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3-Chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinic acid

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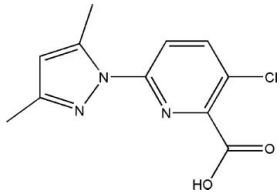
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.041; wR factor = 0.114; data-to-parameter ratio = 13.2.

In the title compound, $C_{11}H_{10}ClN_3O_2$, the dihedral angle between the two rings is 5.6°. The crystal structure is stabilized by O—H···O hydrogen bonds.

Related literature

For related literature, see: Liao *et al.* (2000); Elguero *et al.* (1984); Fun *et al.* (1996); Lu *et al.* (1996); Kai *et al.* (2007).



Experimental

Crystal data

$C_{11}H_{10}ClN_3O_2$
M_r = 251.67
Orthorhombic, $Pna2_1$
a = 17.972 (2) Å
b = 4.5618 (6) Å
c = 14.303 (2) Å
V = 1172.6 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.32 mm^{-1}
T = 298 (2) K
0.53 × 0.50 × 0.36 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.849, T_{max} = 0.894
4435 measured reflections
2038 independent reflections
1806 reflections with $I > 2\sigma(I)$
R_{int} = 0.041

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.114
S = 1.06
2038 reflections
154 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Absolute structure: Flack (1983), 956 Friedel pairs
Flack parameter: −0.03 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N3^{i}	0.82	1.92	2.723 (3)	167

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); 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: SG2207).

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supplementary materials

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3-Chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinic acid

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Comment

The chemical and pharmacological properties of pyrazoles have been investigated extensively, owing to their chelating ability with metal ions and to their potentially beneficial chemical and biological activities, (Elguero *et al.*, 1984;), *e.g*; antitumor, antineoplastic,antibacterial and antimalarial (Liao *et al.*,2000; Fun *et al.*,1996; Lu *et al.*,1996). Recently we reported the 4-(3,5-dimethyl-1*H*-pyrazol-1-yl)phthalazin-1(2*H*)-one; (Kai *et al.*, 2007). We report here the synthesis and crystal structure of 3-chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinic acid. The C—N distances range from 1.332 (4) to 1.411 (3) Å, *i.e.* normal values. The C=O bond length is 1.231 (3) Å, indicating that the molecule is in the keto form.

In the crystal structure, the molecules are interconnected, by intermolecular O—H···O hydrogen bonds (Fig. 2; for symmetry codes see Table1).

Experimental

A solution of 3-chloro-6-hydrazinylpicolinic acid(10 mmol) in 50 ml toluene was added to a solution of pentane-2,4-dione(10 mmol) in 10 ml toluene. The reaction mixture was refluxed for 1 h with stirring. then the resulting pale colorless precipitate was obtained by filtration, washed several times with ethanol and dried *in vacuo* (yield 90%). Analysis calculated for the title compound ($C_{11}H_{10}ClN_3O_2$): C, 52.40; H, 4.11; N, 16.60; O, 12.81; in the crystal, found: C, 52.50; H, 4.01; N, 16.70; O, 12.71. A me thanol solution of the title compound was slowly evaporated and colorless crystals were obtained after one week.

Refinement

The positions of all H atoms were fixed geometrically and refined isotropically using a riding model. The bond lengths for C—H are in the range 0.93–0.96 Å, The bond lengths for N—H are 0.86 Å, respectively.

Data collection: Bruker *SMART*(Siemens, 1996); cell refinement: Bruker *SMART*(Siemens, 1996); data reduction: Bruker *SAINT*(Siemens, 1996); program(*s*) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(*s*) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL* (Sheldrick, 1997*b*).

Figures

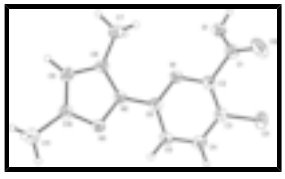


Fig. 1. The structure of the title compound (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

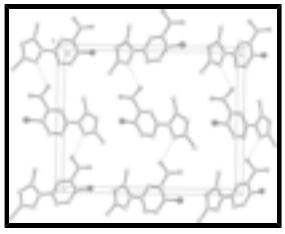


Fig. 2. Crystal packing of (I) showing the hydrogen bonded interactions as dashed lines.

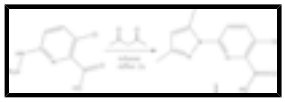


Fig. 3. The formation of the title compound.

3-Chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinic acid

Crystal data

$C_{11}H_{10}ClN_3O_2$	F_{000} = 520
M_r = 251.67	D_x = 1.426 Mg m^{-3}
Orthorhombic, *Pna*2$_1$	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: P 2c -2n	Cell parameters from 2331 reflections
a = 17.972 (2) Å	θ = 2.3–27.0º
b = 4.5618 (6) Å	μ = 0.32 mm^{-1}
c = 14.303 (2) Å	*T* = 298 (2) K
V = 1172.6 (3) Å^3	Block, colorless
Z = 4	0.53 × 0.50 × 0.36 mm

Data collection

Bruker SMART CCD area-detector diffractometer	2038 independent reflections
Radiation source: fine-focus sealed tube	1806 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.041
T = 298(2) K	θ_{max} = 25.0º
phi and ω scans	θ_{min} = 2.3º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	*h* = −21→16
T_{min} = 0.849, T_{max} = 0.894	*k* = −3→5
4435 measured reflections	*l* = −17→16

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.041	$w = 1/[\sigma^2(F_o^2) + (0.0709P)^2 + 0.0549P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.114	$(\Delta/\sigma)_{max} < 0.001$
S = 1.06	$\Delta\rho_{max}$ = 0.25 e Å^{-3}

2038 reflections	$\Delta\rho_{min} = -0.24$ e Å^{-3}
154 parameters	Extinction correction: none
1 restraint	Absolute structure: Flack (1983), 956 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.03 (9)
Secondary atom site location: difference Fourier map	

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 $F^2 > 2\text{sigma}(F^2)$ 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	−0.15772 (4)	1.09661 (17)	0.51407 (7)	0.0586 (3)
N1	0.00189 (14)	0.5293 (6)	0.44703 (17)	0.0400 (6)
N2	0.09799 (11)	0.3047 (5)	0.52919 (16)	0.0376 (5)
N3	0.12733 (14)	0.2224 (6)	0.61406 (17)	0.0405 (6)
O1	−0.05743 (12)	0.7992 (6)	0.28282 (15)	0.0593 (6)
H1	−0.0786	0.7646	0.2332	0.089*
O2	−0.16318 (15)	0.6490 (8)	0.3462 (2)	0.0877 (11)
C1	−0.09889 (17)	0.7136 (8)	0.3518 (2)	0.0500 (8)
C2	−0.05762 (17)	0.7100 (7)	0.4443 (2)	0.0410 (7)
C3	−0.08141 (15)	0.8661 (6)	0.5207 (2)	0.0396 (6)
C4	−0.04237 (18)	0.8392 (7)	0.6036 (2)	0.0461 (8)
H4	−0.0570	0.9460	0.6559	0.055*
C5	0.01755 (17)	0.6565 (7)	0.6090 (2)	0.0414 (7)
H5	0.0442	0.6354	0.6643	0.050*
C6	0.03751 (14)	0.5019 (6)	0.5282 (2)	0.0361 (6)
C7	0.1212 (2)	0.2198 (11)	0.3557 (2)	0.0657 (10)
H7A	0.1556	0.1052	0.3197	0.099*
H7B	0.1269	0.4233	0.3402	0.099*
H7C	0.0713	0.1588	0.3417	0.099*
C8	0.13615 (16)	0.1764 (8)	0.4570 (2)	0.0418 (7)
C9	0.19019 (16)	0.0079 (7)	0.4978 (2)	0.0450 (7)
H9	0.2252	−0.1074	0.4671	0.054*
C10	0.18273 (18)	0.0425 (7)	0.5939 (2)	0.0431 (7)
C11	0.22903 (18)	−0.0922 (8)	0.6711 (3)	0.0571 (9)
H11A	0.2222	0.0176	0.7277	0.086*
H11B	0.2806	−0.0882	0.6536	0.086*
H11C	0.2137	−0.2914	0.6809	0.086*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0498 (4)	0.0487 (4)	0.0773 (6)	0.0094 (3)	0.0004 (4)	0.0100 (4)
N1	0.0391 (12)	0.0466 (13)	0.0342 (14)	−0.0025 (11)	−0.0008 (10)	0.0018 (12)
N2	0.0365 (12)	0.0461 (12)	0.0303 (12)	−0.0009 (10)	0.0001 (10)	0.0017 (12)
N3	0.0390 (13)	0.0494 (15)	0.0330 (13)	0.0017 (11)	−0.0002 (9)	0.0009 (12)
O1	0.0504 (13)	0.0890 (18)	0.0384 (12)	0.0002 (12)	−0.0020 (10)	0.0052 (12)
O2	0.0599 (16)	0.142 (3)	0.0611 (17)	−0.0352 (16)	−0.0180 (12)	0.0307 (18)
C1	0.048 (2)	0.054 (2)	0.0485 (19)	−0.0010 (15)	−0.0042 (14)	0.0097 (15)
C2	0.0392 (16)	0.0421 (16)	0.0416 (16)	−0.0075 (13)	−0.0031 (12)	0.0097 (14)
C3	0.0392 (13)	0.0344 (14)	0.0452 (16)	−0.0036 (11)	0.0002 (14)	0.0071 (14)
C4	0.0546 (19)	0.0421 (16)	0.0414 (18)	0.0020 (14)	0.0058 (14)	0.0003 (13)
C5	0.0486 (17)	0.0419 (15)	0.0336 (16)	−0.0007 (14)	−0.0038 (12)	−0.0001 (12)
C6	0.0395 (13)	0.0357 (13)	0.0331 (14)	−0.0068 (11)	0.0002 (12)	0.0038 (13)
C7	0.067 (2)	0.092 (3)	0.0384 (19)	0.015 (2)	0.0096 (16)	−0.0034 (18)
C8	0.0377 (15)	0.0524 (18)	0.0352 (16)	−0.0034 (14)	0.0059 (12)	−0.0008 (14)
C9	0.0348 (15)	0.0531 (18)	0.0472 (19)	0.0001 (13)	0.0069 (12)	−0.0063 (15)
C10	0.0376 (16)	0.0455 (16)	0.0462 (18)	−0.0023 (14)	0.0018 (13)	0.0018 (15)
C11	0.050 (2)	0.066 (2)	0.055 (2)	0.0165 (16)	−0.0034 (15)	−0.0003 (17)

Geometric parameters (Å, °)

Cl1—C3	1.731 (3)	C4—H4	0.9300
N1—C6	1.332 (4)	C5—C6	1.401 (4)
N1—C2	1.351 (4)	C5—H5	0.9300
N2—C8	1.371 (4)	C7—C8	1.487 (5)
N2—N3	1.376 (3)	C7—H7A	0.9600
N2—C6	1.411 (3)	C7—H7B	0.9600
N3—C10	1.322 (4)	C7—H7C	0.9600
O1—C1	1.297 (4)	C8—C9	1.369 (5)
O1—H1	0.8200	C9—C10	1.390 (5)
O2—C1	1.195 (4)	C9—H9	0.9300
C1—C2	1.516 (4)	C10—C11	1.513 (5)
C2—C3	1.374 (4)	C11—H11A	0.9600
C3—C4	1.383 (5)	C11—H11B	0.9600
C4—C5	1.364 (4)	C11—H11C	0.9600
C6—N1—C2	117.6 (3)	C5—C6—N2	120.7 (2)
C8—N2—N3	110.9 (2)	C8—C7—H7A	109.5
C8—N2—C6	130.5 (3)	C8—C7—H7B	109.5
N3—N2—C6	118.6 (2)	H7A—C7—H7B	109.5
C10—N3—N2	105.4 (2)	C8—C7—H7C	109.5
C1—O1—H1	109.5	H7A—C7—H7C	109.5
O2—C1—O1	125.4 (3)	H7B—C7—H7C	109.5
O2—C1—C2	121.9 (3)	C9—C8—N2	105.8 (3)
O1—C1—C2	112.7 (3)	C9—C8—C7	128.2 (3)
N1—C2—C3	122.6 (3)	N2—C8—C7	125.9 (3)

N1—C2—C1	114.8 (3)	C8—C9—C10	106.8 (3)
C3—C2—C1	122.5 (3)	C8—C9—H9	126.6
C2—C3—C4	118.6 (3)	C10—C9—H9	126.6
C2—C3—Cl1	121.2 (2)	N3—C10—C9	111.0 (3)
C4—C3—Cl1	120.2 (2)	N3—C10—C11	120.5 (3)
C5—C4—C3	120.2 (3)	C9—C10—C11	128.5 (3)
C5—C4—H4	119.9	C10—C11—H11A	109.5
C3—C4—H4	119.9	C10—C11—H11B	109.5
C4—C5—C6	117.6 (3)	H11A—C11—H11B	109.5
C4—C5—H5	121.2	C10—C11—H11C	109.5
C6—C5—H5	121.2	H11A—C11—H11C	109.5
N1—C6—C5	123.3 (3)	H11B—C11—H11C	109.5
N1—C6—N2	116.0 (2)		
C8—N2—N3—C10	−0.5 (3)	C4—C5—C6—N1	1.3 (4)
C6—N2—N3—C10	−179.4 (2)	C4—C5—C6—N2	−178.7 (2)
C6—N1—C2—C3	0.9 (4)	C8—N2—C6—N1	14.4 (4)
C6—N1—C2—C1	−175.7 (2)	N3—N2—C6—N1	−167.1 (2)
O2—C1—C2—N1	120.9 (4)	C8—N2—C6—C5	−165.6 (3)
O1—C1—C2—N1	−60.7 (4)	N3—N2—C6—C5	12.9 (4)
O2—C1—C2—C3	−55.7 (5)	N3—N2—C8—C9	0.5 (3)
O1—C1—C2—C3	122.8 (3)	C6—N2—C8—C9	179.1 (3)
N1—C2—C3—C4	0.7 (4)	N3—N2—C8—C7	−178.6 (4)
C1—C2—C3—C4	176.9 (3)	C6—N2—C8—C7	0.0 (5)
N1—C2—C3—Cl1	179.7 (2)	N2—C8—C9—C10	−0.3 (4)
C1—C2—C3—Cl1	−4.0 (4)	C7—C8—C9—C10	178.8 (4)
C2—C3—C4—C5	−1.2 (4)	N2—N3—C10—C9	0.4 (4)
Cl1—C3—C4—C5	179.7 (2)	N2—N3—C10—C11	179.5 (3)
C3—C4—C5—C6	0.3 (4)	C8—C9—C10—N3	−0.1 (4)
C2—N1—C6—C5	−1.9 (4)	C8—C9—C10—C11	−179.2 (3)
C2—N1—C6—N2	178.2 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N3^{i}	0.82	1.92	2.723 (3)	167

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

Fig. 1

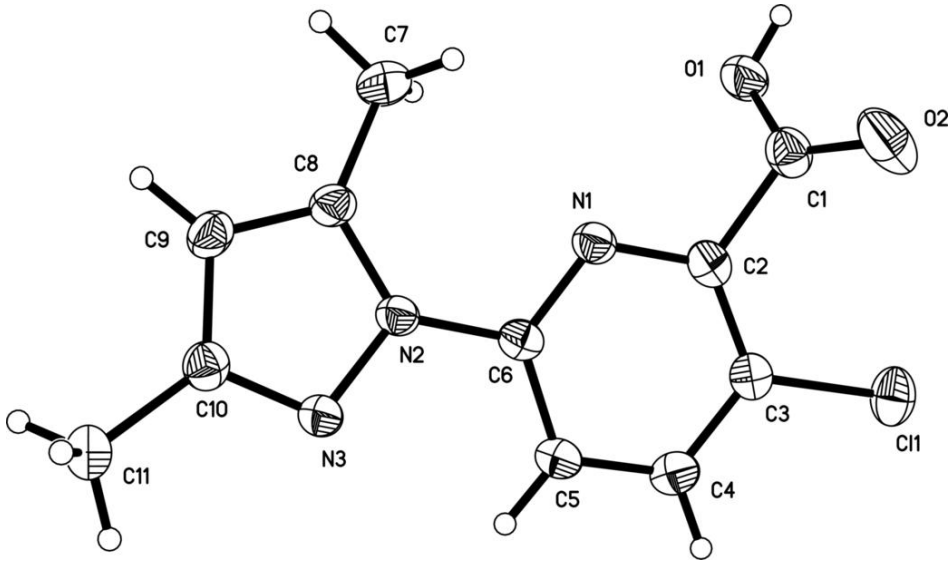


Fig. 2

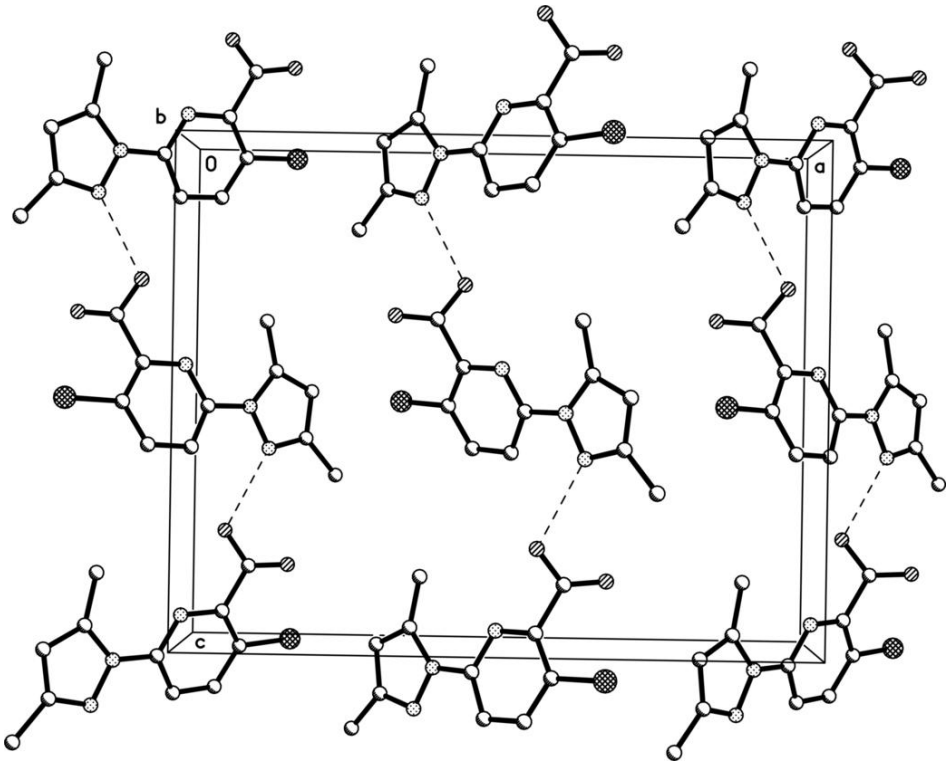
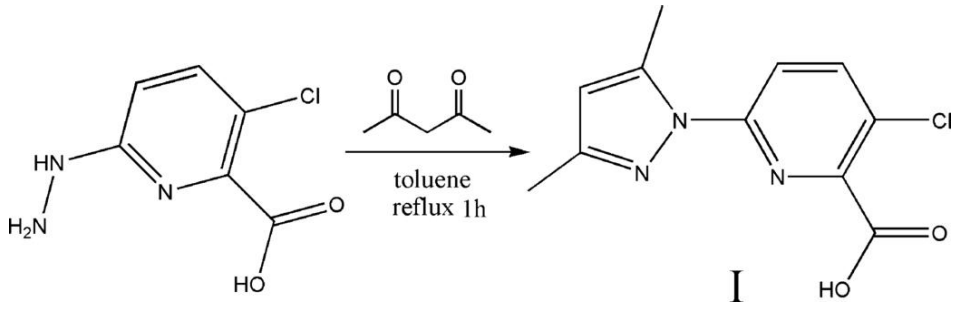


Fig. 3



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