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2-Bromopyridine-3-carboxylic acid

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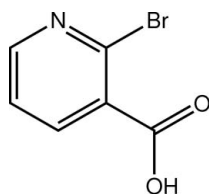
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Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.038; wR factor = 0.093; data-to-parameter ratio = 12.5.

The carboxylic acid residue in the title compound, $\text{C}_6\text{H}_4\text{BrNO}_2$, is twisted out of the plane of the other atoms, as indicated by the $(\text{Br})\text{C}-\text{C}-\text{C}-\text{O}_{\text{carbonyl}}$ torsion angle of -20.1 (9)°. In the crystal, supramolecular chains mediated by $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds are formed with base vector $[201]$ and $\text{C}-\text{H}\cdots\text{O}$ interactions reinforce the packing.

Related literature

For the biological activity of N -heterocyclic compounds, see: de Souza (2005); Cunico *et al.* (2006). For related structures, see: Wright & King (1953); Kutoglu & Scheringer (1983); de Souza *et al.* (2005); Kaiser *et al.* (2009). For the synthesis, see: Bradlow & van der Werf (1949).



Experimental

Crystal data

$\text{C}_6\text{H}_4\text{BrNO}_2$ $V = 650.83$ (8) Å³
 $M_r = 202.01$ $Z = 4$
 Monoclinic, $P2_1/c$ $\text{Mo K}\alpha$ radiation
 $a = 3.9286$ (3) Å $\mu = 6.24$ mm⁻¹
 $b = 12.9737$ (9) Å $T = 120$ K
 $c = 12.8570$ (8) Å $0.10 \times 0.09 \times 0.08$ mm
 $\beta = 96.695$ (4)°

Data collection

Nonius KappaCCD area-detector diffractometer 7699 measured reflections
 Absorption correction: multi-scan (SADABS; Sheldrick, 2007) 1147 independent reflections
 $T_{\text{min}} = 0.453$, $T_{\text{max}} = 0.607$ 882 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.070$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$ 92 parameters
 $wR(F^2) = 0.093$ H-atom parameters constrained
 $S = 1.06$ $\Delta\rho_{\text{max}} = 0.86$ e Å⁻³
 1147 reflections $\Delta\rho_{\text{min}} = -0.62$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1}\cdots\text{N1}^i$	0.84	1.85	2.685 (5)	173
$\text{C5}-\text{H5}\cdots\text{O2}^{ii}$	0.95	2.39	3.258 (7)	152
$\text{C6}-\text{H6}\cdots\text{O2}^{iii}$	0.95	2.47	3.171 (6)	131

Symmetry codes: (i) $x-1, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x+1, -y+\frac{3}{2}, z+\frac{1}{2}$.

Data collection: COLLECT (Hooft, 1998); cell refinement: DENZO (Otwinowski & Minor, 1997) and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997) and DIAMOND (Brandenburg, 2006); software used to prepare material for publication: pubCIF (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5318).

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supporting information

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2-Bromopyridine-3-carboxylic acid

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S1. Comment

The structure of the title compound, (I), was determined in connection with on-going studies of biological activities, e.g. anti-mycobacterial activity, of N-heterocyclic compounds (Cunico *et al.* 2006; de Souza, 2005), as we have embarked on complementary systematic structural investigations in order to ascertain supramolecular aggregation patterns (Kaiser *et al.*, 2009).

In the molecular structure of (I), Fig. 1, the carbonyl-O2 atom is approximately syn to the bromide. The carboxylic acid residue is twisted out of the plane of the pyridine ring as seen in the value of the C2/C3/C7/O1 torsion angle of 161.1 (5)°. In the crystal packing, a supramolecular chain with base vector [2 0 1] is formed through the agency of O–H...N hydrogen bonds, Fig. 2 and Table 1. Additional stabilisation to the chains are afforded by C–H...O_{carbonyl} interactions, Table 1. The chains stack into layers in the ab plane and are consolidated in the crystal structure by further C–H...O_{carbonyl} contacts, Fig. 2 & Table 1. Similar supramolecular chains are found in the crystal structures of nicotinic acid (Wright & King, 1953; Kutoglu & Scheringer, 1983) as well as in 2-chloropyridine-3-carboxylic acid (de Souza *et al.*, 2005).

S2. Experimental

A mixture of 2-bromo-3-methylpyridine (0.77 g, 4.5 mmol), KMnO₄ (0.316 g, 2 mmol) and H₂O (20 ml) was refluxed until the purple colour of the solution disappeared. A second portion of KMnO₄ (0.316 g) and water (10 ml) were added and the reaction mixture was refluxed again until no purple colour remained. The reaction mixture was concentrated to 10 ml, acidified with concentrated hydrochloric acid, and filtered. The precipitate was washed with cold water and cold di-ethylether (20 ml). The yield was 0.79 g (60%), m.p. 520–523 K; lit value 522–523 K (Bradlow & van der Werf, 1949). 2-Bromonicotinic acid was recrystallised from EtOH for the crystallographic study. ¹H NMR [500.00 MHz, DMSO-d₆] δ: 8.50 (1H, dd, *J* = 5.0 and 2.0 Hz, H6), 8.13 (1H, dd, *J* = 7.5 and 2.0 Hz, H4), 7.55 (1H, dd, *J* = 7.5 and 5.0 Hz, H5), 3.44 (1H, s, OH) p.p.m. ¹³C NMR (125.0 MHz, DMSO-d₆) δ: 166.3, 151.8, 139.1, 138.6, 131.1, 123.2 p.p.m.

S3. Refinement

The C-bound H atoms were geometrically placed (C–H = 0.95 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C). The N-bound H atoms were located from a difference map and refined with U_{iso}(H) = 1.5U_{eq}(N).

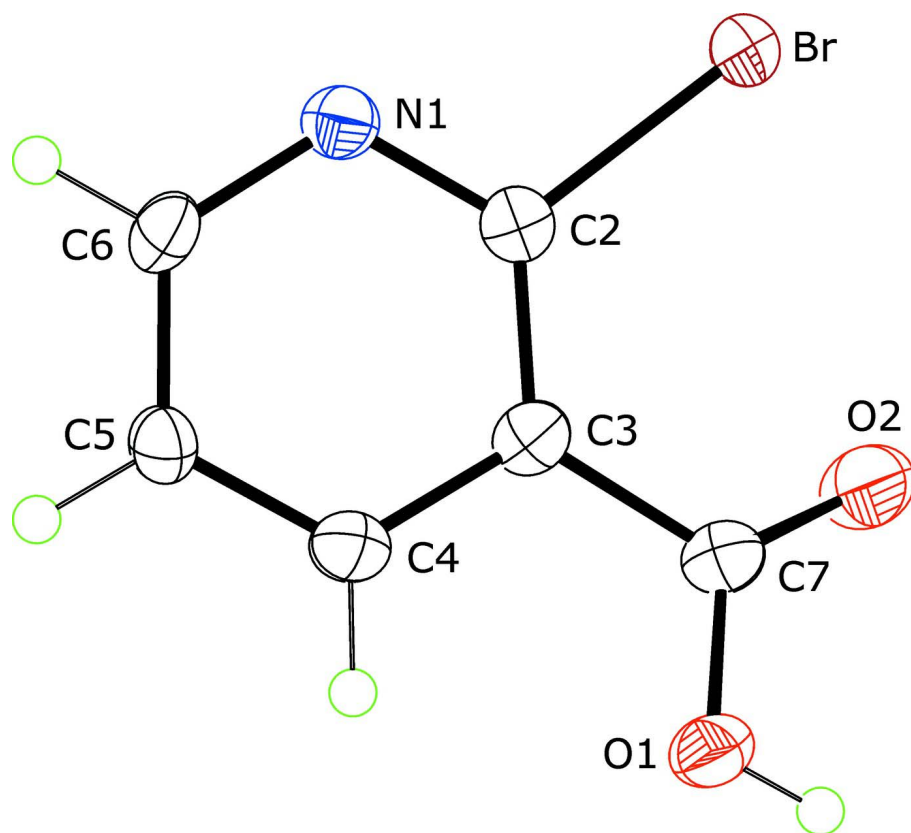


Figure 1

The molecular structure of (I) showing displacement ellipsoids at the 50% probability level.

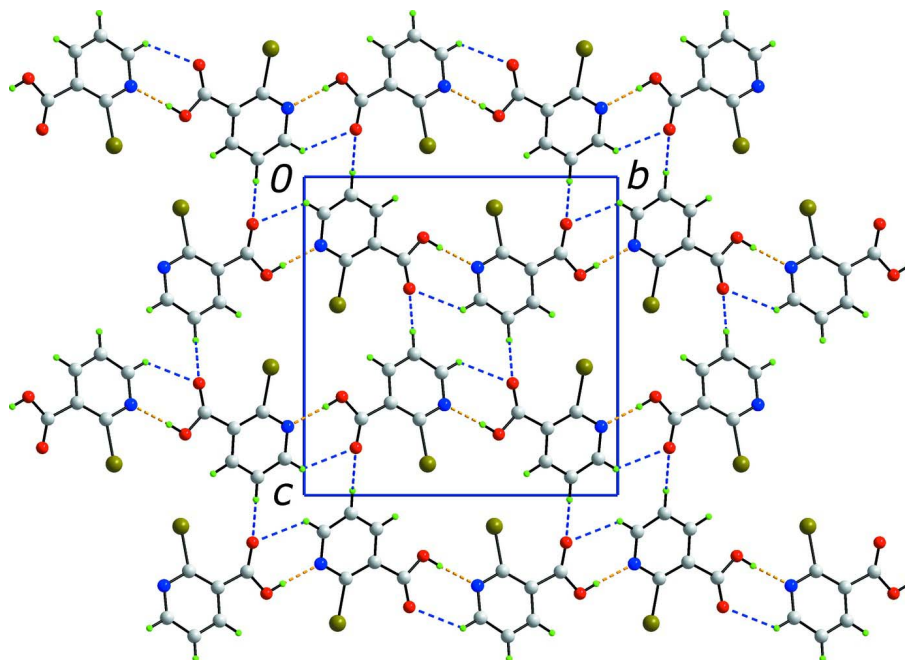


Figure 2

View of the unit cell contents in (I) highlighting the N–H···O hydrogen bonding (orange dashed lines) leading to supramolecular chains, and C–H···O contacts within and between chains (blue dashed lines). Colour code: Br, olive; O, red; N, blue; C, grey; and H, green.

2-Bromopyridine-3-carboxylic acid

Crystal data

$C_6H_4BrNO_2$

$M_r = 202.01$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 3.9286$ (3) Å

$b = 12.9737$ (9) Å

$c = 12.8570$ (8) Å

$\beta = 96.695$ (4)°

$V = 650.83$ (8) Å³

$Z = 4$

$F(000) = 392$

$D_x = 2.062$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 24006 reflections

$\theta = 2.9$ – 27.5 °

$\mu = 6.24$ mm⁻¹

$T = 120$ K

Block, colourless

$0.10 \times 0.09 \times 0.08$ mm

Data collection

Nonius KappaCCD area-detector
diffractometer

Radiation source: Enraf Nonius FR591 rotating
anode

10 cm confocal mirrors monochromator

Detector resolution: 9.091 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 2007)

$T_{\min} = 0.453$, $T_{\max} = 0.607$

7699 measured reflections

1147 independent reflections

882 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.070$

$\theta_{\max} = 25.0$ °, $\theta_{\min} = 3.2$ °

$h = -4 \rightarrow 4$

$k = -15 \rightarrow 15$

$l = -15 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.093$
 $S = 1.06$
 1147 reflections
 92 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0439P)^2 + 1.1585P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.86 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.62 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s 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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br	0.26644 (13)	0.59770 (4)	0.89357 (4)	0.0284 (2)
O1	-0.1485 (10)	0.8088 (3)	0.6204 (3)	0.0329 (9)
H1	-0.2563	0.7783	0.5691	0.049*
O2	0.0225 (11)	0.6488 (3)	0.6647 (3)	0.0484 (12)
N1	0.5499 (10)	0.7843 (3)	0.9471 (3)	0.0257 (10)
C2	0.3563 (13)	0.7384 (4)	0.8676 (4)	0.0237 (11)
C3	0.2287 (12)	0.7899 (4)	0.7756 (4)	0.0246 (11)
C4	0.3069 (14)	0.8942 (4)	0.7698 (4)	0.0303 (12)
H4	0.2193	0.9327	0.7098	0.036*
C5	0.5111 (13)	0.9428 (4)	0.8507 (4)	0.0252 (12)
H5	0.5688	1.0137	0.8461	0.030*
C6	0.6276 (13)	0.8854 (4)	0.9378 (4)	0.0268 (12)
H6	0.7679	0.9179	0.9935	0.032*
C7	0.0240 (13)	0.7406 (4)	0.6822 (4)	0.0290 (12)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.0342 (3)	0.0217 (3)	0.0277 (3)	-0.0033 (2)	-0.0029 (2)	0.0016 (2)
O1	0.042 (2)	0.030 (2)	0.025 (2)	0.0023 (18)	-0.0059 (17)	-0.0007 (16)
O2	0.072 (3)	0.027 (2)	0.041 (2)	0.009 (2)	-0.018 (2)	-0.0066 (19)
N1	0.031 (2)	0.024 (2)	0.023 (2)	0.0023 (19)	0.0034 (19)	-0.0008 (19)
C2	0.021 (2)	0.024 (3)	0.026 (3)	0.002 (2)	0.005 (2)	-0.001 (2)
C3	0.023 (3)	0.026 (3)	0.024 (3)	0.005 (2)	0.002 (2)	-0.003 (2)
C4	0.035 (3)	0.025 (3)	0.029 (3)	0.003 (2)	-0.003 (2)	0.003 (2)

C5	0.030 (3)	0.020 (3)	0.026 (3)	-0.001 (2)	0.003 (2)	-0.003 (2)
C6	0.027 (3)	0.028 (3)	0.024 (3)	0.000 (2)	-0.002 (2)	-0.007 (2)
C7	0.028 (3)	0.031 (3)	0.027 (3)	0.003 (2)	0.000 (2)	0.002 (2)

Geometric parameters (Å, °)

Br—C2	1.897 (5)	C3—C4	1.392 (7)
O1—C7	1.322 (6)	C3—C7	1.507 (7)
O1—H1	0.8400	C4—C5	1.388 (7)
O2—C7	1.213 (6)	C4—H4	0.9500
N1—C2	1.340 (6)	C5—C6	1.378 (7)
N1—C6	1.356 (6)	C5—H5	0.9500
C2—C3	1.400 (7)	C6—H6	0.9500
C7—O1—H1	109.5	C3—C4—H4	119.5
C2—N1—C6	118.4 (4)	C6—C5—C4	118.1 (5)
N1—C2—C3	123.3 (5)	C6—C5—H5	121.0
N1—C2—Br	113.2 (3)	C4—C5—H5	121.0
C3—C2—Br	123.5 (4)	N1—C6—C5	122.6 (4)
C4—C3—C2	116.7 (5)	N1—C6—H6	118.7
C4—C3—C7	118.1 (4)	C5—C6—H6	118.7
C2—C3—C7	125.2 (4)	O2—C7—O1	123.7 (5)
C5—C4—C3	120.9 (5)	O2—C7—C3	123.8 (5)
C5—C4—H4	119.5	O1—C7—C3	112.6 (4)
C2—C3—C7—O1	161.1 (5)	C2—C3—C7—O2	-20.1 (9)
C4—C3—C7—O1	-20.7 (7)	C4—C3—C7—O2	158.1 (6)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1 \cdots N1 ⁱ	0.84	1.85	2.685 (5)	173
C5—H5 \cdots O2 ⁱⁱ	0.95	2.39	3.258 (7)	152
C6—H6 \cdots O2 ⁱⁱⁱ	0.95	2.47	3.171 (6)	131

Symmetry codes: (i) $x-1, -y+3/2, z-1/2$; (ii) $-x+1, y+1/2, -z+3/2$; (iii) $x+1, -y+3/2, z+1/2$.