applications in the preparation of biologically active or pharmaceutical compounds, such as heteroaromatic carboxylic acids (Kiener *et al.*, 1996) and 2-arylamino-substituted pyridinyl nitriles (Guo *et al.*, 2013).

## 2. Structural commentary

4-Chloropyridine-2-carbonitrile, (I) (Fig. 1), and 6-chloropyridine-2-carbonitrile, (II) (Fig. 2), exhibit similar metrical parameters. The nitrile bond length C1–N2 of 1.156 (3) Å in (I) and 1.138 (2) Å in (II) are similar to those seen in the related structure 2-chloropyridine-4-carbonitrile, with the nitrile C≡N distance is 1.141 Å (CSD refcode LOBVIIJ). The nitrile bond lengths in 2- and 3-cyanopyridine [1.145 (2) and 1.150 (1) Å, respectively; Kubiak *et al.*, 2002] and 4-cyanopyridine [1.137 (8) Å; Laing *et al.*, 1971] are also similar to those found in the title compounds. The aromatic chlorine bond lengths, *viz.* C4–Cl and C6–Cl of 1.740 (3) Å in (I) and 1.740 (1) Å in (II), are similar to those seen in the related structures 2-chloropyridine-4-carbonitrile (1.732 Å; CSD refcode LOBVIIJ), 2- and 3-chloropyridine hydrochloride (1.710 and 1.727 Å, respectively; Freytag & Jones, 2001), and 4-chloropyridine hydrochloride (1.730 Å; Freytag *et al.*, 1999).

Both (I) and (II) are almost planar, with r.m.s. deviations from the mean planes of all non-H atoms of 0.0077 and 0.0161 Å, respectively. As may be expected, the heterocyclic rings are slightly wedge shaped as the pyridine C–N bond are shorter than the C–C bonds in each aromatic ring. In (I), the ring C2–N1 and C6–N1 bond lengths of 1.361 (3) and 1.350 (3) Å are similar to those found in (II) of 1.349 (1) and 1.322 (1) Å. The average ring C–C bond lengths are



**Figure 3**  
A view of the intermolecular C–H...N<sub>nitrile</sub> and C–H...N<sub>pyridine</sub> contacts (dashed lines) in 4-chloropyridine-2-carbonitrile, (I), that form a one-dimensional chain. [Symmetry codes: (i)  $-x - 1, -y + 1, -z$ ; (ii)  $-x, -y + 1, -z + 1$ .]

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

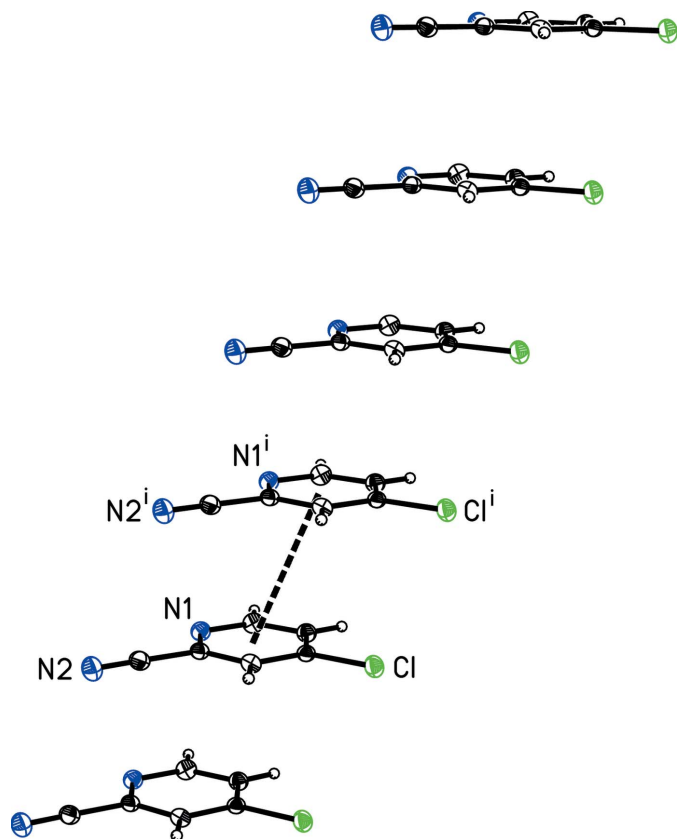
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C3-H3A\cdots N2^i$	0.95	2.64	3.462 (5)	146
$C6-H6A\cdots N1^{ii}$	0.95	2.75	3.493 (5)	136

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

1.403 (2) Å in (I) and 1.391 (5) Å in (II). The lengths are comparable to those found in the parent compound, pyridine, with C–N of 1.34 Å and C–C of 1.38 Å (Mootz & Wussow, 1981), and in the related structure 2-chloropyridine-4-carbonitrile, with C–N bond lengths of 1.328 and 1.340 Å, and an average C–C bond length of 1.377 (7) Å (CSD refcode LOBVIJ).

### 3. Supramolecular features

The molecules of each of the title compounds pack together in the solid state with  $\pi$ -stacking, and intermolecular C–H $\cdots$ N<sub>nitrile</sub> and C–H $\cdots$ N<sub>pyridine</sub> interactions, however, the packing motifs are unique, and also different than those found in the related structure 2-chloropyridine-4-carbonitrile (CSD


**Figure 4**  
 A view of the offset face-to-face  $\pi$ -stacking in 4-chloropyridine-2-carbonitrile, (I), with the thick dashed line indicating a centroid-to-centroid interaction. [Symmetry code: (i)  $x+1, y, z$ .]

**Table 2**  
 Hydrogen-bond geometry (Å, °) for (II).

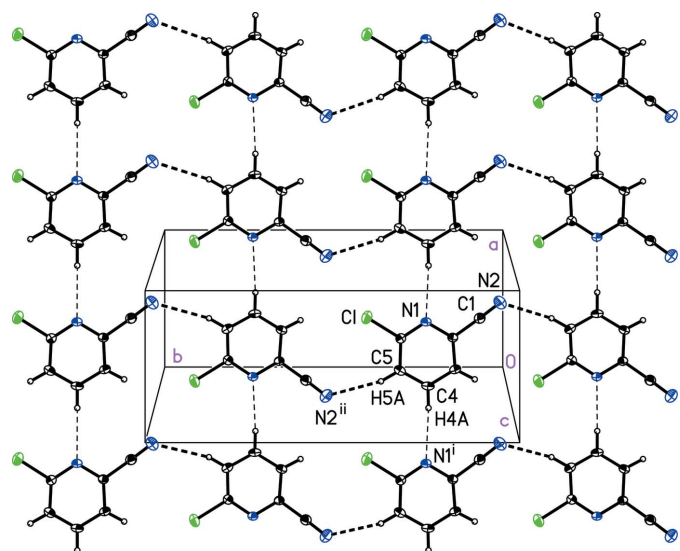
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C4-H4A\cdots N1^i$	0.95	2.49	3.4099 (15)	164
$C5-H5A\cdots N2^{ii}$	0.95	2.70	3.5651 (17)	152

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

refcode LOBVIJ). For a discussion of weak C–H $\cdots$ X interactions, see Desiraju & Steiner (1999).

The molecules of (I) pack together in the solid state *via* alternating centrosymmetric head-to-head intermolecular C–H $\cdots$ N<sub>nitrile</sub> and C–H $\cdots$ N<sub>pyridine</sub> interactions to form a one-dimensional zigzag chain (Fig. 3 and Table 1). The chains further pack together through offset face-to-face  $\pi$ -stacking (Fig. 4). This  $\pi$ -stacking is characterized by a centroid-to-centroid distance of 3.813 (5) Å, a plane-to-centroid distance of 3.454 (4) Å, and a ring offset or ring-slippage distance of 1.615 (3) Å (Hunter & Saunders, 1990; Lueckheide *et al.*, 2013). The  $\pi$ -stacking in (I) is similar to that found in the related unpublished structure 2-chloropyridine-4-carbonitrile (CSD refcode LOBVIJ).

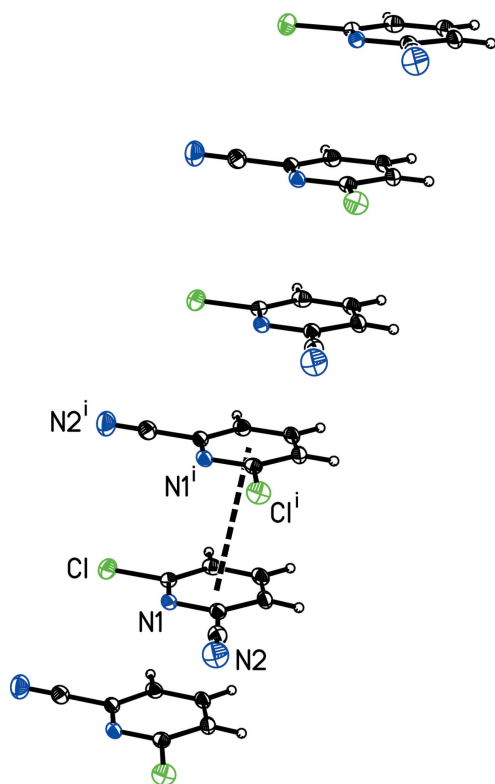
In contrast to (I), the molecules of (II) pack together *via* head-to-tail C–H $\cdots$ N<sub>nitrile</sub> and C–H $\cdots$ N<sub>pyridine</sub> interactions to form two-dimensional sheets that are parallel to the (001) plane (Fig. 5 and Table 2). As in (I), the parallel planes of the molecules engage in offset face-to-face  $\pi$ -stacking between the two-dimensional sheets, which is characterized by a ring centroid-to-centroid distance of 3.7204 (7) Å, a centroid-to-plane distance of 3.41 (1) Å, and a ring-offset slippage of 1.48 (2) Å (Fig. 6). However, in contrast to (I), the  $\pi$ -stacking in (II) is formed between molecules with alternating orienta-


**Figure 5**  
 A view of the intermolecular C–H $\cdots$ N<sub>nitrile</sub> and C–H $\cdots$ N<sub>pyridine</sub> contacts (dashed lines) in 6-chloropyridine-2-carbonitrile, (I), that form a two-dimensional sheet. [Symmetry codes: (i)  $x-1, y, z$ ; (ii)  $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$ .]

**Table 3**  
 Experimental details.

	(I)	(II)
<b>Crystal data</b>		
Chemical formula	C <sub>6</sub> H <sub>3</sub> ClN <sub>2</sub>	C <sub>6</sub> H <sub>3</sub> ClN <sub>2</sub>
<i>M<sub>r</sub></i>	138.55	138.55
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>
Temperature (K)	125	125
<i>a</i> , <i>b</i> , <i>c</i> (Å)	3.813 (5), 14.047 (19), 11.356 (15)	6.1739 (15), 15.238 (4), 7.0123 (18)
$\beta$ (°)	96.806 (19)	112.492 (4)
<i>V</i> (Å <sup>3</sup> )	604.0 (14)	609.5 (3)
<i>Z</i>	4	4
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.52	0.52
Crystal size (mm)	0.25 × 0.10 × 0.04	0.20 × 0.15 × 0.03
<b>Data collection</b>		
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2013)	Multi-scan ( <i>SADABS</i> ; Bruker, 2013)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.67, 0.98	0.82, 0.98
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	12191, 1852, 1498	15460, 1868, 1657
<i>R</i> <sub>int</sub>	0.063	0.031
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.715	0.717
<b>Refinement</b>		
<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>	0.050, 0.135, 1.12	0.028, 0.082, 1.09
No. of reflections	1852	1868
No. of parameters	82	82
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.53, -0.37	0.48, -0.19

Computer programs: *APEX2* and *SAINTE* (Bruker, 2013), *SHELXS2014* and *SHELXTL2014* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008).



**Figure 6**  
 A view of the alternating offset face-to-face  $\pi$ -stacking in 6-chloropyridine-2-carbonitrile, (II), with the thick dashed line indicating a centroid-to-centroid interaction. [Symmetry code: (i)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ]

tions of the chloro and nitrile substituents with a plane-to-plane angle of 0.23 (5)°. For a more thorough description of  $\pi$ -stacking, see Hunter & Saunders (1990) and Lueckheide *et al.* (2013).

Notably, there are no significant Cl $\cdots$ Cl contacts in (I) or (II), in contrast to 2-chloropyridine-4-carbonitrile (CSD refcode LOBVIJ), which exhibits a Cl $\cdots$ Cl contact distance of 3.371 Å that is shorter than the sum of the van der Waals radius of chlorine (3.5 Å; Bondi, 1964). For more information on halide-halide contacts, see Pedireddi *et al.* (1994) and Jelsch *et al.* (2015).

#### 4. Synthesis and crystallization

4-Chloropyridine-2-carbonitrile (97%) and 6-chloropyridine-2-carbonitrile (96%) were purchased from Aldrich Chemical Company, USA. 4-Chloropyridine-2-carbonitrile was recrystallized from 95% ethanol.

#### 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms on C atoms were included in calculated positions and refined using a riding model, with C–H = 0.95 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  of the aryl C atoms.

## Acknowledgements

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## supporting information

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## Crystal structures of 4-chloropyridine-2-carbonitrile and 6-chloropyridine-2-carbonitrile exhibit different intermolecular $\pi$ -stacking, C—H $\cdots$ N<sub>nitrile</sub> and C—H $\cdots$ N<sub>pyridine</sub> interactions

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### Computing details

For both compounds, data collection: *APEX2* (Bruker, 2013); cell refinement: *APEX2* (Bruker, 2013); data reduction: *S SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL2014* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL2014* (Sheldrick, 2008), *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008).

### (I) 4-Chloropyridine-2-carbonitrile

#### Crystal data

C <sub>6</sub> H <sub>3</sub> ClN <sub>2</sub>	$F(000) = 280$
$M_r = 138.55$	$D_x = 1.524 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 3.813 (5) \text{ \AA}$	Cell parameters from 3637 reflections
$b = 14.047 (19) \text{ \AA}$	$\theta = 2.9\text{--}30.3^\circ$
$c = 11.356 (15) \text{ \AA}$	$\mu = 0.52 \text{ mm}^{-1}$
$\beta = 96.806 (19)^\circ$	$T = 125 \text{ K}$
$V = 604.0 (14) \text{ \AA}^3$	Plate, colourless
$Z = 4$	$0.25 \times 0.10 \times 0.04 \text{ mm}$

#### Data collection

Bruker APEXII CCD diffractometer	12191 measured reflections
Radiation source: fine-focus sealed tube	1852 independent reflections
Graphite monochromator	1498 reflections with $I > 2\sigma(I)$
Detector resolution: 8.3333 pixels $\text{mm}^{-1}$	$R_{\text{int}} = 0.063$
$\varphi$ and $\omega$ scans	$\theta_{\text{max}} = 30.6^\circ$ , $\theta_{\text{min}} = 2.3^\circ$
Absorption correction: multi-scan ( <i>SADABS</i> ; Bruker, 2013)	$h = -5 \rightarrow 5$
$T_{\text{min}} = 0.67$ , $T_{\text{max}} = 0.98$	$k = -20 \rightarrow 19$
	$l = -16 \rightarrow 16$

#### Refinement

Refinement on $F^2$	82 parameters
Least-squares matrix: full	0 restraints
$R[F^2 > 2\sigma(F^2)] = 0.050$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.135$	H-atom parameters constrained
$S = 1.12$	
1852 reflections	

$$w = 1/[\sigma^2(F_o^2) + (0.0646P)^2 + 0.4268P]$$

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

$$\Delta\rho_{\max} = 0.53 \text{ e } \text{\AA}^{-3}$$

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

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl	0.27576 (14)	0.79489 (4)	0.15624 (5)	0.02207 (17)
N1	0.0055 (5)	0.52050 (12)	0.33977 (16)	0.0197 (4)
N2	-0.4067 (5)	0.39592 (13)	0.09730 (18)	0.0253 (4)
C1	-0.2642 (5)	0.45592 (15)	0.15388 (19)	0.0204 (4)
C2	-0.0811 (5)	0.53460 (14)	0.22134 (18)	0.0173 (4)
C3	-0.0084 (5)	0.61731 (14)	0.15971 (18)	0.0177 (4)
H3A	-0.0758	0.6235	0.0768	0.021*
C4	0.1688 (5)	0.69050 (13)	0.22646 (18)	0.0163 (4)
C5	0.2634 (5)	0.67930 (15)	0.34888 (18)	0.0192 (4)
H5A	0.383	0.7283	0.3953	0.023*
C6	0.1748 (6)	0.59298 (15)	0.40037 (19)	0.0207 (4)
H6A	0.2382	0.5851	0.4832	0.025*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl	0.0217 (3)	0.0212 (3)	0.0227 (3)	-0.00411 (18)	0.00040 (18)	0.00357 (18)
N1	0.0200 (8)	0.0197 (8)	0.0191 (9)	0.0004 (6)	0.0016 (7)	0.0014 (7)
N2	0.0261 (9)	0.0245 (9)	0.0247 (10)	-0.0046 (7)	0.0003 (8)	-0.0011 (7)
C1	0.0176 (9)	0.0218 (9)	0.0216 (10)	0.0002 (7)	0.0019 (8)	0.0027 (8)
C2	0.0141 (8)	0.0180 (9)	0.0199 (10)	0.0012 (7)	0.0021 (7)	-0.0016 (7)
C3	0.0161 (9)	0.0217 (9)	0.0153 (9)	-0.0004 (7)	0.0020 (7)	-0.0001 (7)
C4	0.0144 (8)	0.0169 (8)	0.0180 (9)	0.0012 (7)	0.0032 (7)	0.0018 (7)
C5	0.0185 (9)	0.0201 (9)	0.0185 (10)	0.0003 (7)	0.0002 (8)	-0.0024 (7)
C6	0.0236 (10)	0.0230 (10)	0.0152 (9)	0.0012 (8)	0.0020 (8)	-0.0004 (7)

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

Cl—C4	1.740 (3)	C3—C4	1.402 (3)
N1—C6	1.350 (3)	C3—H3A	0.95
N1—C2	1.361 (3)	C4—C5	1.403 (3)
N2—C1	1.156 (3)	C5—C6	1.405 (3)
C1—C2	1.473 (3)	C5—H5A	0.95
C2—C3	1.401 (3)	C6—H6A	0.95
C6—N1—C2	116.07 (19)	C3—C4—Cl	119.61 (18)

N2—C1—C2	177.6 (2)	C5—C4—C1	120.11 (16)
N1—C2—C3	125.12 (19)	C4—C5—C6	117.58 (19)
N1—C2—C1	116.70 (19)	C4—C5—H5A	121.2
C3—C2—C1	118.2 (2)	C6—C5—H5A	121.2
C2—C3—C4	116.7 (2)	N1—C6—C5	124.3 (2)
C2—C3—H3A	121.7	N1—C6—H6A	117.9
C4—C3—H3A	121.7	C5—C6—H6A	117.9
C3—C4—C5	120.27 (19)		
C6—N1—C2—C3	-0.1 (3)	C2—C3—C4—C1	178.93 (15)
C6—N1—C2—C1	179.66 (19)	C3—C4—C5—C6	0.1 (3)
N1—C2—C3—C4	0.3 (3)	C1—C4—C5—C6	-179.07 (16)
C1—C2—C3—C4	-179.48 (18)	C2—N1—C6—C5	-0.1 (3)
C2—C3—C4—C5	-0.3 (3)	C4—C5—C6—N1	0.1 (3)

*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>
C3—H3A···N2 <sup>i</sup>	0.95	2.64	3.462 (5)	146
C6—H6A···N1 <sup>ii</sup>	0.95	2.75	3.493 (5)	136

Symmetry codes: (i)  $-x-1, -y+1, -z$ ; (ii)  $-x, -y+1, -z+1$ .**(II) 6-Chloropyridine-2-carbonitrile***Crystal data*C<sub>6</sub>H<sub>3</sub>ClN<sub>2</sub> $M_r = 138.55$ Monoclinic,  $P2_1/n$  $a = 6.1739$  (15) Å $b = 15.238$  (4) Å $c = 7.0123$  (18) Å $\beta = 112.492$  (4)° $V = 609.5$  (3) Å<sup>3</sup> $Z = 4$  $F(000) = 280$  $D_x = 1.510$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 9960 reflections

 $\theta = 2.7$ – $30.5$ ° $\mu = 0.52$  mm<sup>-1</sup> $T = 125$  K

Plate, colourless

 $0.20 \times 0.15 \times 0.03$  mm*Data collection*

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.3333 pixels mm<sup>-1</sup> $\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(SADABS; Bruker, 2013)

 $T_{\min} = 0.82$ ,  $T_{\max} = 0.98$ 

15460 measured reflections

1868 independent reflections

1657 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.031$  $\theta_{\max} = 30.6$ °,  $\theta_{\min} = 2.7$ ° $h = -8 \rightarrow 8$  $k = -21 \rightarrow 21$  $l = -10 \rightarrow 9$ *Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.028$  $wR(F^2) = 0.082$  $S = 1.09$ 

1868 reflections

82 parameters

0 restraints



Hydrogen site location: inferred from  
neighbouring sites  
H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 0.1697P]$$

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

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

$$\Delta\rho_{\max} = 0.48 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$$

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl	1.01050 (5)	0.09596 (2)	0.82065 (4)	0.02803 (10)
N1	0.98012 (14)	0.26545 (6)	0.82258 (13)	0.01720 (17)
N2	1.10287 (19)	0.47889 (7)	0.79286 (18)	0.0351 (2)
C1	1.00059 (18)	0.41966 (8)	0.81170 (17)	0.0232 (2)
C2	0.87412 (16)	0.34169 (7)	0.83298 (15)	0.01728 (19)
C3	0.66223 (17)	0.34787 (7)	0.85770 (15)	0.0198 (2)
H3A	0.5958	0.4032	0.8664	0.024*
C4	0.55044 (17)	0.26976 (8)	0.86928 (16)	0.0210 (2)
H4A	0.4041	0.271	0.8846	0.025*
C5	0.65405 (17)	0.19009 (7)	0.85828 (15)	0.0205 (2)
H5A	0.5818	0.1359	0.8659	0.025*
C6	0.86897 (17)	0.19295 (7)	0.83550 (15)	0.01759 (19)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl	0.03124 (16)	0.02096 (15)	0.03084 (16)	0.00422 (9)	0.01070 (11)	-0.00400 (9)
N1	0.0135 (3)	0.0212 (4)	0.0168 (4)	-0.0004 (3)	0.0058 (3)	-0.0014 (3)
N2	0.0343 (5)	0.0294 (5)	0.0430 (6)	-0.0068 (4)	0.0164 (5)	0.0013 (4)
C1	0.0207 (5)	0.0237 (5)	0.0250 (5)	0.0006 (4)	0.0085 (4)	-0.0006 (4)
C2	0.0148 (4)	0.0199 (4)	0.0167 (4)	-0.0007 (3)	0.0055 (3)	-0.0001 (3)
C3	0.0154 (4)	0.0238 (5)	0.0204 (4)	0.0035 (3)	0.0071 (3)	0.0010 (4)
C4	0.0135 (4)	0.0317 (5)	0.0187 (4)	-0.0012 (4)	0.0072 (3)	0.0010 (4)
C5	0.0182 (4)	0.0246 (5)	0.0186 (4)	-0.0051 (3)	0.0068 (3)	0.0004 (4)
C6	0.0175 (4)	0.0193 (4)	0.0151 (4)	0.0004 (3)	0.0052 (3)	-0.0012 (3)

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

Cl—C6	1.7402 (11)	C3—C4	1.3938 (15)
N1—C6	1.3218 (13)	C3—H3A	0.95
N1—C2	1.3490 (13)	C4—C5	1.3881 (16)
N2—C1	1.1378 (16)	C4—H4A	0.95
C1—C2	1.4604 (15)	C5—C6	1.3965 (14)
C2—C3	1.3870 (14)	C5—H5A	0.95

C6—N1—C2	116.15 (9)	C5—C4—H4A	120.2
N2—C1—C2	177.99 (12)	C3—C4—H4A	120.2
N1—C2—C3	124.44 (9)	C4—C5—C6	117.21 (9)
N1—C2—C1	113.94 (9)	C4—C5—H5A	121.4
C3—C2—C1	121.62 (9)	C6—C5—H5A	121.4
C2—C3—C4	117.46 (9)	N1—C6—C5	125.09 (9)
C2—C3—H3A	121.3	N1—C6—Cl	114.83 (8)
C4—C3—H3A	121.3	C5—C6—Cl	120.07 (8)
C5—C4—C3	119.65 (9)		
C6—N1—C2—C3	0.62 (14)	C3—C4—C5—C6	-0.07 (15)
C6—N1—C2—C1	-178.24 (8)	C2—N1—C6—C5	0.12 (15)
N1—C2—C3—C4	-1.03 (15)	C2—N1—C6—Cl	179.80 (7)
C1—C2—C3—C4	177.74 (9)	C4—C5—C6—N1	-0.38 (15)
C2—C3—C4—C5	0.71 (15)	C4—C5—C6—Cl	179.96 (7)

*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>
C4—H4A $\cdots$ N1 <sup>i</sup>	0.95	2.49	3.4099 (15)	164
C5—H5A $\cdots$ N2 <sup>ii</sup>	0.95	2.70	3.5651 (17)	152

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