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Methyl 4,6-dichloropyridine-3-carboxylate

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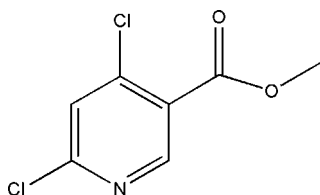
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 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.053; wR factor = 0.136; data-to-parameter ratio = 13.9.

The title compound, $\text{C}_7\text{H}_5\text{Cl}_2\text{NO}_2$, crystallizes with two independent molecules in the asymmetric unit. The bond lengths and angles in both molecules are within normal ranges. In the crystal structure, weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds link the molecules into layers parallel to the [010] plane.

Related literature

For details of the biological activity of the title compound, see: Wallace *et al.* (2006); Bondinell *et al.* (2002). For a related structure, see: McArdle *et al.* (1982).



Experimental

Crystal data

 $\text{C}_7\text{H}_5\text{Cl}_2\text{NO}_2$
 $M_r = 206.02$

 Monoclinic, $P2_1/c$
 $a = 8.033$ (4) Å

 $b = 18.974$ (9) Å
 $c = 11.240$ (6) Å
 $\beta = 95.224$ (8)°
 $V = 1705.9$ (15) Å³
 $Z = 8$

 Mo $K\alpha$ radiation
 $\mu = 0.71$ mm⁻¹
 $T = 298$ (2) K
 $0.45 \times 0.19 \times 0.06$ mm

Data collection

 Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
 $T_{\min} = 0.739$, $T_{\max} = 0.958$
 8532 measured reflections
 3012 independent reflections
 2289 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.135$
 $S = 1.08$
 3012 reflections
 217 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.25$ e Å⁻³
 $\Delta\rho_{\min} = -0.18$ e Å⁻³

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C6}-\text{H6A}\cdots\text{O3}^i$	0.93	2.41	3.309 (4)	162
$\text{C11}-\text{H11A}\cdots\text{O2}^ii$	0.93	2.60	3.513 (4)	168

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2396).

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supplementary materials

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Methyl 4,6-dichloropyridine-3-carboxylate

Y. Ma and J. Liu

Comment

Methyl 4,6-dichloropyridine-3-carboxylate is a useful intermediate for the synthesis of different kinase inhibitors (Wallace *et al.*, 2006; Bondinell *et al.*, 2002). In this paper, we report the crystal structure of the title compound (I).

Compound (I) crystallizes with two independent molecules in the asymmetric unit (Fig. 1), all bond lengths and angles are normal and in a good agreement with those reported previously (McArdle *et al.*, 1982). The dihedral angles between the planes of the methoxycarbonyl group (C1/C2/O1/O2; C8/C9/O3/O4) and pyridine rings in the two independent molecules are 10.9 (2) and 8.1 (4)°. In the crystal structure, weak intermolecular C—H···O hydrogen bonds link the molecules into layers parallel to the *b* axis.

Experimental

Methyl 4,6-dichloropyridine-3-carboxylate was synthesized from Methyl 4,6-dihydroxypyridine-3-carboxylate *via* chlorination with POCl₃. The desired compound was obtained as a low melting yellow solid in 89% yield. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution in a hexane/dichloromethane mixture (1:4 *v/v*) at room temperature over a period of one week.

Refinement

All H atoms were placed in calculated positions, with C—H = 0.93 or 0.96 Å, and included in the final cycles of refinement using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2$ times $U_{\text{eq}}(\text{C})$.

Figures

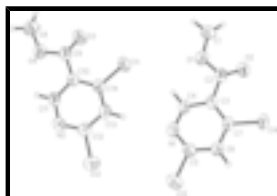


Fig. 1. View of the title compound (I), with displacement ellipsoids drawn at the 40% probability level.

Methyl 4,6-dichloropyridine-3-carboxylate

Crystal data

C₇H₅Cl₂NO₂

$M_r = 206.02$

Monoclinic, $P2_1/c$

$F_{000} = 832$

$D_x = 1.604 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

supplementary materials

Hall symbol: -P 2ybc	$\lambda = 0.71073 \text{ \AA}$
$a = 8.033 (4) \text{ \AA}$	Cell parameters from 1274 reflections
$b = 18.974 (9) \text{ \AA}$	$\theta = 2.8\text{--}27.9^\circ$
$c = 11.240 (6) \text{ \AA}$	$\mu = 0.72 \text{ mm}^{-1}$
$\beta = 95.224 (8)^\circ$	$T = 298 (2) \text{ K}$
$V = 1705.9 (15) \text{ \AA}^3$	Block, colorless
$Z = 8$	$0.45 \times 0.19 \times 0.06 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	3012 independent reflections
Radiation source: fine-focus sealed tube	2289 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.035$
$T = 298(2) \text{ K}$	$\theta_{\text{max}} = 25.0^\circ$
φ and ω scans	$\theta_{\text{min}} = 2.1^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -9 \rightarrow 9$
$T_{\text{min}} = 0.739$, $T_{\text{max}} = 0.958$	$k = -16 \rightarrow 22$
8532 measured reflections	$l = -12 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.052$	H-atom parameters constrained
$wR(F^2) = 0.135$	$w = 1/[\sigma^2(F_o^2) + (0.0645P)^2 + 0.3441P]$
$S = 1.08$	where $P = (F_o^2 + 2F_c^2)/3$
3012 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
217 parameters	$\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$
	Extinction correction: none

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	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.31475 (11)	0.33695 (5)	0.64891 (7)	0.0715 (3)
Cl4	0.81189 (12)	0.14450 (4)	1.15267 (7)	0.0730 (3)
Cl3	0.49419 (14)	0.01243 (5)	0.78099 (8)	0.0883 (4)
Cl2	0.16454 (16)	0.07877 (5)	0.49234 (11)	0.1033 (4)
O4	0.0012 (3)	0.39718 (12)	0.3185 (2)	0.0810 (7)
O1	0.6147 (3)	0.33347 (11)	0.9518 (2)	0.0761 (7)
C3	0.6515 (3)	0.21244 (15)	0.9614 (2)	0.0494 (7)
C4	0.5571 (4)	0.20765 (17)	0.8514 (3)	0.0629 (8)
H4A	0.5253	0.2497	0.8133	0.075*
O2	0.7987 (3)	0.29383 (12)	1.0946 (2)	0.0859 (8)
C6	0.6496 (4)	0.08658 (16)	0.9608 (3)	0.0586 (8)
H6A	0.6799	0.0434	0.9955	0.070*
N1	0.5088 (4)	0.14837 (15)	0.7965 (2)	0.0676 (7)
C10	0.1250 (3)	0.30967 (15)	0.4395 (2)	0.0496 (7)
C11	0.0479 (4)	0.25996 (16)	0.3617 (3)	0.0570 (8)
H11A	-0.0152	0.2765	0.2940	0.068*
C13	0.2303 (4)	0.21170 (16)	0.5586 (3)	0.0585 (8)
H13A	0.2924	0.1930	0.6251	0.070*
O3	0.1841 (4)	0.43167 (13)	0.4631 (2)	0.1010 (10)
C5	0.5558 (4)	0.09031 (17)	0.8522 (3)	0.0603 (8)
C7	0.6965 (4)	0.14869 (15)	1.0159 (2)	0.0504 (7)
C9	0.1096 (4)	0.38562 (17)	0.4109 (3)	0.0574 (8)
C1	0.6574 (6)	0.40446 (18)	0.9884 (4)	0.0940 (13)
H1B	0.5889	0.4371	0.9405	0.141*
H1C	0.7730	0.4131	0.9781	0.141*
H1D	0.6388	0.4105	1.0710	0.141*
N2	0.0578 (3)	0.19055 (14)	0.3773 (2)	0.0640 (7)
C14	0.2165 (4)	0.28322 (15)	0.5410 (2)	0.0505 (7)
C2	0.6989 (4)	0.28237 (16)	1.0116 (3)	0.0552 (7)
C8	-0.0218 (5)	0.46966 (19)	0.2809 (3)	0.0893 (12)
H8A	-0.1038	0.4719	0.2133	0.134*
H8B	0.0823	0.4883	0.2591	0.134*
H8C	-0.0592	0.4969	0.3453	0.134*
C12	0.1485 (4)	0.16916 (16)	0.4737 (3)	0.0612 (8)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0777 (6)	0.0746 (6)	0.0578 (5)	-0.0105 (4)	-0.0170 (4)	-0.0072 (4)
Cl4	0.0903 (7)	0.0682 (5)	0.0546 (5)	0.0025 (4)	-0.0261 (4)	0.0098 (4)
Cl3	0.1127 (9)	0.0703 (6)	0.0774 (6)	-0.0146 (5)	-0.0161 (5)	-0.0120 (4)
Cl2	0.1327 (10)	0.0557 (5)	0.1145 (8)	0.0077 (6)	-0.0265 (7)	-0.0019 (5)
O4	0.0964 (19)	0.0624 (14)	0.0776 (15)	-0.0033 (13)	-0.0278 (14)	0.0115 (12)
O1	0.0920 (18)	0.0560 (13)	0.0748 (15)	0.0027 (12)	-0.0222 (12)	0.0056 (11)

supplementary materials

C3	0.0457 (17)	0.0590 (18)	0.0425 (15)	0.0017 (13)	-0.0020 (12)	0.0062 (13)
C4	0.072 (2)	0.0584 (19)	0.0548 (18)	-0.0003 (16)	-0.0144 (15)	0.0074 (15)
O2	0.107 (2)	0.0698 (16)	0.0729 (15)	-0.0033 (14)	-0.0369 (14)	-0.0034 (12)
C6	0.064 (2)	0.0565 (18)	0.0530 (18)	0.0022 (15)	-0.0044 (15)	0.0079 (14)
N1	0.076 (2)	0.0683 (18)	0.0538 (15)	-0.0015 (14)	-0.0175 (13)	0.0034 (13)
C10	0.0448 (17)	0.0594 (18)	0.0444 (15)	-0.0022 (14)	0.0035 (12)	-0.0019 (13)
C11	0.059 (2)	0.064 (2)	0.0466 (16)	-0.0005 (15)	-0.0042 (14)	-0.0028 (14)
C13	0.0565 (19)	0.066 (2)	0.0509 (17)	0.0018 (15)	-0.0056 (14)	0.0038 (14)
O3	0.136 (3)	0.0614 (16)	0.0958 (19)	-0.0204 (15)	-0.0430 (18)	0.0030 (13)
C5	0.064 (2)	0.063 (2)	0.0528 (17)	-0.0050 (16)	-0.0029 (15)	-0.0045 (15)
C7	0.0465 (17)	0.0616 (18)	0.0418 (15)	0.0028 (14)	-0.0031 (12)	0.0062 (13)
C9	0.058 (2)	0.064 (2)	0.0501 (17)	-0.0045 (16)	-0.0014 (15)	0.0015 (15)
C1	0.133 (4)	0.053 (2)	0.090 (3)	0.003 (2)	-0.020 (2)	-0.0003 (18)
N2	0.0729 (19)	0.0568 (16)	0.0602 (16)	-0.0026 (13)	-0.0062 (13)	-0.0087 (13)
C14	0.0462 (17)	0.0586 (18)	0.0464 (16)	-0.0040 (13)	0.0034 (13)	-0.0036 (13)
C2	0.061 (2)	0.0597 (18)	0.0445 (16)	0.0022 (15)	0.0002 (14)	0.0054 (14)
C8	0.105 (3)	0.068 (2)	0.090 (3)	0.002 (2)	-0.016 (2)	0.0210 (19)
C12	0.064 (2)	0.0546 (18)	0.064 (2)	0.0040 (15)	-0.0002 (16)	-0.0012 (15)

Geometric parameters (\AA , $^\circ$)

C11—C14	1.720 (3)	N1—C5	1.306 (4)
C14—C7	1.723 (3)	C10—C11	1.392 (4)
C13—C5	1.731 (3)	C10—C14	1.393 (4)
C12—C12	1.731 (3)	C10—C9	1.479 (4)
O4—C9	1.313 (4)	C11—N2	1.330 (4)
O4—C8	1.446 (4)	C11—H11A	0.9300
O1—C2	1.329 (4)	C13—C12	1.371 (4)
O1—C1	1.441 (4)	C13—C14	1.374 (4)
C3—C7	1.389 (4)	C13—H13A	0.9300
C3—C4	1.393 (4)	O3—C9	1.184 (4)
C3—C2	1.478 (4)	C1—H1B	0.9600
C4—N1	1.324 (4)	C1—H1C	0.9600
C4—H4A	0.9300	C1—H1D	0.9600
O2—C2	1.194 (4)	N2—C12	1.314 (4)
C6—C7	1.368 (4)	C8—H8A	0.9600
C6—C5	1.376 (4)	C8—H8B	0.9600
C6—H6A	0.9300	C8—H8C	0.9600
C9—O4—C8	116.6 (3)	C3—C7—C14	122.1 (2)
C2—O1—C1	116.2 (3)	O3—C9—O4	122.6 (3)
C7—C3—C4	115.7 (3)	O3—C9—C10	125.7 (3)
C7—C3—C2	124.4 (2)	O4—C9—C10	111.8 (3)
C4—C3—C2	119.8 (3)	O1—C1—H1B	109.5
N1—C4—C3	125.6 (3)	O1—C1—H1C	109.5
N1—C4—H4A	117.2	H1B—C1—H1C	109.5
C3—C4—H4A	117.2	O1—C1—H1D	109.5
C7—C6—C5	117.6 (3)	H1B—C1—H1D	109.5
C7—C6—H6A	121.2	H1C—C1—H1D	109.5
C5—C6—H6A	121.2	C12—N2—C11	115.9 (3)

C5—N1—C4	115.7 (3)	C13—C14—C10	120.2 (3)
C11—C10—C14	116.2 (3)	C13—C14—C11	117.2 (2)
C11—C10—C9	120.0 (3)	C10—C14—C11	122.5 (2)
C14—C10—C9	123.8 (3)	O2—C2—O1	122.5 (3)
N2—C11—C10	124.8 (3)	O2—C2—C3	126.4 (3)
N2—C11—H11A	117.6	O1—C2—C3	111.2 (3)
C10—C11—H11A	117.6	O4—C8—H8A	109.5
C12—C13—C14	117.0 (3)	O4—C8—H8B	109.5
C12—C13—H13A	121.5	H8A—C8—H8B	109.5
C14—C13—H13A	121.5	O4—C8—H8C	109.5
N1—C5—C6	125.4 (3)	H8A—C8—H8C	109.5
N1—C5—C13	116.1 (2)	H8B—C8—H8C	109.5
C6—C5—C13	118.5 (2)	N2—C12—C13	125.9 (3)
C6—C7—C3	120.0 (3)	N2—C12—C12	115.8 (2)
C6—C7—C14	117.9 (2)	C13—C12—C12	118.2 (2)
C7—C3—C4—N1	-0.2 (5)	C11—C10—C9—O4	8.7 (4)
C2—C3—C4—N1	179.1 (3)	C14—C10—C9—O4	-172.4 (3)
C3—C4—N1—C5	-0.1 (5)	C10—C11—N2—C12	-0.3 (5)
C14—C10—C11—N2	-0.9 (4)	C12—C13—C14—C10	-1.1 (4)
C9—C10—C11—N2	178.0 (3)	C12—C13—C14—C11	178.5 (2)
C4—N1—C5—C6	-0.1 (5)	C11—C10—C14—C13	1.6 (4)
C4—N1—C5—C13	-179.7 (2)	C9—C10—C14—C13	-177.3 (3)
C7—C6—C5—N1	0.6 (5)	C11—C10—C14—C11	-178.0 (2)
C7—C6—C5—C13	-179.8 (2)	C9—C10—C14—C11	3.1 (4)
C5—C6—C7—C3	-0.9 (5)	C1—O1—C2—O2	3.5 (5)
C5—C6—C7—C14	179.3 (2)	C1—O1—C2—C3	-176.6 (3)
C4—C3—C7—C6	0.7 (4)	C7—C3—C2—O2	11.1 (5)
C2—C3—C7—C6	-178.5 (3)	C4—C3—C2—O2	-168.0 (3)
C4—C3—C7—C14	-179.5 (2)	C7—C3—C2—O1	-168.8 (3)
C2—C3—C7—C14	1.3 (4)	C4—C3—C2—O1	12.0 (4)
C8—O4—C9—O3	1.1 (5)	C11—N2—C12—C13	0.9 (5)
C8—O4—C9—C10	-178.8 (3)	C11—N2—C12—C12	-178.8 (2)
C11—C10—C9—O3	-171.2 (3)	C14—C13—C12—N2	-0.2 (5)
C14—C10—C9—O3	7.7 (5)	C14—C13—C12—C12	179.5 (2)

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>
C6—H6A...O3 ⁱ	0.93	2.41	3.309 (4)	162
C11—H11A...O2 ⁱⁱ	0.93	2.60	3.513 (4)	168

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

Fig. 1

