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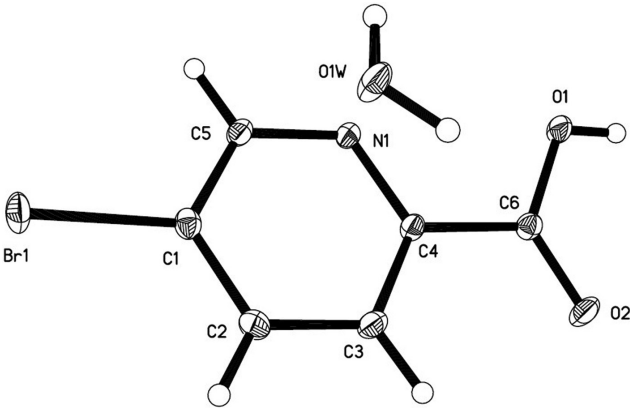
The crystal structure of 5-bromopicolinic acid monohydrate, $C_6H_6BrNO_3$



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Abstract

$C_6H_6BrNO_3$, triclinic, $P\bar{1}$ (no. 2), $a = 7.0407(5)$ Å, $b = 7.1597(6)$ Å, $c = 8.3808(7)$ Å, $\alpha = 75.844(4)°$, $\beta = 94.562(4)°$, $\gamma = 76.306(4)°$, $V = 373.61(5)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0205$, $wR_{ref}(F^2) = 0.0527$, $T = 150(2)$ 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.

Source of material

All of the starting materials were used as received. 2.01 g (0.01 mol) 5-bromopicolinic acid was added to a solution mixed by 10 mL THF and 1 mL double-destilled water under room temperature. After stirring for 10 min, the solution was filtered and let evaporate automatically. Many colorless block crystals were harvested, which are suitable for single XRD measurement, yield 68.5% (based on 5-bromopicolinic acid).

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.26 × 0.22 × 0.10 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	5.46 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	25.2°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6538, 1352, 0.035
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1226
$N(param)_{refined}$:	112
Programs:	Bruker [1], SHELX [2], Olex2 [3, 4]

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

Atom	x	y	z	U_{iso}*/U_{eq}
Br1	0.87131(4)	0.89027(4)	0.91538(3)	0.02585(11)
C1	0.7000(4)	0.8024(4)	0.8297(3)	0.0179(5)
C2	0.7346(4)	0.5969(4)	0.8438(3)	0.0230(5)
H2	0.845136	0.495181	0.896357	0.028*
C3	0.6028(4)	0.5432(4)	0.7787(3)	0.0210(5)
H3	0.620305	0.403050	0.786730	0.025*
C4	0.4453(3)	0.6974(3)	0.7019(3)	0.0166(5)
C5	0.5386(3)	0.9485(4)	0.7523(3)	0.0182(5)
H5	0.516523	1.089667	0.744780	0.022*
C6	0.3008(3)	0.6445(3)	0.6290(3)	0.0177(5)
N1	0.4137(3)	0.8975(3)	0.6882(2)	0.0163(4)
O1	0.1922(3)	0.7977(3)	0.5303(2)	0.0226(4)
O2	0.2925(3)	0.4724(3)	0.6625(3)	0.0278(4)
O1W	0.9172(3)	0.7506(3)	0.4137(3)	0.0291(5)
H1	0.114(5)	0.768(5)	0.499(4)	0.037(9)*
H1WA	0.834(5)	0.850(5)	0.394(4)	0.036(10)*
H1WB	0.873(5)	0.658(6)	0.405(5)	0.053(11)*

Experimental details

The structure was solved by direct methods with the SHELXS-2018 program. All H-atoms from C atoms were positioned with idealized geometry and refined isotropically ($U_{iso}(H) = 1.2U_{eq}(C)$) using a riding model with C—H = 0.950 Å. The H-atom from O1 atom was positioned in accordance with a difference electron density peak and refined isotropic freely ($U_{iso}(H) = 1.5U_{eq}(O)$, O—H = 0.776 Å).

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Comment

5-Bromopicolinic acid, one of the derivatives of picolinic acid, attracted attention over a long period of time and acted as organic ligand to form metal-organic complexes [5–11]. One of the derivatives, the methyl-5-bromo-6-methylpicolinate, has been reported as single crystal structure elsewhere [12]. To the best of our knowledge, the single crystal structure of 5-bromopicolinic acid has not been published.

As shown in the figure, the asymmetric unit is made of one neutral 5-bromopicolinic acid molecule and one water molecule, given the molecule formula of $C_6H_6BrNO_3$. All of the atoms are nearly co-planar, except the carboxyl group. The two C—O bond lengths from carboxyl group are 1.217 and 1.299 Å, indicating that the H atom from the carboxyl group is not removed. Furthermore, the refinement resulted that the N atom from the pyridine is not protonated and acts as an acceptor of the intermolecular O—H···N hydrogen bond. There is a dimer formed by two 5-bromopicolinic acid molecules which are bridged by two water molecules through two O—H···O hydrogen bonds. These dimers are linked with O—H···N hydrogen bonds to generate a hydrogen bonded strand, which runs along the crystallographic *b* axis. All bond lengths and angles of 5-bromopicolinic acid are comparable with its analogues [5–11].

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