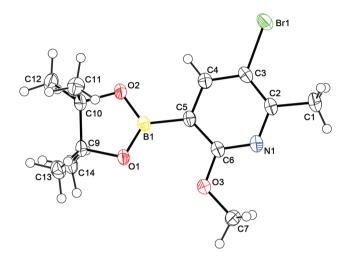
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Ji-Run Zhang, Hao Deng and Tong Liu*

The crystal structure of 3-bromo-6-methoxy-2methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine, C₁₃H₁₉BBrNO₃



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Abstract

 $C_{13}H_{19}BBrNO_3$, triclinic, $P\bar{1}$ (no. 2), a = 6.5459(3) Å, $\alpha = 106.938(2)^{\circ}$ b = 11.2565(5) Åc = 11.8529(5) Å, $\beta = 105.657(2)^{\circ}$, $\gamma = 106.628(2)^{\circ}$, $V = 738.71(6) \text{ Å}^3$, Z = 2, $R_{\rm gt}(F) = 0.0286$, $wR_{\rm ref}(F^2) = 0.0641$, T = 173 K.

CCDC no.: 1958725

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.

Source of material

All chemicals, reagents and solvents are of analytical grade and commercially available. To a 3 mouth bis(pinacolato)diboron (6.91 g, bipyridine (0.19 g, 1.21 mmol) and bis[(1,5-cyclooctadiene)

Ji-Run Zhang and Hao Deng: School of Chemistry and Chemical Engineering, Guizhou University, Guiyang 550025, P.R. China

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.16 \times 0.11 \times 0.08~\text{mm}$
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	$2.79 \; \text{mm}^{-1}$
Diffractometer, scan mode:	Bruker APEX-II, $oldsymbol{arphi}$ and $oldsymbol{\omega}$
$\theta_{\sf max}$, completeness:	27.5°, 99%
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}, R_{\text{int}}$:	9092, 3356, 0.031
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{\rm obs} > 2 \ \sigma(I_{\rm obs})$, 2931
$N(param)_{refined}$:	178
Programs:	Bruker [1], SHELX [2, 3], Olex2 [4]

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

Atom	X	у	Z	U _{iso} */U _{eq}
B1	0.6832(4)	0.2552(2)	0.46623(19)	0.0235(4)
Br1	0.48104(4)	0.29330(2)	0.01250(2)	0.03610(8)
C1	0.7962(4)	0.1217(2)	-0.02188(18)	0.0359(5)
H1A	0.888080	0.206264	-0.023754	0.054*
H1B	0.648763	0.076348	-0.095781	0.054*
H1C	0.880997	0.062582	-0.024993	0.054*
C2	0.7514(3)	0.15211(19)	0.09884(17)	0.0259(4)
С3	0.6202(3)	0.22479(19)	0.12749(17)	0.0261(4)
C4	0.5935(3)	0.25312(19)	0.24355(17)	0.0262(4)
H4	0.503053	0.302869	0.262392	0.031*
C5	0.6984(3)	0.20908(18)	0.33224(16)	0.0237(4)
C6	0.8221(3)	0.13227(18)	0.29263(16)	0.0236(4)
C7	1.0333(4)	-0.0014(2)	0.33081(19)	0.0318(4)
H7A	0.929361	-0.074235	0.247196	0.048*
H7B	1.078136	-0.040533	0.392499	0.048*
H7C	1.171592	0.053372	0.323600	0.048*
C9	0.7191(3)	0.28905(19)	0.67033(16)	0.0245(4)
C10	0.6096(3)	0.38222(19)	0.62608(16)	0.0253(4)
C11	0.7802(4)	0.5269(2)	0.6734(2)	0.0354(5)
H11A	0.918540	0.526928	0.656276	0.053*
H11B	0.823345	0.572655	0.765534	0.053*
H11C	0.708844	0.574643	0.628886	0.053*
C12	0.3928(4)	0.3792(2)	0.65081(19)	0.0345(5)
H12A	0.335480	0.439467	0.619151	0.052*
H12B	0.428760	0.409383	0.742832	0.052*
H12C	0.274290	0.286730	0.606405	0.052*
C13	0.9224(4)	0.3610(2)	0.79788(18)	0.0348(5)
H13A	0.985013	0.296413	0.816562	0.052*

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^{*}Corresponding author: Tong Liu, School of Chemistry and Chemical Engineering, Guizhou University, Guiyang 550025, P.R. China, e-mail: 544930407@qq.com. https://orcid.org/0000-0001-9737-3847

Table 2 (continued)

Atom	х	у	Z	U _{iso} */U _{eq}
H13B	0.871152	0.399121	0.865187	0.052*
H13C	1.042345	0.433840	0.794377	0.052*
C14	0.5439(4)	0.1645(2)	0.66675(18)	0.0321(4)
H14A	0.414104	0.119498	0.583598	0.048*
H14B	0.487182	0.191329	0.734652	0.048*
H14C	0.617113	0.102204	0.679675	0.048*
N1	0.8487(3)	0.10511(16)	0.18210(14)	0.0262(3)
01	0.8042(2)	0.24100(13)	0.57073(11)	0.0259(3)
02	0.5450(2)	0.32268(13)	0.48730(11)	0.0271(3)
03	0.9169(2)	0.08245(13)	0.37358(12)	0.0276(3)

(methanolato)iridium] (0.041 g, 0.062 mmol) were added and n-hexane (100 mL) was injected into the 3 mouth flask at 25 °C then the reaction mixture was stirred under a nitrogen atmosphere. After stirring for an hour, 3-bromo-6-methoxy-2methylpyridine (5.0 g, 24.74 mmol) was added under a nitrogen atmosphere. The reaction mixture was stirred at 60 °C for 1 hour under nitrogen. The progress of the reaction was monitored by TLC. On completion, the reaction mixture was poured into water and filtered, then the filtrate was extracted with ethyl acetate. The organic phase was evaporated with vacuum distillation to afford the crude product (8.01 g). The crude product was recrystallized from n-hexane (100 mL) twice to afford a crystalline solid (7.23 g, 89.03%). ¹H NMR (400 MHz, CDCl₃) δ [ppm] 8.12 (s, 1H), 4.02 (s, 3H), 2.47 (s, 3H), 1.39 (s, 12H).

Experimental details

All hydrogen atoms were placed in geometrically calculated positions. The $U_{\rm iso}$ values of the hydrogen atoms of methyl groups were set to 1.5 $U_{eq}(C_{methyl})$ and the U_{iso} values of all other hydrogen atoms were set to 1.2 U_{eq} .

Comment

The compound 3-bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine, which shows some similarities with the title compound has applications in the field of medicine, organic synthesis and fine chemicals. It is an important intermediate for the synthesis of cholinergic drugs which can treat gastrointestinal diseases [5]. Similar compounds participate in the synthesis of oxazolidinone derivatives for modulators of mGluR5 [6]. In the synthesis of organic electroluminescent devices [7].

The structure of the title compound was clarified by spectroscopy and X-ray diffraction. The crystal structure shows that there is one molecule in the asymmetric unit. The crystal structure shows that the molecules are stabilized by intermolecular hydrogen bonds which are C14-H14C···C7 (distance = 2.846 Å). C7–H7B···O1 (distance = 2.695 Å). C11– H11C···O2 (distance = 2.605 Å) and the intermolecular packing is stabilized by the van der Waals forces. All bond lengths and angles are comparable to those in the literature [8, 9].

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