Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

7-Chloro-5-(chloromethyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile

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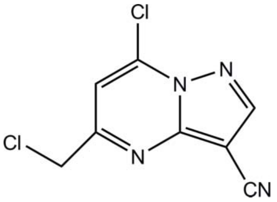
Received 23 February 2012; accepted 18 March 2012

Key indicators: single-crystal X-ray study; *T* = 301 K; mean σ(C–C) = 0.003 Å; *R* factor = 0.038; *wR* factor = 0.104; data-to-parameter ratio = 16.6.

All non-H atoms of the title compound, $C_8H_4Cl_2N_4$, are essentially coplanar, with an r.m.s. deviation of 0.011 Å. In the crystal, weak C—H⋯N hydrogen bonds link the molecules into infinite sheets parallel to the *bc* plane.

Related literature

For details of the synthesis, see: Li *et al.* (2006). For applications of pyrazolo[1,5-*a*]pyrimidines as pharmacophores or building blocks in anti-tumor drug design, see: Li *et al.* (2006); Di Grandi *et al.* (2009); Powell *et al.* (2007); Gopalsamy *et al.* (2005).



Experimental

Crystal data

$C_8H_4Cl_2N_4$
M_r = 227.05
Monoclinic, $P2_1/c$
a = 4.9817 (4) Å
b = 18.4025 (15) Å
c = 10.1526 (9) Å
β = 95.924 (1)°
V = 925.78 (13) Å^3
Z = 4
Mo *K*α radiation
μ = 0.66 mm^{-1}
T = 301 K
0.60 × 0.48 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.693, T_{max} = 0.879
5429 measured reflections
2111 independent reflections
1749 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.104
S = 1.04
2111 reflections
127 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C8—H8⋯N2^{i}	0.93	2.50	3.337 (3)	150
C2—H2⋯N2^{ii}	0.93	2.70	3.515 (3)	146

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; 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*.

This project was sponsored by the National Natural Science Foundation of China (No.21071022) and the Fundamental Research Funds for the Central Universities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2361).

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supplementary materials

Acta Cryst. (2012). E**68**, o1161   [doi:10.1107/S160053681201166X]

7-Chloro-5-(chloromethyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile

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Comment

Pyrazolo[1,5-*a*]pyrimidines are widely applied as important pharmacophores or building blocks in anti-tumor drug design (Di Grandi *et al.*, 2009; Powell *et al.*, 2007; Gopalsamy *et al.*, 2005; Li *et al.*, 2006). Thus, the synthesis of the title compound may lead to the development of further pyrazolo[1,5-*a*]pyrimidine derivatives as new anti-tumor drugs. Here we report the crystal structure of the title compound.

The molecular structure of the title compound is shown in Fig. 1. The complete molecule is essentially planar, except the H atoms of the methylene group. Each molecule acts as a donor and a acceptor of weak intermolecular C—H···N hydrogen-bond interactions linking the molecules into infinite sheets (Fig. 2).

Experimental

The title compound can prepared by the reaction of 5-(chloromethyl)-7-hydroxypyrazolo[1,5-*a*]pyrimidine-3-carbonitrile with phosphorus oxychloride (Li *et al.*, 2006). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of the crude product in ethyl acetate at ambient temperature.

Refinement

All H atoms attached to C atoms were fixed geometrically and treated as riding with C—H = 0.93 Å (CH) and C—H = 0.97 Å (CH_2) with $U_{iso}(H) = 1.2U_{eq}(C)$.

Computing details

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT* (Bruker, 2005); 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).

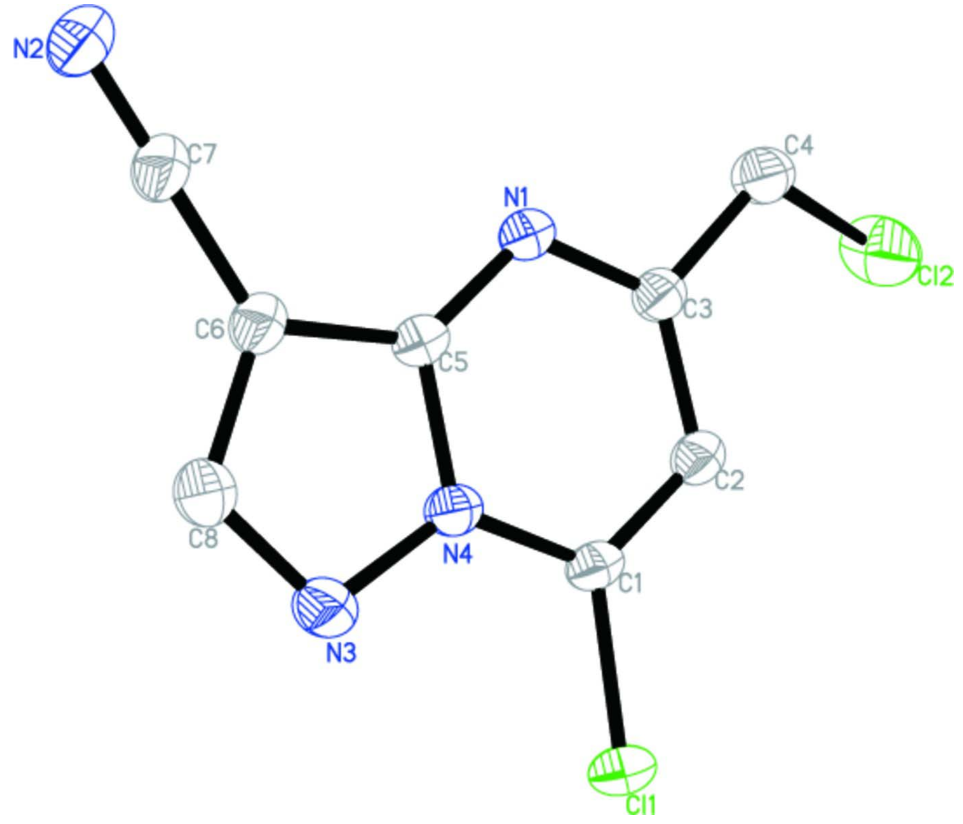

Figure 1

Molecular structure of the title compound showing displacement ellipsoids at the 45% probability level.

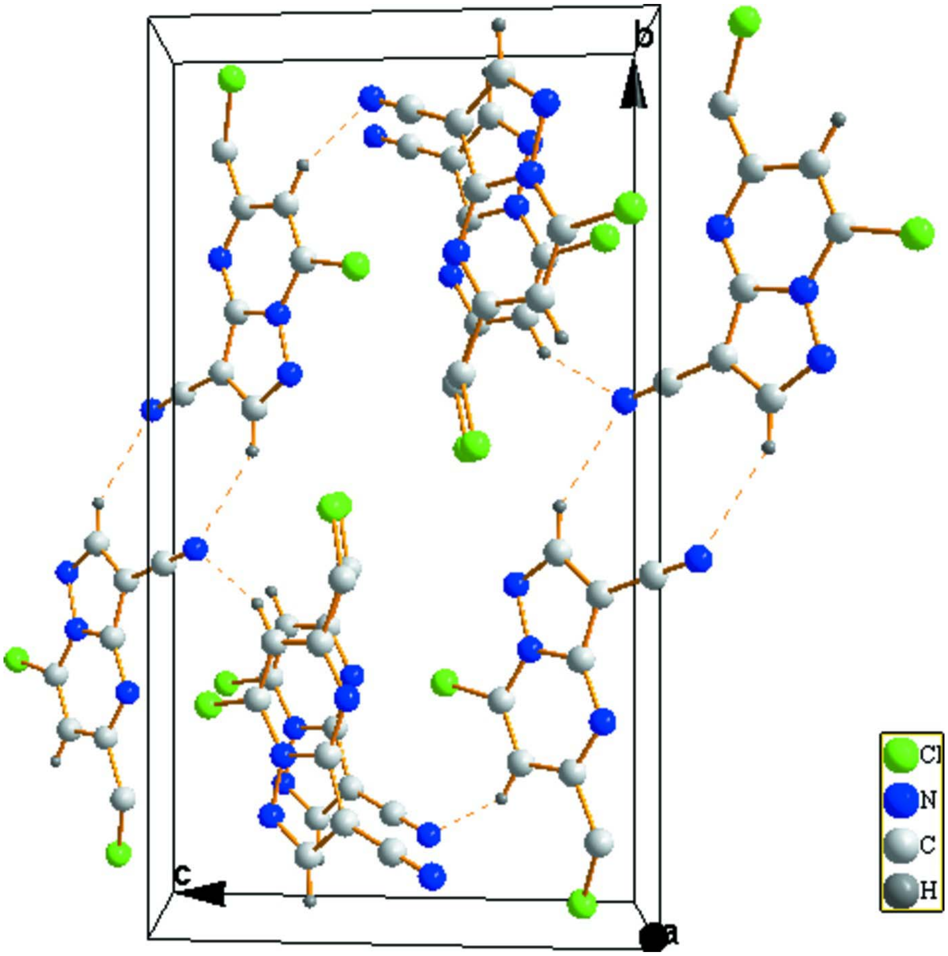

Figure 2

Packing diagram of the title compound, viewed along the *a* axis. Dashed lines indicate hydrogen bonds.

7-Chloro-5-(chloromethyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile

Crystal data

$C_8H_4Cl_2N_4$	$F(000) = 456$
$M_r = 227.05$	$D_x = 1.629$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2237 reflections
$a = 4.9817$ (4) Å	$\theta = 3.9$–$27.6°$
$b = 18.4025$ (15) Å	$\mu = 0.66$ mm^{-1}
$c = 10.1526$ (9) Å	$T = 301$ K
$\beta = 95.924$ (1)°	Block, red
$V = 925.78$ (13) Å^3	0.60 × 0.48 × 0.20 mm
$Z = 4$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
Radiation source: fine-focus sealed tube	$T_{min} = 0.693$, $T_{max} = 0.879$
Graphite monochromator	5429 measured reflections
phi and ω scans	2111 independent reflections

1749 reflections with $I > 2\sigma(I)$	$h = -6 \rightarrow 6$
$R_{\text{int}} = 0.017$	$k = -13 \rightarrow 23$
$\theta_{\text{max}} = 27.6°$, $\theta_{\text{min}} = 2.3°$	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.104$	$w = 1/[\sigma^2(F_o^2) + (0.050P)^2 + 0.3703P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2111 reflections	$\Delta\rho_{\text{max}} = 0.46$ e Å^{-3}
127 parameters	$\Delta\rho_{\text{min}} = -0.53$ e Å^{-3}
0 restraints	
Primary atom site location: structure-invariant direct methods	

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	0.32935 (9)	0.26419 (3)	0.40816 (5)	0.04533 (17)
Cl2	0.73176 (14)	0.03358 (3)	0.13931 (8)	0.0784 (3)
N1	0.9223 (3)	0.23861 (8)	0.10690 (15)	0.0376 (3)
N2	1.2065 (4)	0.41634 (10)	−0.0585 (2)	0.0636 (5)
N3	0.5932 (4)	0.38077 (9)	0.26671 (18)	0.0503 (4)
N4	0.6551 (3)	0.31043 (8)	0.24035 (15)	0.0374 (3)
C1	0.5553 (4)	0.25052 (10)	0.29599 (18)	0.0363 (4)
C2	0.6391 (4)	0.18420 (10)	0.25839 (18)	0.0390 (4)
H2	0.5762	0.1420	0.2952	0.047*
C3	0.8249 (4)	0.18073 (10)	0.16175 (18)	0.0378 (4)
C4	0.9331 (5)	0.10975 (11)	0.1153 (2)	0.0554 (6)
H4A	1.1109	0.1018	0.1615	0.066*
H4B	0.9540	0.1138	0.0216	0.066*
C5	0.8380 (3)	0.30370 (10)	0.14617 (17)	0.0352 (4)
C6	0.8930 (4)	0.37484 (10)	0.11144 (19)	0.0423 (4)
C7	1.0677 (4)	0.39787 (10)	0.0175 (2)	0.0473 (5)
C8	0.7377 (5)	0.41835 (11)	0.1879 (2)	0.0520 (5)
H8	0.7362	0.4688	0.1837	0.062*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0409 (3)	0.0559 (3)	0.0418 (3)	−0.0012 (2)	0.01678 (19)	−0.0018 (2)

Cl2	0.0764 (4)	0.0456 (3)	0.1169 (6)	−0.0135 (3)	0.0270 (4)	−0.0184 (3)
N1	0.0376 (8)	0.0389 (8)	0.0378 (8)	0.0000 (6)	0.0108 (6)	0.0019 (6)
N2	0.0747 (13)	0.0502 (11)	0.0710 (13)	−0.0039 (10)	0.0321 (11)	0.0098 (10)
N3	0.0591 (11)	0.0374 (9)	0.0574 (10)	0.0019 (8)	0.0213 (8)	−0.0043 (8)
N4	0.0381 (8)	0.0379 (8)	0.0377 (8)	−0.0003 (6)	0.0110 (6)	−0.0009 (6)
C1	0.0323 (8)	0.0449 (10)	0.0328 (8)	−0.0023 (7)	0.0089 (7)	0.0012 (7)
C2	0.0403 (9)	0.0381 (10)	0.0398 (9)	−0.0032 (8)	0.0099 (8)	0.0035 (8)
C3	0.0403 (9)	0.0364 (9)	0.0376 (9)	−0.0009 (7)	0.0075 (7)	0.0007 (7)
C4	0.0654 (14)	0.0379 (11)	0.0676 (14)	0.0002 (10)	0.0292 (11)	−0.0003 (10)
C5	0.0333 (8)	0.0391 (9)	0.0341 (9)	−0.0023 (7)	0.0078 (7)	0.0007 (7)
C6	0.0458 (10)	0.0368 (10)	0.0458 (10)	−0.0045 (8)	0.0114 (8)	0.0033 (8)
C7	0.0549 (12)	0.0360 (10)	0.0527 (12)	−0.0045 (9)	0.0137 (10)	0.0047 (9)
C8	0.0621 (13)	0.0350 (10)	0.0612 (13)	−0.0022 (9)	0.0177 (11)	−0.0011 (9)

Geometric parameters (Å, º)

Cl1—C1	1.7006 (18)	C2—C3	1.418 (2)
Cl2—C4	1.755 (2)	C2—H2	0.9300
N1—C3	1.318 (2)	C3—C4	1.507 (3)
N1—C5	1.343 (2)	C4—H4A	0.9700
N2—C7	1.139 (3)	C4—H4B	0.9700
N3—C8	1.325 (3)	C5—C6	1.390 (3)
N3—N4	1.364 (2)	C6—C8	1.402 (3)
N4—C1	1.356 (2)	C6—C7	1.421 (3)
N4—C5	1.393 (2)	C8—H8	0.9300
C1—C2	1.357 (3)		

C3—N1—C5	117.09 (15)	C3—C4—H4A	108.6
C8—N3—N4	103.25 (16)	Cl2—C4—H4A	108.6
C1—N4—N3	126.15 (15)	C3—C4—H4B	108.6
C1—N4—C5	120.50 (15)	Cl2—C4—H4B	108.6
N3—N4—C5	113.35 (15)	H4A—C4—H4B	107.5
N4—C1—C2	118.49 (16)	N1—C5—C6	133.52 (16)
N4—C1—Cl1	117.07 (14)	N1—C5—N4	121.99 (15)
C2—C1—Cl1	124.44 (14)	C6—C5—N4	104.50 (15)
C1—C2—C3	118.48 (16)	C5—C6—C8	105.24 (17)
C1—C2—H2	120.8	C5—C6—C7	126.97 (18)
C3—C2—H2	120.8	C8—C6—C7	127.79 (19)
N1—C3—C2	123.45 (17)	N2—C7—C6	179.6 (3)
N1—C3—C4	114.14 (16)	N3—C8—C6	113.67 (19)
C2—C3—C4	122.40 (16)	N3—C8—H8	123.2
C3—C4—Cl2	114.86 (15)	C6—C8—H8	123.2

C8—N3—N4—C1	−179.43 (19)	C3—N1—C5—C6	−179.6 (2)
C8—N3—N4—C5	0.3 (2)	C3—N1—C5—N4	−0.2 (3)
N3—N4—C1—C2	−179.90 (18)	C1—N4—C5—N1	0.0 (3)
C5—N4—C1—C2	0.4 (3)	N3—N4—C5—N1	−179.71 (17)
N3—N4—C1—Cl1	0.6 (3)	C1—N4—C5—C6	179.58 (16)
C5—N4—C1—Cl1	−179.05 (13)	N3—N4—C5—C6	−0.1 (2)
N4—C1—C2—C3	−0.6 (3)	N1—C5—C6—C8	179.4 (2)

Cl1—C1—C2—C3	178.78 (14)	N4—C5—C6—C8	0.0 (2)
C5—N1—C3—C2	−0.1 (3)	N1—C5—C6—C7	0.0 (4)
C5—N1—C3—C4	−178.66 (18)	N4—C5—C6—C7	−179.5 (2)
C1—C2—C3—N1	0.5 (3)	N4—N3—C8—C6	−0.3 (3)
C1—C2—C3—C4	178.98 (19)	C5—C6—C8—N3	0.2 (3)
N1—C3—C4—Cl2	−159.03 (16)	C7—C6—C8—N3	179.7 (2)
C2—C3—C4—Cl2	22.4 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···N2^{i}	0.93	2.50	3.337 (3)	150
C2—H2···N2^{ii}	0.93	2.70	3.515 (3)	146

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*; (ii) *x*−1, −*y*+1/2, *z*+1/2.