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3-Bromopyridine-2-carbonitrile

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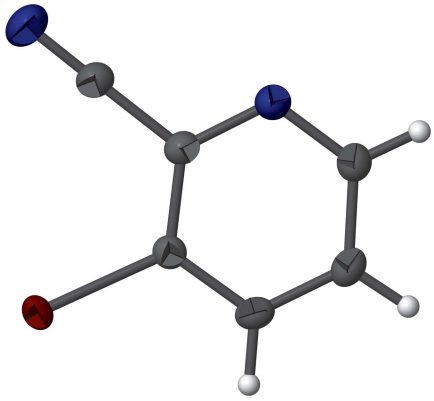
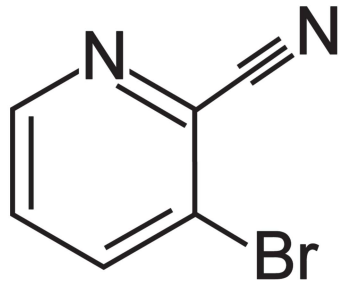
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_6H_3BrN_2$, also known as 3-bromopicolinonitrile, was synthesized by cyanation of 2,3-dibromopyridine. In the solid state, short intermolecular Br···N contacts are observed. Additionally, the crystal packing is consolidated by π–π stacking interactions with centroid–centroid distances of 3.7893 (9) Å.

3D view



Chemical scheme



Structure description

The new title compound is a pyridine derivative with a cyano group in the *ortho* and a bromine atom in the *meta* position. Its molecular structure is shown in Fig. 1. Non-H short intermolecular contacts along the *b* axis are observed [Br1···N2 = 3.1237 (17) Å, Fig. 2]. Additionally the crystal packing is stabilized by π–π stacking interactions between the pyridine rings along the *c* axis [centroid–centroid distance: 3.7893 (9) Å, dihedral angle between the planes of the pyridine rings: 4.01 (7)°, ring slippage 1.32 and 1.16 Å, respectively; Fig. 3].

Synthesis and crystallization

The title compound was obtained as the main product by synthesizing the mono- and dicyano derivatives of 2,3-dibromopyridine. The reaction was carried out in an Ace pressure tube. A mixture of 2,3-dibromopyridine (1.0 mmol, 237 mg), $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.4 mmol, 169 mg), Na_2CO_3 (1.2 mmol, 127 mg), CuI (0.1 mmol, 19 mg), 1-butyl-imidazole (2.0 mmol, 248 mg) and *o*-xylene (2 ml) was stirred at 160°C for 24 h. Afterwards the reaction mixture was quenched with water and diluted with dichloromethane. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 20 ml). The combined organic layers were dried on anhydrous Na_2SO_4. After filtering, the solvent was removed *in vacuo*, and the product was purified

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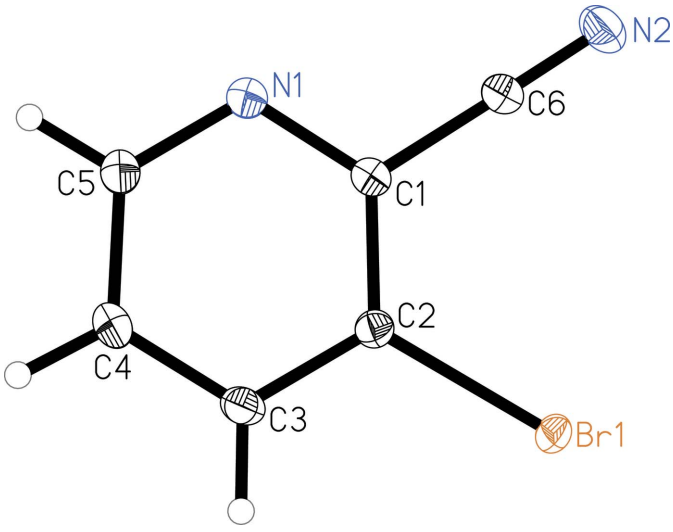

Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 30% probability level.

by column chromatography (silica gel, ethyl acetate/*n*-hexane 1:1 *v*/*v;* yield: 20%, 37 mg). Crystals suitable for X-ray analysis were obtained by recrystallization from an ethyl acetate/*n*-heptane (1:1 *v*/*v*) solution. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (*dd*, 1H, *J* = 744 Hz), 2.09 (*s*, 3H), 8.03 (*dd*, 1H, *J* = 8.03 Hz), 8.63 (*dd*, 1H, *J* = 744 Hz); ^{13}C NMR ($CDCl_3$): δ = 115.7 (C), 124.6 (C), 127.8 (CH), 135.1 (C), 149.2 (CH), 149.2 (CH); GC–MS (EI, 70 eV): *m*/*z* = 184 (M^+, 96), 181 (100), 103 (99), 76 (49), 75 (29), 51 (22), 50 (21).

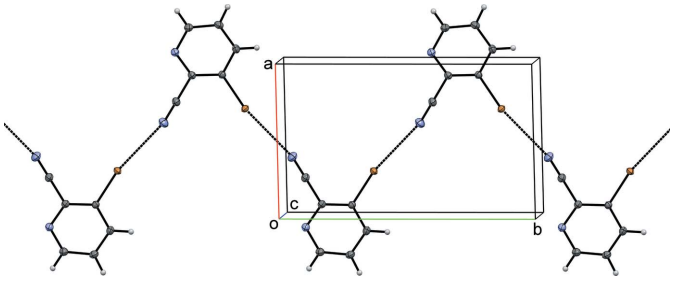

Figure 2
Partial packing diagram of the title compound showing the intermolecular Br···N contacts as dashed lines. Displacement ellipsoids are drawn at the 30% probability level.

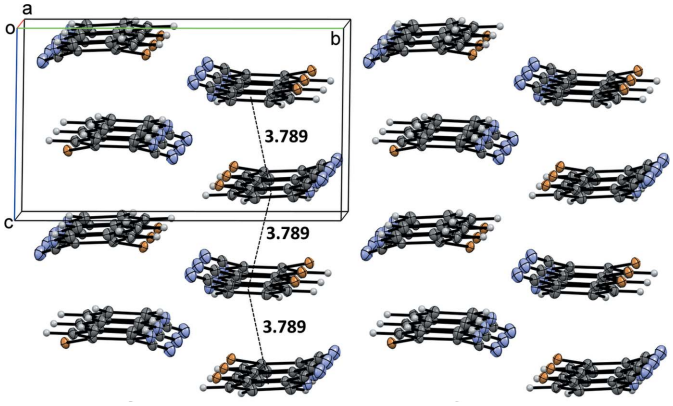

Figure 3
Packing diagram of the title compound showing the π–π stacking interactions (dashed lines). Displacement ellipsoids are drawn at the 30% probability level.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_6H_3BrN_2$
M_r	183.01
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, *b*, *c* (Å)	7.8821 (2), 11.7480 (3), 7.4169 (2)
β (°)	113.906 (1)
V (Å^3)	627.88 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	6.44
Crystal size (mm)	0.43 × 0.39 × 0.22
Data collection	
Diffractometer	Bruker Kappa APEXII DUO
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.17, 0.34
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18621, 1637, 1577
R_{int}	0.020
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.679
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.016, 0.042, 1.16
No. of reflections	1637
No. of parameters	82
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.38, −0.37

Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2013), *XP* in *SHELXTL* and *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2006), *publCIF* (Westrip, 2010) and *PLATON* (Spek, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. One outlier (100) was omitted in the last cycles of refinement.

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full crystallographic data

IUCrData (2019). **4**, x191326 [https://doi.org/10.1107/S2414314619013269]

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Crystal data

$C_6H_3BrN_2$
M_r = 183.01
Monoclinic, $P2_1/c$
a = 7.8821 (2) Å
b = 11.7480 (3) Å
c = 7.4169 (2) Å
β = 113.906 (1)°
V = 627.88 (3) Å^3
Z = 4
$F(000)$ = 352
D_x = 1.936 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9981 reflections
θ = 2.8–28.8°
μ = 6.44 mm^{-1}
T = 150 K
Part of a needle, colourless
0.43 × 0.39 × 0.22 mm

Data collection

Bruker Kappa APEXII DUO diffractometer
Radiation source: fine-focus sealed tube
Curved graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
ω and phi scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.17, T_{max} = 0.34
18621 measured reflections
1637 independent reflections
1577 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 28.8°, θ_{min} = 3.3°
h = −10→10
k = −15→15
l = −10→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.016
$wR(F^2)$ = 0.042
S = 1.16
1637 reflections
82 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0198P)^2 + 0.3045P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Special details

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

Refinement. The H atoms were refined as riding, with C–H = 0.95 Å and U_{iso}(H) = -1.2U_{eq}(C).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.30145 (2)	0.36783 (2)	0.19853 (2)	0.02306 (6)
C1	0.0879 (2)	0.16246 (12)	0.1697 (2)	0.0229 (3)
C2	0.08389 (19)	0.28060 (12)	0.1631 (2)	0.0219 (3)
C3	−0.0811 (2)	0.33623 (13)	0.1323 (2)	0.0272 (3)
H3	−0.0885	0.4170	0.1274	0.033*
C4	−0.2344 (2)	0.27070 (14)	0.1088 (2)	0.0286 (3)
H4	−0.3499	0.3058	0.0860	0.034*
C5	−0.2173 (2)	0.15295 (14)	0.1192 (3)	0.0287 (3)
H5	−0.3235	0.1090	0.1037	0.034*
C6	0.2574 (2)	0.10001 (14)	0.2049 (2)	0.0274 (3)
N1	−0.05951 (18)	0.09830 (12)	0.1497 (2)	0.0280 (3)
N2	0.3907 (2)	0.05012 (14)	0.2363 (2)	0.0384 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02029 (8)	0.02140 (8)	0.02829 (9)	−0.00458 (5)	0.01069 (6)	−0.00295 (5)
C1	0.0233 (6)	0.0217 (6)	0.0235 (7)	0.0023 (5)	0.0094 (5)	0.0002 (5)
C2	0.0219 (6)	0.0213 (6)	0.0222 (6)	−0.0009 (5)	0.0087 (5)	−0.0011 (5)
C3	0.0277 (7)	0.0211 (6)	0.0314 (8)	0.0040 (5)	0.0104 (6)	0.0003 (6)
C4	0.0226 (6)	0.0301 (8)	0.0330 (8)	0.0053 (6)	0.0110 (6)	0.0015 (6)
C5	0.0231 (7)	0.0278 (7)	0.0354 (8)	0.0006 (6)	0.0121 (6)	0.0022 (6)
C6	0.0273 (7)	0.0238 (7)	0.0320 (8)	0.0017 (6)	0.0129 (6)	−0.0017 (6)
N1	0.0255 (6)	0.0233 (6)	0.0362 (7)	0.0013 (5)	0.0136 (5)	0.0023 (5)
N2	0.0311 (7)	0.0354 (8)	0.0485 (9)	0.0077 (6)	0.0161 (7)	−0.0040 (7)

Geometric parameters (Å, º)

Br1—C2	1.9220 (14)	C3—H3	0.9500
C1—N1	1.3418 (19)	C4—C5	1.389 (2)
C1—C2	1.389 (2)	C4—H4	0.9500
C1—C6	1.452 (2)	C5—N1	1.335 (2)
C2—C3	1.390 (2)	C5—H5	0.9500
C3—C4	1.382 (2)	C6—N2	1.141 (2)
N1—C1—C2	123.46 (14)	C3—C4—C5	119.18 (14)
N1—C1—C6	115.37 (13)	C3—C4—H4	120.4
C2—C1—C6	121.15 (14)	C5—C4—H4	120.4
C1—C2—C3	118.83 (13)	N1—C5—C4	123.44 (15)
C1—C2—Br1	121.45 (11)	N1—C5—H5	118.3
C3—C2—Br1	119.71 (11)	C4—C5—H5	118.3
C4—C3—C2	118.08 (14)	N2—C6—C1	178.55 (19)
C4—C3—H3	121.0	C5—N1—C1	117.00 (14)
C2—C3—H3	121.0		

N1—C1—C2—C3	−0.6 (2)	C2—C3—C4—C5	0.7 (2)
C6—C1—C2—C3	−178.91 (14)	C3—C4—C5—N1	−0.4 (3)
N1—C1—C2—Br1	178.61 (11)	C4—C5—N1—C1	−0.5 (2)
C6—C1—C2—Br1	0.3 (2)	C2—C1—N1—C5	1.0 (2)
C1—C2—C3—C4	−0.3 (2)	C6—C1—N1—C5	179.35 (14)
Br1—C2—C3—C4	−179.52 (12)		