organic compounds

2-Chloro-5-nitropyridin-4-amine

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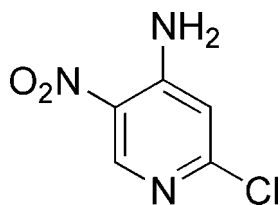Correspondence e-mail: jlheyc@163.com

The title molecule, $C_5H_4ClN_3O_2$, possesses mirror symmetry, with all of the atoms lying in the mirror plane. There is an intramolecular N—H⋯O hydrogen bond involving the adjacent –NO_2 and –NH_2 groups. A short C—H⋯O interaction is also observed. In the crystal, adjacent molecules are linked via N—H⋯Cl and N—H⋯N hydrogen bonds, forming chains propagating along [100].

Related literature

For details concerning the importance of the title compound as an intermediate in organic synthesis, and for the synthetic procedure, see: Hu et al. (2011). For bond-length data, see: Allen et al. (1987).

Experimental

Crystal data

$C_5H_4ClN_3O_2$	b = 6.2782 (10) Å
M_r = 173.5	c = 7.3018 (12) Å
Orthorhombic, $Pnma$	V = 669.11 (18) Å^3
a = 14.596 (2) Å	Z = 4

Mo $K\alpha$ radiation	T = 296 K
μ = 0.52 mm^{-1}	$0.18 \times 0.17 \times 0.15$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	663 independent reflections
Absorption correction: multi-scan (North et al., 1968)	625 reflections with $I > 2\sigma(I)$
T_{min} = 0.913, T_{max} = 0.927	R_{int} = 0.034
3496 measured reflections	3 standard reflections every 200 reflections
	intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028	67 parameters
$wR(F^2)$ = 0.082	H-atom parameters constrained
S = 1.16	$\Delta\rho_{max}$ = 0.21 e Å^{-3}
663 reflections	$\Delta\rho_{min}$ = −0.35 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2B⋯O2	0.85	2.06	2.673 (3)	128
C5—H5⋯O1	0.93	2.34	2.682 (2)	101
N2—H2A⋯Cl1^i	0.80	2.77	3.3023 (18)	126
N2—H2B⋯N1^i	0.85	2.61	3.213 (2)	128

Symmetry code: (i) $x, y, z − 1$.

Data collection: CAD-4 Software (Enraf–Nonius, 1985); cell refinement: CAD-4 Software; data reduction: XCAD4 (Harms & Wocadlo, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2408).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). J. Chem. Soc. Perkin Trans. 2, pp. S1–19.
Enraf–Nonius (1985). CAD-4 Software. Enraf–Nonius, Delft, The Netherlands.
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Comment

The title compound is an important nitropyridine compound which is widely used in organic synthesis, especially in the synthesis of heterocyclic drugs and cytokine inhibitors (Hu *et al.*, 2011).

The molecular structure of the title compound is shown in Fig. 1. The molecule lies in a mirror plane. In the molecule there is an N-H···O hydrogen bond involving the adjacent NO_2 and NH_2 groups (Table 1). A short C-H···O interaction is also observed. The bond lengths (Allen *et al.*, 1987) and angles are within normal ranges.

In the crystal, adjacent molecules are linked via N–H···Cl and N–H···N hydrogen bonds so forming chains propagating along the a axis direction. (Table 1 and Fig. 2).

Experimental

The title compound was prepared by the literature procedure (Hu *et al.*, 2011). To a solution of *tert*-butyl 2-chloro-5-nitropyridin-4-ylcarbamate (5 g, 18.3 mmol) in dichloromethane (30 ml) in a 100 mL flask was added slowly a solution of trifluoroaceticacid (10 ml). After being stirred for 4 h at the room temperature, the solvent was evaporated on a rotary evaporator. The pH of the remaining mixture was then adjusted to 7 with saturated sodium bicarbonate solution, giving the title compound. Colourless block-like crytsals were grown in ethanol (30 ml) by evaporating the solvent slowly at room temperature for about 8 d.

Refinement

The NH H atoms were located in a difference Fourier map and were treated as riding atoms. The C-bound H-atoms were included in calculated positions and treated as riding atoms: C-H = 0.93 Å. For all H atoms $U_{iso}(H) = 1.2U_{eq}(N,C)$.

Computing details

Data collection: *CAD-4 Software* (Enraf–Nonius, 1985); cell refinement: *CAD-4 Software* (Enraf–Nonius, 1985); data reduction: *XCAD4* (Harms & Wocadlo,1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).
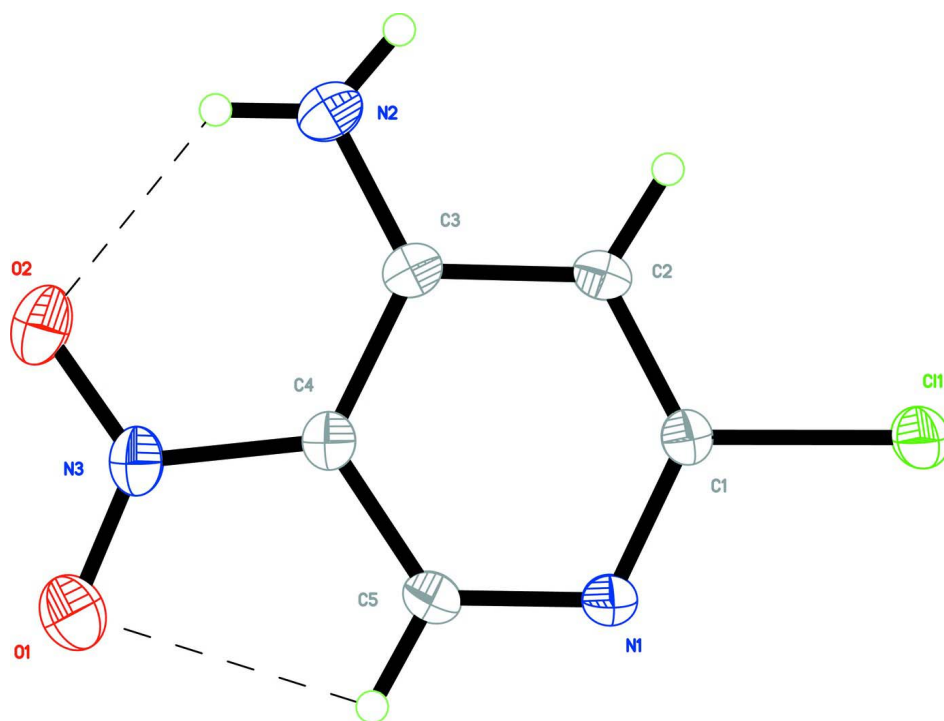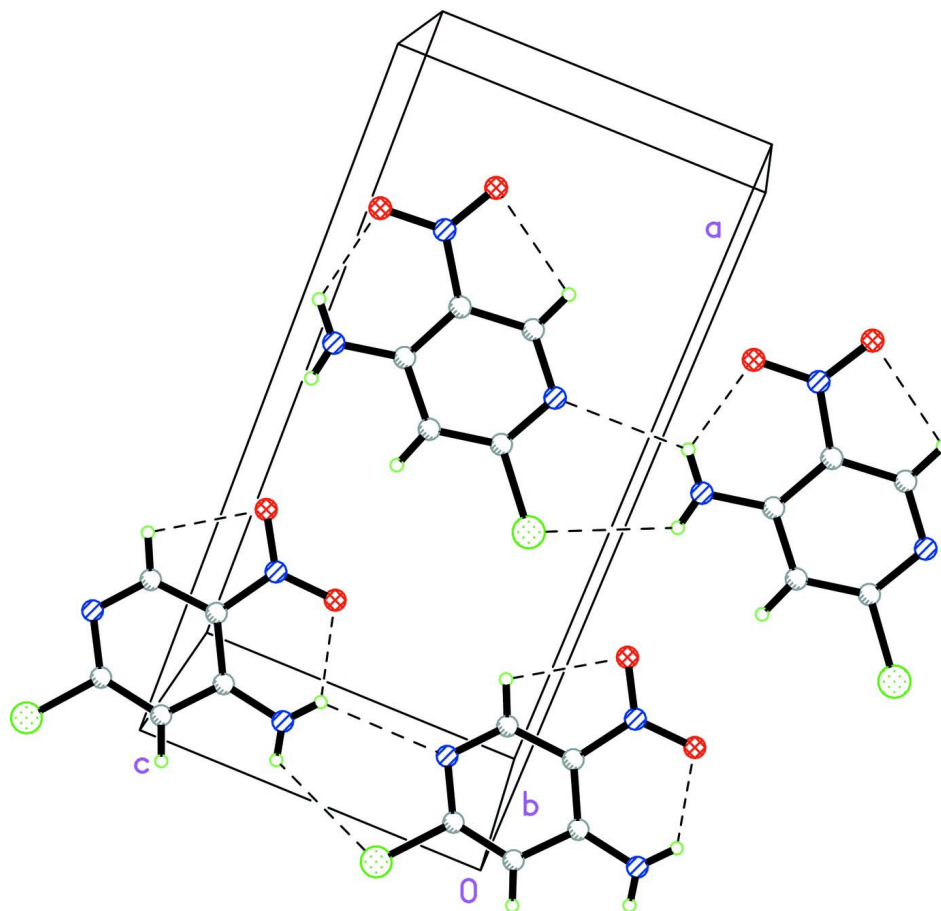
Figure 1

The molecular structure of the title molecule, with the atom-numbering. Displacement ellipsoids are drawn at the 50% probability level.

Figure 2

A view along the b axis of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines [H atoms not involved in hydrogen bonding have been omitted for clarity].

2-Chloro-5-nitropyridin-4-amine

Crystal data

$C_5H_4ClN_3O_2$	$F(000) = 352$
$M_r = 173.5$	$D_x = 1.723$ Mg m^{-3}
Orthorhombic, *Pnma*	Mo *Kα* radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ac 2n	Cell parameters from 2718 reflections
$a = 14.596$ (2) Å	$\theta = 2.8–29.8°$
$b = 6.2782$ (10) Å	$\mu = 0.52$ mm^{-1}
$c = 7.3018$ (12) Å	$T = 296$ K
$V = 669.11$ (18) Å^3	Block, colourless
$Z = 4$	$0.18 \times 0.17 \times 0.15$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	Absorption correction: multi-scan (North *et al.*, 1968)
Radiation source: fine-focus sealed tube	$T_{min} = 0.913$, $T_{max} = 0.927$
Graphite monochromator	3496 measured reflections
$\omega/2\theta$ scans	663 independent reflections
	625 reflections with $I > 2\sigma(I)$

$R_{int} = 0.034$

$\theta_{max} = 25.2°$, $\theta_{min} = 2.8°$

$h = -17→17$

$k = -6→7$

$l = -8→7$

3 standard reflections every 200 reflections

intensity decay: 1%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.028$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.082$	
$S = 1.16$	H-atom parameters constrained
663 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0499P)^2 + 0.1012P]$ where $P = (F_o^2 + 2F_c^2)/3$
67 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.21$ e Å^{-3}
	$\Delta\rho_{min} = -0.35$ e Å^{-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 (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Cl1	0.49841 (3)	0.2500	0.77100 (7)	0.0475 (2)
O1	0.10325 (10)	0.2500	0.3741 (2)	0.0610 (5)
O2	0.18179 (10)	0.2500	0.12421 (19)	0.0495 (4)
N1	0.32242 (10)	0.2500	0.70422 (19)	0.0329 (4)
N2	0.36482 (14)	0.2500	0.1360 (2)	0.0492 (5)
H2A	0.4186	0.2500	0.1145	0.059*
H2B	0.3196	0.2500	0.0623	0.059*
N3	0.17674 (11)	0.2500	0.2932 (2)	0.0377 (4)
C1	0.40493 (11)	0.2500	0.6229 (2)	0.0317 (4)
C2	0.42218 (12)	0.2500	0.4395 (2)	0.0350 (4)
H2	0.4821	0.2500	0.3964	0.042*
C3	0.34767 (13)	0.2500	0.3155 (3)	0.0329 (4)
C4	0.26029 (11)	0.2500	0.3989 (2)	0.0311 (4)
C5	0.25209 (11)	0.2500	0.5895 (2)	0.0330 (4)
H5	0.1934	0.2500	0.6392	0.040*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0280 (3)	0.0797 (4)	0.0347 (4)	0.000	−0.00544 (16)	0.000
O1	0.0275 (8)	0.0978 (12)	0.0575 (10)	0.000	−0.0049 (7)	0.000
O2	0.0551 (9)	0.0551 (8)	0.0384 (8)	0.000	−0.0163 (7)	0.000

N1	0.0277 (8)	0.0446 (8)	0.0264 (8)	0.000	0.0025 (5)	0.000
N2	0.0451 (10)	0.0759 (12)	0.0266 (9)	0.000	0.0030 (7)	0.000
N3	0.0346 (9)	0.0395 (8)	0.0390 (10)	0.000	−0.0097 (7)	0.000
C1	0.0261 (8)	0.0403 (9)	0.0288 (8)	0.000	−0.0020 (6)	0.000
C2	0.0262 (8)	0.0479 (10)	0.0310 (9)	0.000	0.0059 (7)	0.000
C3	0.0359 (10)	0.0355 (8)	0.0272 (8)	0.000	0.0020 (7)	0.000
C4	0.0296 (9)	0.0327 (8)	0.0311 (9)	0.000	−0.0026 (7)	0.000
C5	0.0258 (9)	0.0397 (9)	0.0333 (10)	0.000	0.0046 (6)	0.000

Geometric parameters (Å, º)

Cl1—C1	1.7410 (16)	N3—C4	1.443 (2)
O1—N3	1.225 (2)	C1—C2	1.363 (2)
O2—N3	1.236 (2)	C2—C3	1.415 (3)
N1—C5	1.325 (2)	C2—H2	0.9300
N1—C1	1.343 (2)	C3—C4	1.413 (2)
N2—C3	1.335 (3)	C4—C5	1.397 (3)
N2—H2A	0.8009	C5—H5	0.9300
N2—H2B	0.8515		
C5—N1—C1	114.55 (14)	C1—C2—H2	120.4
C3—N2—H2A	112.1	C3—C2—H2	120.4
C3—N2—H2B	118.4	N2—C3—C4	126.34 (18)
H2A—N2—H2B	129.5	N2—C3—C2	118.97 (16)
O1—N3—O2	122.27 (16)	C4—C3—C2	114.70 (16)
O1—N3—C4	118.81 (16)	C5—C4—C3	120.44 (16)
O2—N3—C4	118.92 (16)	C5—C4—N3	117.42 (15)
N1—C1—C2	126.90 (15)	C3—C4—N3	122.14 (17)
N1—C1—Cl1	115.35 (12)	N1—C5—C4	124.29 (14)
C2—C1—Cl1	117.75 (13)	N1—C5—H5	117.9
C1—C2—C3	119.13 (16)	C4—C5—H5	117.9

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*B*···O2	0.85	2.06	2.673 (3)	128
C5—H5···O1	0.93	2.34	2.682 (2)	101
N2—H2*A*···Cl1[i]	0.80	2.77	3.3023 (18)	126
N2—H2*B*···N1[i]	0.85	2.61	3.213 (2)	128

Symmetry code: (i) *x*, *y*, *z*−1.