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The crystal structure of (*E*)-2-chloro-5-((2-(nitromethylene)imidazolidin-1-yl)methyl)pyridine, C₁₀H₁₁ClN₄O₂

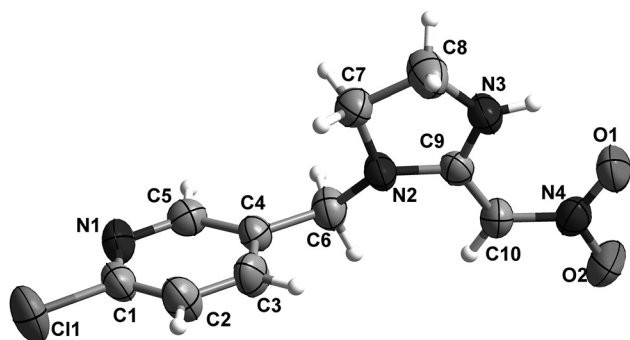


Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.20 × 0.10 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.32 mm ⁻¹
Diffractometer, scan mode:	Bruker Smart Apex II, φ and ω
$\theta_{\max}$, completeness:	25.0°, >99 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	17,187, 2047, 0.071
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1242
$N(\text{param})_{\text{refined}}$:	154
Programs:	Bruker [1], Olex2 [2], Shelx [3, 4], Diamond [5]

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Abstract

C₁₀H₁₁ClN₄O₂, monoclinic, $P2_1/c$ (no. 14), $a = 12.7802(17)$ Å, $b = 7.6211(12)$ Å, $c = 12.0486(17)$ Å, $\beta = 95.551(4)^\circ$, $V = 1168.0(3)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0562$, $wR_{\text{ref}}(F^2) = 0.1172$, $T = 273(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of materials

We started the synthesis of 2-chloro-5-((2-(nitromethylene)imidazolidin-1-yl)methyl)pyridine from 1,1-dimethylthio-2-nitroethylene and N-2(chloro-5-pyridylmethyl)ethylenediamine according to the literature reported by Li [6]. A mixture of 1,1-dimethylthio-2-nitroethylene (662 mg 4.0 mmol) prepared

from nitromethane and carbon disulfide and N-2(chloro-5-pyridylmethyl)ethylenediamine (754 mg 4.1 mmol) in anhydrous ethanol (9 mL) was refluxed for 8 h affording a clear yellow solution. The solvent was removed in vacuo after cooling to ambient temperature. The crude product was purified by silica gel chromatography using dichloromethane:acetone (4:1, v/v) as eluant to give a white power. Then a certain amount of white powder was dissolved in ethyl acetate. After solvent slowly evaporated at room temperature, the crystals were obtained.

2 Experimental details

The structure was solved by Direct Methods with the SHELX program system [3]. All H-atoms were positioned geometrically and refined using a riding model with $d(\text{N-H}) = 0.86$ Å, $d(\text{C-H}) = 0.93$ Å (aromatic and olefin CH), 0.97 Å (methylene CH₂). For all H atoms, isotropic displacement parameters were assigned as $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{N, C})$.

3 Comment

Nitrogen-containing heterocyclic insecticide has successful established its place in the field of insecticides research and development [7]. Especially, the neonicotinic insecticides are widely concerned and studied in the field of crop protection

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Cl1	−0.05579 (8)	−0.73366 (15)	0.85293 (8)	0.0838 (4)
O1	0.53016 (17)	−0.8124 (3)	0.28131 (19)	0.0634 (7)
O2	0.5971 (2)	−0.5955 (3)	0.3834 (2)	0.0741 (8)
N1	0.1315 (2)	−0.8538 (4)	0.8340 (2)	0.0520 (7)
N2	0.31630 (19)	−0.9053 (3)	0.5092 (2)	0.0477 (7)
N3	0.3704 (2)	−0.9947 (4)	0.3525 (2)	0.0540 (7)
H3	0.407054	−0.999009	0.296406	0.065 [*]
N4	0.5304 (2)	−0.7188 (4)	0.3678 (2)	0.0533 (7)
C1	0.0537 (3)	−0.7680 (5)	0.7795 (3)	0.0518 (9)
C2	0.0527 (3)	−0.7055 (5)	0.6729 (3)	0.0618 (10)
H2	−0.006112	−0.649300	0.637910	0.074 [*]
C3	0.1421 (3)	−0.7291 (4)	0.6195 (3)	0.0560 (9)
H3A	0.145117	−0.686529	0.547542	0.067 [*]
C4	0.2275 (2)	−0.8162 (4)	0.6730 (2)	0.0425 (8)
C5	0.2170 (2)	−0.8778 (4)	0.7788 (2)	0.0463 (8)
H5	0.272945	−0.940372	0.814573	0.056 [*]
C6	0.3296 (2)	−0.8386 (5)	0.6230 (2)	0.0533 (9)
H6A	0.365395	−0.726346	0.623439	0.064 [*]
H6B	0.373882	−0.919001	0.668914	0.064 [*]
C7	0.2547 (3)	−1.0645 (4)	0.4823 (3)	0.0552 (9)
H7A	0.179953	−1.041521	0.480825	0.066 [*]
H7B	0.273775	−1.157219	0.535618	0.066 [*]
C8	0.2846 (3)	−1.1123 (5)	0.3672 (3)	0.0741 (12)
H8A	0.306815	−1.233801	0.364420	0.089 [*]
H8B	0.226358	−1.093064	0.310714	0.089 [*]
C9	0.3868 (2)	−0.8800 (4)	0.4345 (2)	0.0419 (8)
C10	0.4627 (2)	−0.7474 (4)	0.4453 (3)	0.0488 (8)
H10	0.466792	−0.676188	0.508198	0.059 [*]

[8]. In addition, how to construct nitrogen heterocyclic ring and polycyclic compounds is also a classical subject in the field of synthesis. Title compound (*I*) is a key intermediate in the synthesis of complicated neonicotinic insecticides [8–11]. It is not only a nitrogen-containing heterocyclic compound in itself, but also a precursor to construct polycyclic compounds through cyclization with unsaturated aldehydes. In view of the excellent potential of this compound, it is worth studying its synthesis optimization and structural characteristics.

The asymmetric unit of (*I*) is shown in the figure. The C=C bond length is 1.398(4) Å and the C=C double bond in compound (*I*) will lead to geometrical isomerism. Single crystal X-ray diffraction confirmed that the title compound is the (*E*)-diastereomer. The C–Cl bond is 1.747(3) Å. The C–N bond lengths are between 1.312(4) and 1.466(4) Å. The N–O bond lengths are between 1.262(3) and 1.270(3) Å. The O–N–O bond angle is 119.2(3)°. All these values are in the normal range [12, 13]. The dihedral angle between the mean planes

passing through the pyridine ring and the imidazoline ring is 81.79(3). The C4–C6–N2 bond angle 113.024(6)° is smaller than the value for this bond angle in the similar structure (*E*)-2-[1-[(6-chloropyridin-3-yl)methyl]-2-imidazolidinylidene]-2-nitroacetonitrile [14]. The torsion angle of C4–C6–N2–C7 is −52.253(9)° which is obviously different with the value 88.1° observed in similar structure 2(*E*)-2-[1-[(6-chloropyridin-3-yl)methyl]-2-imidazolidinylidene]-2-nitroacetonitrile, which may be due to the space effect and interaction of cyano group in comparative structure. There exist intramolecular interactions [N3...O1 = 2.684(4) Å and N3–H3...O1 = 120.147(7)°] and intermolecular interactions [N3...O2_{*i*} = 3.012(3) Å and N3–H3...O2_{*i*} = 142.543(8)° (*i* = 1 – *X*, –1/2 + *Y*, 1/2 – *Z*)] between N–H donors from imidazoline ring and the oxygen atoms from nitro group. The presence of intermolecular hydrogen bonds results in the formation of one-dimensional chain-like structure along the (010) direction. There are four non-classical hydrogen bonds between C–H donors and the oxygen atoms from nitro group. The intermolecular interactions [C6...O2_{*ii*} = 3.441(4) Å and C6–H6A...O2_{*ii*} = 162.998(6)° (*ii* = 1 – *X*, –1 – *Y*, 1 – *Z*)] and [C6...O1_{*iii*} = 3.349(4) Å and C6–H6B...O1_{*iii*} = 157.636(6)° (*iii* = 1 – *X*, –2 – *Y*, 1 – *Z*)] lead the extension of one-dimensional chain structure along the (001) direction to two-dimensional (2D) supramolecular layer. The existence of intermolecular interactions [C10...O2_{*ii*} = 3.462(4) Å and C10–H10...O2_{*ii*} = 150.724(6)° and C7...O2_{*iii*} = 3.511(4) Å and C7–H7B...O2_{*iii*} = 151.176(6)°] enhanced the stability of this structure.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

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