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5-Chloro-1,3-dimethyl-1*H*-pyrazole-4-carbaldehyde

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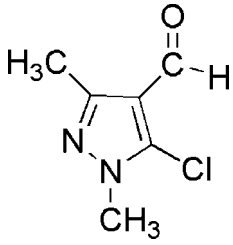
Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.003 Å; R factor = 0.027; wR factor = 0.081; data-to-parameter ratio = 14.2.

In the title compound, $C_6H_7ClN_2O$, the molecules are situated on mirror planes, so H atoms of two methyl groups were treated as rotationally disordered over two orientations each. The crystal packing exhibits weak intermolecular C—H···O interactions and short Cl···N contacts of 3.046 (2) Å.

Related literature

For the biological activity of pyrazole derivatives, see: Hamaguchi *et al.* (1995); Motoba *et al.* (1992). For a related structure, see: Yokoyama *et al.* (2004).



Experimental

Crystal data

$C_6H_7ClN_2O$
M_r = 158.59
Orthorhombic, *Pnma*
a = 13.167 (9) Å
b = 6.463 (5) Å
c = 8.190 (6) Å
V = 696.9 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.47 mm^{-1}
T = 113 K
0.24 × 0.22 × 0.18 mm

Data collection

Rigaku Saturn724 CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2008)
T_{min} = 0.895, T_{max} = 0.920
7166 measured reflections
897 independent reflections
726 reflections with $I > 2\sigma(I)$
R_{int} = 0.049

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.081
S = 1.05
897 reflections
63 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5A···O1^{i}	0.98	2.58	3.220 (3)	123

Symmetry code: (i) $x, y, z+1$.

Data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5167).

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Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Yokoyama, Y., Kurimoto, Y., Saito, Y., Katsurada, M., Okada, I., Osano, Y. T., Sasaki, C., Yokoyama, Y., Tukada, H., Adachi, M., Nakamura, S., Murayama, T., Harazono, T. & Kodaira, T. (2004). *Chem. Lett.* **33**, 106–107.

supporting information

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5-Chloro-1,3-dimethyl-1*H*-pyrazole-4-carbaldehyde

Yong-Jun Shen, Mei Xu and Chong-Guang Fan

S1. Comment

The pyrazole ring is a prominent heterocyclic scaffold in numerous bioactive molecules. Many pyrazole-based compounds are reported to possess diverse biological activities (Motoba *et al.*, 1992; Hamaguchi *et al.*, 1995). The title compound (I), is an important intermediate for the synthesis of agrochemicals and drugs. Details of its crystal structure may be helpful for the design of novel bioactive molecules.

In (I) (Fig. 1), all bond lengths and angles are normal and comparable with those observed in ethyl 4-formyl-1,3-dimethylpyrazole-5-carboxylate (Yokoyama *et al.*, 2004). All molecules in (I) are situated on mirror planes. The crystal packing exhibits weak intermolecular C—H···O interactions (Table 1) and short Cl···N contacts of 3.046 (2) Å.

S2. Experimental

To a well stirred cold solution of DMF(60 mmol) was added dropwise phosphoryl trichloride (90 mmol). The resulting mixture was stirred at 273 K for another 20 min. To the above solution was added 1,3-dimethyl- 1*H*-pyrazol-5(4*H*)-one (30 mmol), then it was heated to 363 k for 4 h. Completion of the reaction was checked by TLC, the reaction mixture was cooled and poured into cold water(100 ml). The pH of the mixture was adjusted to 7 by sodium hydroxide solution. The resulting solution was extracted with ethyl acetate (3 * 30 ml). The organic layer was dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure, then the residue was recrystallized from ethyl acetate/petroleum ether to give a colourless crystal.

S3. Refinement

All H atoms were placed in calculated positions, with C–H = 0.95, and 0.98 ° A, and included in the final cycles of refinement using a riding model, with U_{iso}(H) = 1.2U_{eq}(C). H atoms of two methyl groups were treated as rotationally disordered over two orientations each with occupancies fixed to 0.5.

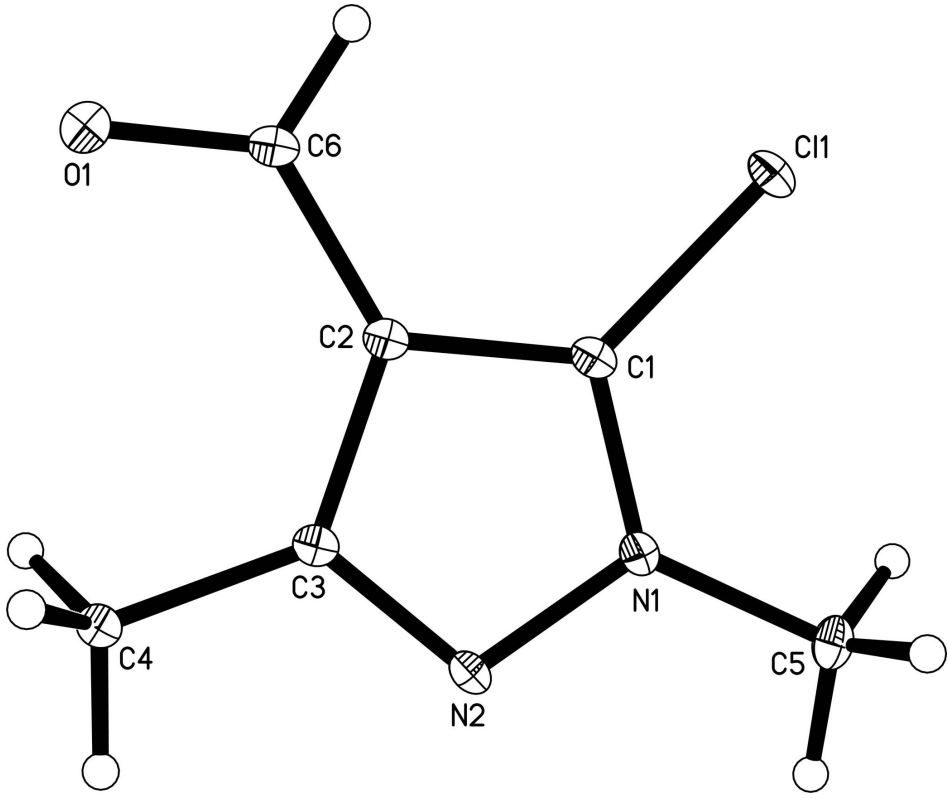

Figure 1

The molecular structure of (I) showing the atomic labels and 30% probability displacement ellipsoids.

5-Chloro-1,3-dimethyl-1*H*-pyrazole-4-carbaldehyde

Crystal data

$C_6H_7ClN_2O$
M_r = 158.59
Orthorhombic, *Pnma*
Hall symbol: -P 2ac 2n
a = 13.167 (9) Å
b = 6.463 (5) Å
c = 8.190 (6) Å
V = 696.9 (8) Å^3
Z = 4
$F(000)$ = 328
D_x = 1.511 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2460 reflections
θ = 2.5–27.8°
μ = 0.47 mm^{-1}
T = 113 K
Prism, colourless
0.24 × 0.22 × 0.18 mm

Data collection

Rigaku Saturn724 CCD diffractometer
Radiation source: rotating anode
Multilayer monochromator
Detector resolution: 14.22 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2008)
T_{min} = 0.895, T_{max} = 0.920
7166 measured reflections
897 independent reflections
726 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 27.8°, θ_{min} = 2.9°
h = −16→17
k = −8→8
l = −10→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.081$
$S = 1.05$
897 reflections
63 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0516P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cl1	0.41884 (3)	0.2500	0.25597 (5)	0.01825 (17)	
O1	0.48840 (10)	0.2500	−0.28470 (15)	0.0222 (3)	
N1	0.62098 (12)	0.2500	0.23171 (16)	0.0159 (4)	
N2	0.70015 (10)	0.2500	0.12266 (17)	0.0166 (3)	
C1	0.53190 (11)	0.2500	0.1537 (2)	0.0146 (4)	
C2	0.54995 (11)	0.2500	−0.0124 (2)	0.0141 (4)	
C3	0.65799 (11)	0.2500	−0.0242 (2)	0.0142 (4)	
C4	0.72306 (11)	0.2500	−0.1739 (2)	0.0178 (4)	
H4A	0.7015	0.3620	−0.2468	0.027*	0.50
H4B	0.7161	0.1170	−0.2303	0.027*	0.50
H4C	0.7942	0.2710	−0.1426	0.027*	0.50
C5	0.63988 (14)	0.2500	0.4067 (2)	0.0234 (4)	
H5A	0.5928	0.3457	0.4603	0.035*	0.50
H5B	0.7099	0.2942	0.4276	0.035*	0.50
H5C	0.6297	0.1102	0.4500	0.035*	0.50
C6	0.47278 (12)	0.2500	−0.1387 (2)	0.0167 (4)	
H6	0.4039	0.2500	−0.1041	0.020*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0131 (3)	0.0215 (3)	0.0202 (3)	0.000	0.00588 (14)	0.000
O1	0.0198 (7)	0.0291 (8)	0.0177 (6)	0.000	−0.0013 (5)	0.000
N1	0.0138 (8)	0.0210 (8)	0.0130 (7)	0.000	0.0020 (5)	0.000
N2	0.0119 (7)	0.0226 (8)	0.0153 (7)	0.000	0.0035 (6)	0.000

C1	0.0119 (8)	0.0145 (9)	0.0175 (8)	0.000	0.0017 (6)	0.000
C2	0.0124 (8)	0.0137 (8)	0.0163 (8)	0.000	0.0001 (6)	0.000
C3	0.0125 (8)	0.0137 (9)	0.0163 (8)	0.000	0.0000 (6)	0.000
C4	0.0135 (8)	0.0239 (10)	0.0159 (8)	0.000	0.0008 (6)	0.000
C5	0.0237 (9)	0.0354 (12)	0.0111 (9)	0.000	0.0000 (7)	0.000
C6	0.0119 (8)	0.0182 (9)	0.0199 (8)	0.000	−0.0006 (7)	0.000

Geometric parameters (Å, º)

Cl1—C1	1.7081 (18)	C3—C4	1.495 (2)
O1—C6	1.213 (2)	C4—H4A	0.9800
N1—C1	1.336 (2)	C4—H4B	0.9800
N1—N2	1.373 (2)	C4—H4C	0.9800
N1—C5	1.455 (2)	C5—H5A	0.9800
N2—C3	1.325 (2)	C5—H5B	0.9800
C1—C2	1.381 (2)	C5—H5C	0.9800
C2—C3	1.426 (2)	C6—H6	0.9500
C2—C6	1.450 (2)		
C1—N1—N2	110.83 (14)	C3—C4—H4B	109.5
C1—N1—C5	128.43 (15)	H4A—C4—H4B	109.5
N2—N1—C5	120.74 (15)	C3—C4—H4C	109.5
C3—N2—N1	105.82 (13)	H4A—C4—H4C	109.5
N1—C1—C2	108.67 (14)	H4B—C4—H4C	109.5
N1—C1—Cl1	122.06 (14)	N1—C5—H5A	109.5
C2—C1—Cl1	129.27 (13)	N1—C5—H5B	109.5
C1—C2—C3	103.80 (14)	H5A—C5—H5B	109.5
C1—C2—C6	125.60 (15)	N1—C5—H5C	109.5
C3—C2—C6	130.61 (15)	H5A—C5—H5C	109.5
N2—C3—C2	110.88 (14)	H5B—C5—H5C	109.5
N2—C3—C4	120.27 (14)	O1—C6—C2	125.74 (15)
C2—C3—C4	128.84 (15)	O1—C6—H6	117.1
C3—C4—H4A	109.5	C2—C6—H6	117.1
C1—N1—N2—C3	0.0	Cl1—C1—C2—C6	0.0
C5—N1—N2—C3	180.0	N1—N2—C3—C2	0.0
N2—N1—C1—C2	0.0	N1—N2—C3—C4	180.0
C5—N1—C1—C2	180.0	C1—C2—C3—N2	0.0
N2—N1—C1—Cl1	180.0	C6—C2—C3—N2	180.0
C5—N1—C1—Cl1	0.0	C1—C2—C3—C4	180.0
N1—C1—C2—C3	0.0	C6—C2—C3—C4	0.0
Cl1—C1—C2—C3	180.0	C1—C2—C6—O1	180.0
N1—C1—C2—C6	180.0	C3—C2—C6—O1	0.0

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

C5—H5*A*···O1^{i}	0.98	2.58	3.220 (3)	123

Symmetry code: (i) *x*, *y*, *z*+1.