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(*E*)-1-[(2-Chloro-5-methylpyridin-3-yl)-methylene]thiosemicarbazide

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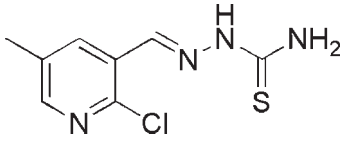
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.004 Å; R factor = 0.037; wR factor = 0.105; data-to-parameter ratio = 14.3.

The title compound, $C_8H_9ClN_4S$, which has potential insecticidal activity, was synthesized by the reaction of 2-chloro-5-methylnicotinaldehyde and thiosemicarbazide. In the crystal structure, the molecules are linked *via* intermolecular N—H···N, N—H···S and N—H···Cl hydrogen bonds, forming a three-dimensional network stacked down *a*.

Related literature

Tyrosinase is a key enzyme in the moulting process of insects, see: Kramer & Knost (2001). For the inhibitory activity on tyrosinase of benzaldehyde thiosemicarbazones, see: Xue *et al.* (2007). For the synthesis of the title compound, see: Liu *et al.* (2008).



Experimental

Crystal data

$C_8H_9ClN_4S$
M_r = 228.70
Monoclinic, $P2_1/c$
a = 8.776 (3) Å
b = 15.523 (4) Å
c = 7.540 (2) Å
β = 96.193 (16)°
V = 1021.2 (5) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 4.95 mm^{-1}
T = 173 K
0.45 × 0.30 × 0.30 mm

Data collection

Rigaku R-AXIS Rapid diffractometer
Absorption correction: numerical (*ABSCOR*; Higashi, 1995)
T_{min} = 0.214, T_{max} = 0.319
6565 measured reflections
1847 independent reflections
1598 reflections with $I > 2\sigma(I)$
R_{int} = 0.048

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.105
S = 1.11
1847 reflections
129 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3B···S1^{i}	0.88	2.52	3.379 (2)	166
N4—H4B···N1^{ii}	0.88	2.15	3.012 (3)	168
N4—H4B···Cl1^{ii}	0.88	2.98	3.609 (2)	130

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

Data collection: *RAPID-AUTO* (Rigaku, 2001); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DS2018).

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Xue, C.-B., Zhang, L., Luo, W.-C., Xie, X.-Y., Jiang, L. & Xiao, T. (2007). *Bioorg. Med. Chem.* **15**, 2006–2015.

supplementary materials

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(*E*)-1-[(2-Chloro-5-methylpyridin-3-yl)methylene]thiosemicarbazide

Z. Wang, Y. Ma, Y. Xu, Y. Ling and X. Yang

Comment

Tyrosinase is a key enzyme in the molting process of insect (Kramer & Knost 2001), and benzaldehyde thiosemicarbazones have inhibitory activity on tyrosinase (Xue *et al.*, 2007). In order to look for highly potent tyrosinase inhibitors, the title compound was synthesized by the reaction of thiosemicarbazide and 2-chloro-5-methylnicotinaldehyde (Liu *et al.*, 2008). Finally in the preliminary bioassay, we found that it showed obvious inhibitory activity against tyrosinase from cotton bollworm. To get more information about the structure, we prepared a single crystal of the title compound and its crystal will be reported herein.

The bond distances between N2 and C7 is 1.277 (3) Å, which is in the range of typical bond length of imine double bond. The bond distance of 1.683 (2) Å for the thiocarbonyl group (S1–C8) is about the average value of the typical C=S double bond (1.56 Å) and C–S single bond (1.82 Å), showing a partial double bond character in feature. The partial double bond character also appears between N3 and C8 as well as N4 and C8, which show the distance of 1.355 (3) and 1.322 (3) Å, respectively. In the cryatal structure, there are three intermolecular hydrogen bonds: N3–H3···S1, N4–H4···N1, N4–H4···Cl1 (Table 1).

Experimental

1.6 g (10 mmol) 2-Chloro-5-methylnicotinaldehyde was dissolved in anhydrous ethanol (15 ml). To this solution, 0.91 g (10 mmol) thiosemicarbazide and 0.5 mL acetic acid were added. The mixture was refluxed for 24 h and then cooled to room temperatur. The precipitate was formed and collected after filteration. The title compound was obtained in 89% yield after recrystallization of the precipitate from anhydrous MeOH. The colourless crystals suitable for X-ray crystallography was carefully grown from anhydrous methanolic solution.

Refinement

All H atoms were placed in geometrically idealized positions(C—H = 0.93-0.96 Å, N—H=0.86 Å) and treated as riding on their parent atoms, with U_{iso}(H) = 1.2-1.5U_{eq}(C,*N*).

Figures

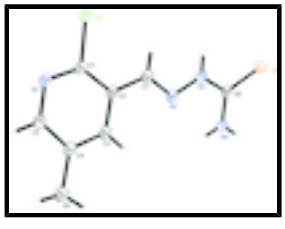

Fig. 1. The molecular structure of the title compound , showing the labelling scheme. Displacement ellipsoids are drawn at the 30% probability level for all non-H atoms.

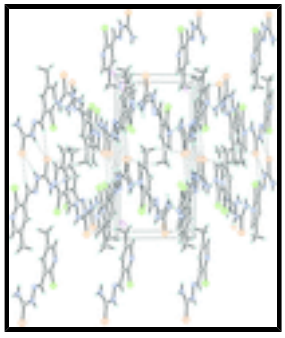

Fig. 2. Packing diagram for the title compound viewed along the a axis.

(*E*)-1-[(2-Chloro-5-methylpyridin-3-yl)methylene]thiosemicarbazide

Crystal data

$C_8H_9ClN_4S$	$F(000) = 472$
$M_r = 228.70$	$D_x = 1.488$ Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.54186$ Å
Hall symbol: -P 2ybc	Cell parameters from 658 reflections
$a = 8.776$ (3) Å	$\theta = 3.1$–$66.2°$
$b = 15.523$ (4) Å	$\mu = 4.95$ mm^{-1}
$c = 7.540$ (2) Å	$T = 173$ K
$\beta = 96.193$ (16)°	Block, colorless
$V = 1021.2$ (5) Å^3	0.45 × 0.30 × 0.30 mm
$Z = 4$	

Data collection

Rigaku R-AXIS Rapid diffractometer	1847 independent reflections
Radiation source: rotating anode	1598 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.048$
ω scans at fixed $\chi = 45°$	$\theta_{max} = 68.3°$, $\theta_{min} = 5.1°$
Absorption correction: numerical (ABSCOR; Higashi, 1995)	$h = -10 \rightarrow 9$
$T_{min} = 0.214$, $T_{max} = 0.319$	$k = -18 \rightarrow 17$
6565 measured reflections	$l = -8 \rightarrow 9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.037$	H-atom parameters constrained
$wR(F^2) = 0.105$	$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.4188P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} = 0.001$

1847 reflections	$\Delta\rho_{max}$ = 0.27 e Å^{-3}
129 parameters	$\Delta\rho_{min}$ = −0.22 e Å^{-3}
0 restraints	Extinction correction: SHELXL, $Fc^{*}=kFc[1+0.001xFc^{2}\lambda^{3}/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0051 (7)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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	0.50443 (6)	0.31852 (4)	0.16529 (8)	0.0385 (2)
S1	1.21803 (7)	0.48033 (4)	−0.12061 (9)	0.0413 (2)
N1	0.5116 (2)	0.15225 (14)	0.1900 (3)	0.0341 (5)
N2	0.9510 (2)	0.28984 (13)	−0.0128 (2)	0.0309 (5)
N3	1.0139 (2)	0.36918 (13)	−0.0313 (3)	0.0349 (5)
H3B	0.9687	0.4145	0.0097	0.042*
N4	1.2069 (2)	0.31191 (13)	−0.1757 (3)	0.0380 (5)
H4A	1.1645	0.2609	−0.1669	0.046*
H4B	1.2914	0.3171	−0.2281	0.046*
C1	0.5935 (3)	0.21864 (16)	0.1461 (3)	0.0308 (5)
C2	0.7391 (2)	0.21399 (15)	0.0899 (3)	0.0289 (5)
C3	0.7996 (3)	0.13151 (16)	0.0783 (3)	0.0315 (5)
H3A	0.8979	0.1246	0.0385	0.038*
C4	0.7192 (3)	0.05922 (17)	0.1237 (3)	0.0336 (5)
C5	0.5753 (3)	0.07344 (16)	0.1798 (3)	0.0357 (6)
H5A	0.5186	0.0249	0.2129	0.043*
C6	0.7836 (3)	−0.03035 (16)	0.1176 (3)	0.0407 (6)
H6A	0.8908	−0.0302	0.1699	0.061*
H6B	0.7779	−0.0498	−0.0067	0.061*
H6C	0.7241	−0.0694	0.1854	0.061*
C7	0.8228 (3)	0.29122 (16)	0.0529 (3)	0.0340 (5)
H7A	0.7804	0.3455	0.0787	0.041*
C8	1.1438 (3)	0.38067 (15)	−0.1105 (3)	0.0305 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0293 (3)	0.0389 (4)	0.0493 (4)	0.0043 (2)	0.0141 (3)	0.0027 (2)
S1	0.0337 (4)	0.0357 (4)	0.0589 (4)	−0.0051 (3)	0.0259 (3)	−0.0051 (3)
N1	0.0275 (10)	0.0380 (11)	0.0387 (11)	0.0010 (9)	0.0119 (8)	0.0023 (9)
N2	0.0255 (10)	0.0368 (11)	0.0313 (10)	−0.0025 (8)	0.0063 (8)	0.0003 (8)
N3	0.0256 (10)	0.0369 (12)	0.0449 (12)	−0.0032 (8)	0.0155 (9)	−0.0046 (9)
N4	0.0283 (11)	0.0369 (12)	0.0519 (13)	−0.0026 (8)	0.0184 (9)	−0.0073 (9)
C1	0.0266 (12)	0.0381 (14)	0.0284 (11)	0.0031 (10)	0.0057 (9)	−0.0013 (9)
C2	0.0242 (11)	0.0374 (14)	0.0263 (11)	−0.0030 (9)	0.0075 (9)	−0.0010 (9)
C3	0.0230 (11)	0.0434 (14)	0.0293 (12)	0.0010 (10)	0.0080 (9)	−0.0014 (10)
C4	0.0290 (12)	0.0422 (14)	0.0307 (12)	0.0001 (10)	0.0080 (9)	−0.0007 (10)
C5	0.0311 (13)	0.0357 (14)	0.0422 (13)	−0.0027 (10)	0.0122 (10)	0.0020 (10)
C6	0.0385 (14)	0.0381 (15)	0.0474 (15)	0.0015 (11)	0.0138 (12)	0.0007 (11)
C7	0.0283 (12)	0.0341 (13)	0.0413 (14)	−0.0017 (10)	0.0115 (10)	−0.0002 (10)
C8	0.0230 (11)	0.0371 (14)	0.0325 (12)	−0.0019 (9)	0.0078 (9)	−0.0004 (9)

Geometric parameters (Å, °)

Cl1—C1	1.749 (2)	C2—C3	1.392 (3)
S1—C8	1.683 (2)	C2—C7	1.449 (3)
N1—C1	1.319 (3)	C3—C4	1.388 (3)
N1—C5	1.350 (3)	C3—H3A	0.9500
N2—C7	1.277 (3)	C4—C5	1.393 (3)
N2—N3	1.363 (3)	C4—C6	1.503 (3)
N3—C8	1.355 (3)	C5—H5A	0.9500
N3—H3B	0.8800	C6—H6A	0.9800
N4—C8	1.322 (3)	C6—H6B	0.9800
N4—H4A	0.8800	C6—H6C	0.9800
N4—H4B	0.8800	C7—H7A	0.9500
C1—C2	1.391 (3)		
C1—N1—C5	117.0 (2)	C3—C4—C6	122.5 (2)
C7—N2—N3	114.1 (2)	C5—C4—C6	120.8 (2)
C8—N3—N2	122.2 (2)	N1—C5—C4	123.7 (2)
C8—N3—H3B	118.9	N1—C5—H5A	118.1
N2—N3—H3B	118.9	C4—C5—H5A	118.1
C8—N4—H4A	120.0	C4—C6—H6A	109.5
C8—N4—H4B	120.0	C4—C6—H6B	109.5
H4A—N4—H4B	120.0	H6A—C6—H6B	109.5
N1—C1—C2	125.4 (2)	C4—C6—H6C	109.5
N1—C1—Cl1	114.30 (17)	H6A—C6—H6C	109.5
C2—C1—Cl1	120.30 (19)	H6B—C6—H6C	109.5
C1—C2—C3	115.8 (2)	N2—C7—C2	123.2 (2)
C1—C2—C7	121.2 (2)	N2—C7—H7A	118.4
C3—C2—C7	123.0 (2)	C2—C7—H7A	118.4
C4—C3—C2	121.4 (2)	N4—C8—N3	117.7 (2)

C4—C3—H3A	119.3	N4—C8—S1	123.06 (18)
C2—C3—H3A	119.3	N3—C8—S1	119.29 (18)
C3—C4—C5	116.7 (2)		
C7—N2—N3—C8	−175.1 (2)	C2—C3—C4—C6	−178.2 (2)
C5—N1—C1—C2	0.2 (3)	C1—N1—C5—C4	−1.0 (3)
C5—N1—C1—Cl1	−179.23 (17)	C3—C4—C5—N1	0.7 (4)
N1—C1—C2—C3	0.8 (3)	C6—C4—C5—N1	179.4 (2)
Cl1—C1—C2—C3	−179.73 (16)	N3—N2—C7—C2	−177.63 (19)
N1—C1—C2—C7	−177.0 (2)	C1—C2—C7—N2	−174.1 (2)
Cl1—C1—C2—C7	2.5 (3)	C3—C2—C7—N2	8.3 (4)
C1—C2—C3—C4	−1.2 (3)	N2—N3—C8—N4	2.0 (3)
C7—C2—C3—C4	176.6 (2)	N2—N3—C8—S1	−177.57 (16)
C2—C3—C4—C5	0.5 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3B···S1^{i}	0.88	2.52	3.379 (2)	166.
N4—H4B···N1^{ii}	0.88	2.15	3.012 (3)	168.
N4—H4B···Cl1^{ii}	0.88	2.98	3.609 (2)	130.

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

Fig. 1

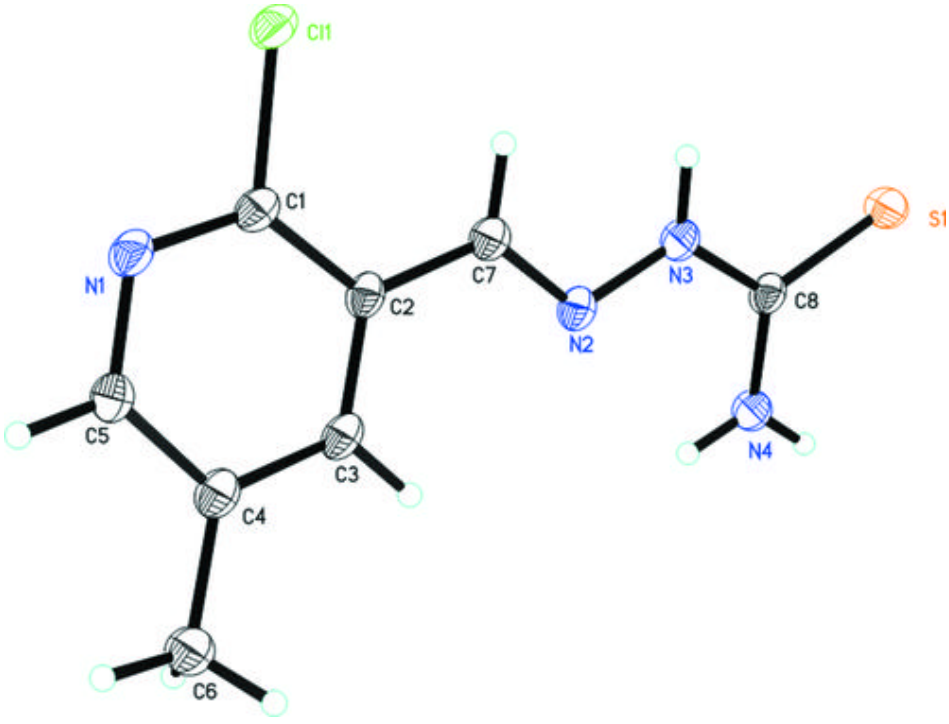

Fig. 2