

2,6-Dichloropyridine-3,5-dicarbonitrile

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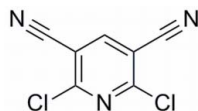
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Key indicators: single-crystal X-ray study; $T = 297$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.067; wR factor = 0.133; data-to-parameter ratio = 13.0.

In the crystal, essentially planar (r.m.s. deviation = 0.003 Å) molecules of the title compound, $\text{C}_7\text{HCl}_2\text{N}_3$, form chains along the b axis by means of $\text{C}-\text{H}\cdots\text{N}$ interactions. These chains are further linked into layers parallel to the ab plane by $\text{C}-\text{Cl}\cdots\text{N}$ interactions.

Related literature

For the structures of related pyridine derivatives, see: Boer *et al.* (1972); Clegg *et al.* (1997); Julia *et al.* (1983); Schlosser *et al.* (2006); Schmidt *et al.* (2005); Smith *et al.* (2008). For more information on the synthesis of 2,6-dichloropyridine-3,5-dicarbonitrile, see: Duindam *et al.* (1993). For compounds obtained from 2,6-dichloropyridine-3,5-dicarbonitrile, see: Katz *et al.* (2005); Vilarelle *et al.* (2004).



Experimental

Crystal data

$\text{C}_7\text{HCl}_2\text{N}_3$
 $M_r = 198.01$
Orthorhombic, $Pbca$
 $a = 6.8473$ (9) Å
 $b = 12.1307$ (15) Å
 $c = 19.430$ (3) Å

$V = 1613.9$ (4) Å³
 $Z = 8$
Mo $K\alpha$ radiation
 $\mu = 0.74$ mm⁻¹
 $T = 297$ K
 $0.41 \times 0.39 \times 0.39$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\min} = 0.751$, $T_{\max} = 0.761$
10614 measured reflections
1420 independent reflections
1328 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.067$
 $wR(F^2) = 0.133$
 $S = 1.29$
1420 reflections
109 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Table 1

Intermolecular interactions (Å, °).

$D-X\cdots A$	$D-X$	$X\cdots A$	$D\cdots A$	$D-X\cdots A$
$\text{C3}-\text{H3}\cdots\text{N1}^{\text{i}}$	0.93	2.54	3.412 (5)	157
$\text{C1}-\text{Cl1}\cdots\text{N2}^{\text{ii}}$	1.71 (1)	3.24 (1)	4.820 (5)	152 (1)
$\text{C5}-\text{Cl2}\cdots\text{N3}^{\text{iii}}$	1.72 (1)	3.28 (1)	4.851 (6)	151 (1)

Symmetry codes: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, z$; (ii) $-x + \frac{5}{2}, y + \frac{1}{2}, z$; (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, z$.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg & Putz, 2006); software used to prepare material for publication: publCIF (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: YA2129).

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supplementary materials

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2,6-Dichloropyridine-3,5-dicarbonitrile

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Comment

Some pyridine derivatives are known to be important intermediates in pharmaceutical and medicinal chemistry. They can be used for the synthesis of various compounds having antibacterial, antianaphilactic, antipyretic, antiallergic or anticancer properties (Vilarelle *et al.*, 2004). Lately, pyridine derivatives were used in the synthesis of cage molecules, supramolecular structures which are important as tools for the study of molecular encapsulation and host–guest interactions (Katz *et al.*, 2005).

Relatively few crystal structures of pyridines substituted in positions 2 and 6 with chlorine atoms were published (Boer *et al.*, 1972; Clegg *et al.*, 1997; Julia *et al.*, 1983; Schlosser *et al.*, 2006; Schmidt *et al.*, 2005; Smith *et al.*, 2008). The synthesis of the title compound has been reported some years ago (Duindam *et al.*, 1993), however its crystal structure has not yet been determined, even though electron withdrawing CN groups, causing considerable acidity of the H atom in position 4, as well as chlorine substituents at the pyridine atoms adjacent to the endocyclic N atom, may give rise to important non-conventional intermolecular interactions. Therefore, one may expect that structural study of the title compound may provide some non-trivial information.

Molecule of the title compound (Fig. 1) is essentially planar; the N2 and N3 atoms deviate from the pyridine plane by 0.060 (4) Å and 0.026 (4) Å respectively.

The molecules are linked by means of C3—H3···N1ⁱ interactions (Table 1) into infinite chains running along the *b* axis. The pyridine rings in the adjacent molecules of these chains are not coplanar, but rather form substantial dihedral angle with one another [56.5 (1)°]. The chains are further linked *via* C1—C11···N2ⁱⁱ and C5—C12···N3ⁱⁱⁱ interactions into layers parallel to the *ab*-plane (Table 1; Fig. 2).

Experimental

A mixture of malononitrile (5 g, 75.69 mmol, 2 equiv.), triethyl orthoformate (5.61 g, 37.84 mmol, 1 equiv.) and pyridine (2.99 g, 37.84 mmol, 1 equiv.) was allowed to reflux for 20 minutes, then concentrated HCl was added at 80°C. The mixture was cooled to room temperature and water (20 ml) was added. The formed precipitate was collected by filtration, washed successively with water, ethanol and diethylether to afford the intermediate 2-amino-6-chloropyridine-3,5-dicarbonitrile (9.74 g, 96%). To a solution of 2-amino-6-chloropyridine-3,5-dicarbonitrile (3 g, 16.8 mmol, 1 equiv.) and CuCl₂ (3.39 g, 25.2 mmol, 1.5 equiv.) in dry CH₃CN (150 ml), isopentyl nitrite was added (2.95 g, 25.2 mmol, 1.5 equiv.). The mixture was heated at 65°C for 5 h. The solution was acidified (HCl, 2 N) to pH=3, extracted with CH₂Cl₂ (3×50 ml) and dried with Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography using CH₂Cl₂ as eluent to yield 2,6-dichloropyridine-3,5-dicarbonitrile as a colourless solid (2.97 g, 89%). The crystals were obtained by slow evaporation of the solvent from solution of the title compound in dichloromethane.

Refinement

The H3 atom was placed in calculated position ($C-H = 0.93 \text{ \AA}$) and treated in the subsequent refinement using the riding model approximation with $U_{\text{iso}} = 1.2U_{\text{eq}}(C)$.

Figures

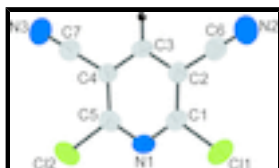


Fig. 1. Molecular structure of the title compound; displacement ellipsoids are drawn at the 50% probability level, and the H3 atom is shown as a circle of arbitrary small radius.

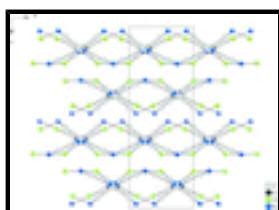


Fig. 2. Packing diagram for the crystal of the title compound viewed down the b axis. The $C-H \cdots N$ and $Cl \cdots N$ interactions are shown as dashed lines.

2,6-Dichloropyridine-3,5-dicarbonitrile

Crystal data

$C_7HCl_2N_3$

$M_r = 198.01$

Orthorhombic, $Pbca$

Hall symbol: $-P\ 2ac\ 2ab$

$a = 6.8473\ (9)\ \text{\AA}$

$b = 12.1307\ (15)\ \text{\AA}$

$c = 19.430\ (3)\ \text{\AA}$

$V = 1613.9\ (4)\ \text{\AA}^3$

$Z = 8$

$F(000) = 784$

$D_x = 1.630\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 4078 reflections

$\theta = 3.1\text{--}26.1^\circ$

$\mu = 0.74\ \text{mm}^{-1}$

$T = 297\ \text{K}$

Block, colourless

$0.41 \times 0.39 \times 0.39\ \text{mm}$

Data collection

Bruker SMART APEX CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

phi and ω scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2000)

$T_{\text{min}} = 0.751$, $T_{\text{max}} = 0.761$

10614 measured reflections

1420 independent reflections

1328 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.049$

$\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 2.1^\circ$

$h = -8 \rightarrow 8$

$k = -14 \rightarrow 14$

$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.067$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.133$	H-atom parameters constrained
$S = 1.29$	$w = 1/[\sigma^2(F_o^2) + (0.0317P)^2 + 2.8365P]$
1420 reflections	where $P = (F_o^2 + 2F_c^2)/3$
109 parameters	$(\Delta/\sigma)_{\max} < 0.001$
0 restraints	$\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$

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.

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.9151 (5)	0.3589 (3)	0.4007 (2)	0.0375 (9)
C2	0.8734 (5)	0.2479 (3)	0.40946 (19)	0.0364 (9)
C3	0.7015 (5)	0.2084 (3)	0.38179 (18)	0.0368 (9)
H3	0.6687	0.1343	0.3861	0.044*
C4	0.5791 (5)	0.2801 (3)	0.34764 (18)	0.0332 (8)
C5	0.6383 (6)	0.3884 (3)	0.34168 (19)	0.0390 (9)
C6	1.0034 (6)	0.1770 (4)	0.4467 (2)	0.0474 (10)
C7	0.3992 (6)	0.2425 (3)	0.3184 (2)	0.0438 (10)
Cl1	1.12351 (16)	0.41416 (10)	0.43512 (6)	0.0578 (4)
Cl2	0.49486 (18)	0.48205 (10)	0.29881 (6)	0.0604 (4)
N1	0.8014 (5)	0.4280 (3)	0.36795 (16)	0.0404 (8)
N2	1.1049 (6)	0.1222 (3)	0.4775 (2)	0.0683 (12)
N3	0.2550 (6)	0.2128 (4)	0.29590 (19)	0.0630 (11)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.033 (2)	0.040 (2)	0.039 (2)	-0.0043 (18)	0.0058 (17)	-0.0067 (17)

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C2	0.035 (2)	0.0368 (19)	0.0372 (19)	0.0031 (18)	-0.0002 (16)	-0.0039 (17)
C3	0.042 (2)	0.0271 (18)	0.041 (2)	-0.0021 (17)	0.0037 (18)	-0.0046 (16)
C4	0.0343 (19)	0.0314 (19)	0.0339 (19)	0.0003 (16)	0.0020 (16)	-0.0033 (15)
C5	0.041 (2)	0.037 (2)	0.039 (2)	0.0048 (18)	0.0058 (18)	0.0025 (17)
C6	0.048 (2)	0.047 (2)	0.048 (2)	0.003 (2)	-0.003 (2)	-0.009 (2)
C7	0.048 (2)	0.041 (2)	0.042 (2)	-0.001 (2)	-0.003 (2)	-0.0012 (18)
C11	0.0412 (6)	0.0622 (7)	0.0699 (8)	-0.0128 (5)	-0.0045 (5)	-0.0138 (6)
C12	0.0611 (7)	0.0487 (6)	0.0714 (8)	0.0081 (6)	-0.0105 (6)	0.0191 (5)
N1	0.0417 (19)	0.0334 (17)	0.0461 (19)	-0.0030 (15)	0.0061 (16)	-0.0011 (15)
N2	0.067 (3)	0.064 (3)	0.074 (3)	0.025 (2)	-0.020 (2)	-0.007 (2)
N3	0.054 (2)	0.075 (3)	0.060 (2)	-0.014 (2)	-0.013 (2)	0.002 (2)

Geometric parameters (Å, °)

C1—N1	1.309 (5)	C4—C5	1.380 (5)
C1—C2	1.387 (5)	C4—C7	1.430 (5)
C1—C11	1.713 (4)	C5—N1	1.319 (5)
C2—C3	1.380 (5)	C5—C12	1.717 (4)
C2—C6	1.434 (6)	C6—N2	1.133 (5)
C3—C4	1.378 (5)	C7—N3	1.139 (5)
C3—H3	0.9300		
N1—C1—C2	124.0 (4)	C3—C4—C5	117.6 (3)
N1—C1—C11	115.8 (3)	C3—C4—C7	120.9 (3)
C2—C1—C11	120.2 (3)	C5—C4—C7	121.6 (3)
C3—C2—C1	117.7 (3)	N1—C5—C4	124.3 (4)
C3—C2—C6	121.2 (4)	N1—C5—C12	115.5 (3)
C1—C2—C6	121.1 (4)	C4—C5—C12	120.2 (3)
C4—C3—C2	119.1 (3)	N2—C6—C2	178.4 (5)
C4—C3—H3	120.4	N3—C7—C4	179.2 (5)
C2—C3—H3	120.4	C1—N1—C5	117.3 (3)
N1—C1—C2—C3	0.1 (6)	C3—C4—C5—N1	-1.8 (6)
C11—C1—C2—C3	178.7 (3)	C7—C4—C5—N1	179.4 (4)
N1—C1—C2—C6	-179.2 (4)	C3—C4—C5—C12	179.1 (3)
C11—C1—C2—C6	-0.6 (5)	C7—C4—C5—C12	0.3 (5)
C1—C2—C3—C4	-0.6 (5)	C2—C1—N1—C5	-0.3 (6)
C6—C2—C3—C4	178.7 (4)	C11—C1—N1—C5	-179.0 (3)
C2—C3—C4—C5	1.4 (5)	C4—C5—N1—C1	1.2 (6)
C2—C3—C4—C7	-179.8 (3)	C12—C5—N1—C1	-179.6 (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>
C3—H3 \cdots N1 ⁱ	0.93	2.54	3.412 (5)	157
C1—C11 \cdots N2 ⁱⁱ	1.713 (4)	3.241 (4)	4.820 (5)	151.9 (2)
C5—C12 \cdots N3 ⁱⁱⁱ	1.717 (4)	3.281 (5)	4.851 (6)	150.6 (2)

Symmetry codes: (i) $-x+3/2, y-1/2, z$; (ii) $-x+5/2, y+1/2, z$; (iii) $-x+1/2, y+1/2, z$.

Fig. 1

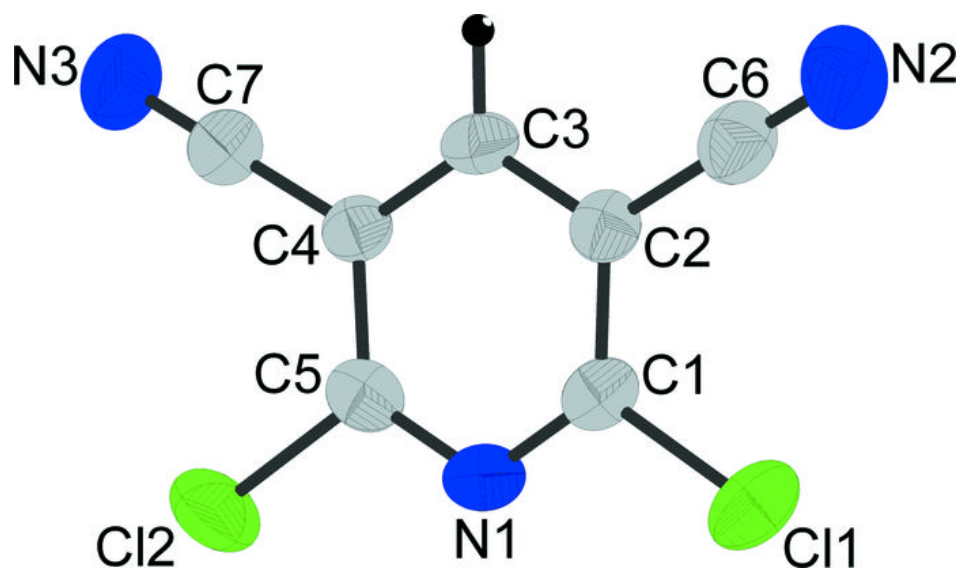


Fig. 2

