Yun-Lian Shi, Xu-Liang Nie, Tao Huang, Jin-Hui Xie, Da-Yong Peng*, Xu-Gen Shi and Bao-Tong Li*

Crystal structure of 3-methyl-*N*-(pyrimidin-5-ylmethyl)pyridin-2-amine, C₁₁H₁₂N₄

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.17 × 0.15 × 0.13 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.08 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
$\theta_{\max}$, completeness:	25.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	3997, 1914, 0.024
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1704
$N(\text{param})_{\text{refined}}$:	138
Programs:	Bruker programs [1], SHELX [2]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
N1	0.22652(15)	0.30465(12)	−0.08218(11)	0.0459(3)
N2	0.03137(15)	0.33502(13)	0.10314(12)	0.0509(3)
H2	−0.0791	0.3110	0.1363	0.061*
N3	0.70141(17)	0.32686(15)	0.30310(14)	0.0610(4)
N4	0.4954(2)	0.26181(15)	0.47924(13)	0.0634(4)
C1	0.05619(17)	0.25951(13)	−0.03250(13)	0.0402(3)
C2	−0.09646(18)	0.14156(14)	−0.11425(14)	0.0452(3)
C3	−0.0631(2)	0.07492(16)	−0.25164(15)	0.0567(4)
H3	−0.1600	−0.0021	−0.3101	0.068*
C4	0.1129(2)	0.12059(17)	−0.30478(15)	0.0587(4)
H4	0.1359	0.0749	−0.3977	0.070*
C5	0.2507(2)	0.23415(16)	−0.21690(14)	0.0513(3)
H5	0.3689	0.2648	−0.2523	0.062*
C6	−0.2837(2)	0.09282(18)	−0.05320(18)	0.0609(4)
H6A	−0.3679	0.0111	−0.1235	0.091*
H6B	−0.3585	0.1792	−0.0379	0.091*
H6C	−0.2446	0.0569	0.0409	0.091*
C7	0.6646(2)	0.26637(18)	0.42313(16)	0.0623(4)
H7	0.7705	0.2221	0.4734	0.075*
C8	0.3451(2)	0.32414(16)	0.40451(15)	0.0531(3)
H8	0.2228	0.3239	0.4406	0.064*
C9	0.36044(18)	0.38898(13)	0.27669(13)	0.0414(3)
C10	0.5463(2)	0.38793(15)	0.23136(14)	0.0497(3)
H10	0.5652	0.4319	0.1466	0.060*
C11	0.1842(2)	0.45392(15)	0.19308(14)	0.0499(3)
H11A	0.1213	0.5156	0.2649	0.060*
H11B	0.2353	0.5215	0.1281	0.060*

<https://doi.org/10.1515/ncrs-2019-0395>

Received June 9, 2019; accepted July 12, 2019; available online August 2, 2019

Abstract

[C₁₁H₁₂N₄], triclinic, $P\bar{1}$, $a = 6.6939(10)$ Å, $b = 8.8034(13)$ Å, $c = 9.1140(13)$ Å, $\alpha = 97.749(2)^\circ$, $\beta = 99.285(2)^\circ$, $\gamma = 95.917(2)^\circ$, $V = 520.90(13)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0381$, $wR_{\text{ref}}(F^2) = 0.1030$, $T = 296(2)$ K.

CCDC no.: 1940076

The crystal 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.

Source of materials

The synthesis of 3-methyl-*N*-(pyrimidin-5-ylmethyl)pyridin-2-amine was carried out using 3-methylpyridin-2-amine

*Corresponding authors: Da-Yong Peng, College of Sciences, Jiangxi Agricultural University, Nanchang 330045, P.R. China, e-mail: dayongpeng@163.com; and Bao-Tong Li, College of Agronomy, Jiangxi Agricultural University, Nanchang 330045, P.R. China, e-mail: libt66@163.com

Yun-Lian Shi and Xu-Gen Shi: College of Agronomy, Jiangxi Agricultural University, Nanchang 330045, P.R. China

Xu-Liang Nie, Tao Huang and Jin-Hui Xie: College of Sciences, Jiangxi Agricultural University, Nanchang 330045, P.R. China. <https://orcid.org/0000-0002-9449-8932> (X.-L. Nie)

and pyrimidine-5-carbaldehyde, using a modified literature known reaction [3–6]. The 3-methylpyridin-2-amine (1.47 g, 15.62 mmol), pyrimidine-5-carbaldehyde (1.70 g, 15.72 mmol) and *p*-toluenesulfonic acid (0.1 g, 0.58 mmol) were added to

the reaction flask with toluene as solvent. The mixture was refluxed for 4 h, then the toluene was removed under reduced pressure. 15 mL methanol was added for next step. And the sodium tetrahydroborate (0.6 g, 15.86 mmol) was slowly added to the above solution and then stirred at room temperature. The reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure. The products were extract with ethyl acetate and adjust pH to 7 with dilute hydrochloric acid. The residue was purified by column chromatography (ethyl acetate/Hexane = 1/1) to give title compound (1.3 g), Yield 45.33 %. The product was recrystallized from Acetone. m.p. 118 °C–120 °C. **MS** (ES I) m/z: 200.35. Elemental Anal. Calcd. (%) for C₁₁H₁₂N₄: C, 65.98; H, 6.04; Found(%): C, 65.88; H, 5.99. **¹H NMR** (500 MHz, CDCl₃) δ 9.10 (s, 1H), 8.75 (s, 2H), 7.99 (d, J = 4.7 Hz, 1H), 7.28 (d, J = 2.4 Hz, 1H), 6.60 (dd, J = 7.0, 5.2 Hz, 1H), 4.71 (d, J = 5.8 Hz, 2H), 4.59 (bs, 1H), 2.11 (s, 3H). **¹³C NMR** (125 MHz, CDCl₃) δ 157.47, 156.42, 155.75, 145.37, 137.17, 133.62, 116.62, 113.80, 40.75, 16.83.

Experimental details

All H atoms were included in calculated positions and refined as riding atoms, with C–H = 0.93 Å with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2 U_{\text{eq}}(\text{C})$ for all other H atoms.

Comment

Triflumezopyrim is a new type of mesoionic insecticide developed by DuPont. It can be used to control rice Delphacidae, Cicadellidae etc., especially for Nilaparvata lugens [7, 8]. 3-methyl-*N*-(pyrimidin-5-ylmethyl) pyridin-2-amine is an important intermediate for the synthesis of mesoionic compounds. The synthetic route was further optimized and then a series of triflumezopyrim analogs (which are mesoionic compounds) were synthesized, which are expected to have good biological activity [9, 10]. Herein we report the synthesis and crystal structure of 3-methyl-*N*-(pyrimidin-5-ylmethyl) pyridin-2-amine, which provides a more efficient synthesis method of such compounds.

There is one crystallographic independent molecules in the asymmetric unit (shown in the figure). In the molecule of the title compound bond lengths and angles are very similar to those given in the literature for pyrimidine derivatives [11, 12]. The dihedral angle of the pyrimidine plane and the pyridine plane is 72.778(334)°, 53.230(575)° and 57.419(610)°.

Acknowledgements: X-ray data were collected at Instrumental Analysis Center Nanchang Hangkong University,

Nanchang, 330063, People's Republic of China. This research has been supported by the China National Key R and D Program during the 13th Five-year Plan Period (Grant No. 2017YFD0301604), The National Natural Science Foundation of China (Grant No. 21562022), The Natural Science Foundation of Jiangxi Province (Grant No. 20181BAB203015), The Research Foundation of Educational Department of Jiangxi Province [No. GJJ160379, GJJ180204].

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