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3,5-Dibromo-4-methylpyridine

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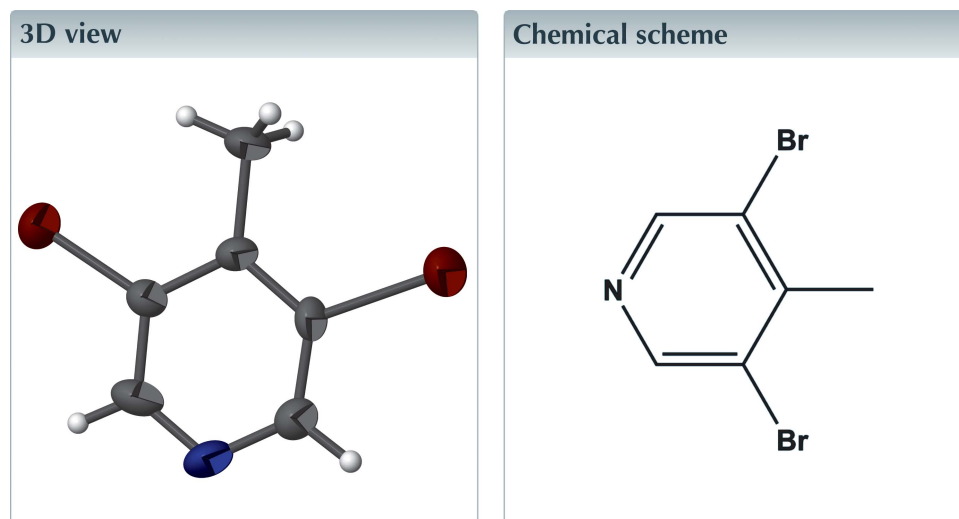
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Keywords: crystal structure; pyridine; Br...N interactions; halogen bonds; offset π - π interactions; framework structure.

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

The title compound, C₆H₅Br₂N, lies on a mirror plane. In the crystal, molecules are linked by Br...N and Br...Br interactions, forming zigzag chains along [010]. The chains are linked by offset π - π interactions [intercentroid distance = 3.5451 (3) Å], forming a three-dimensional framework.



Structure description

Pyridine has been used very frequently as a proton acceptor in studies involving hydrogen-bonded complexes (Zeegers-Huyskens *et al.*, 1981; Gur'yanova *et al.*, 1976). Pyridine derivatives are used as non-linear optical materials (Tomaru *et al.*, 1991) and photochemicals (Kaneko *et al.*, 1966). The main use of 4-methylpyridine is in the production of the anti-tuberculosis agent, isoniazid (isonicotinic acid hydrazide). Another use of this substance is the production of 4-vinylpyridine used in the manufacture of polymers, especially in the production of anion exchangers (Shimizu *et al.*, 2007).

The molecular structure of the title compound is shown in Fig. 1. The molecule is planar, with all atoms, except the methyl H atoms, lying in a mirror plane.

In the crystal, molecules are linked by Br...N interactions [$\text{Br}3 \cdots \text{N}1^i = 3.253 (7) \text{ \AA}$; symmetry code: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{2}$], and Br...Br halogen bonds [$\text{Br}3 \cdots \text{Br}5^{ii} = 3.6579 (15) \text{ \AA}$; symmetry code: (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{5}{2}$], forming zigzag chains along [010]. These chains are further interconnected by offset π - π interactions [$\text{Cg}1 \cdots \text{Cg}1^{iii/iv} = 3.5451 (3) \text{ \AA}$, Cg1 is the centroid of the pyridine ring N1/C2-C6, interplanar distance = 3.4594 Å, slippage = 0.775 Å, symmetry codes: (iii) $-x + 2, y + \frac{1}{2}, -z + 2$; (iv) $-x + 2, -y + 1, -z + 2$], forming a three-dimensional framework (Fig. 2).

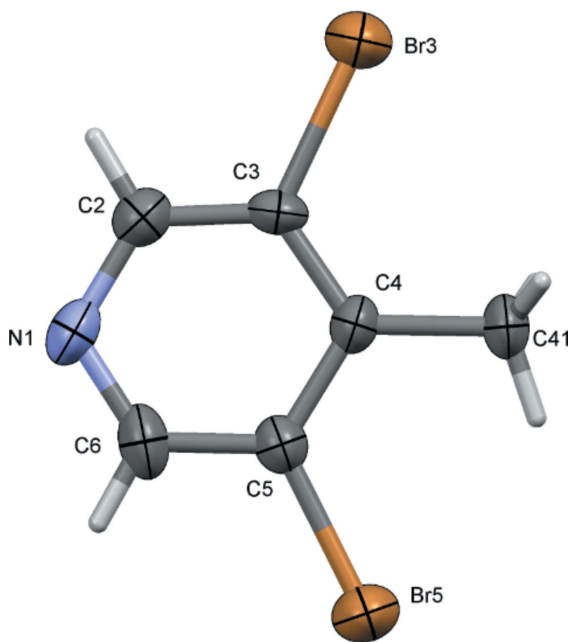


Figure 1
The molecular structure of the title compound, with atom labelling. Displacement ellipsoids drawn at the 50% probability level.

Synthesis and crystallization

The commercially available title compound (Sigma–Aldrich) was recrystallized from ethanol solution giving colourless prismatic crystals.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Acknowledgements

Thanks are due to MESRS and DG–RSDT (Ministère de l’Enseignement Supérieur et de la Recherche Scientifique et la

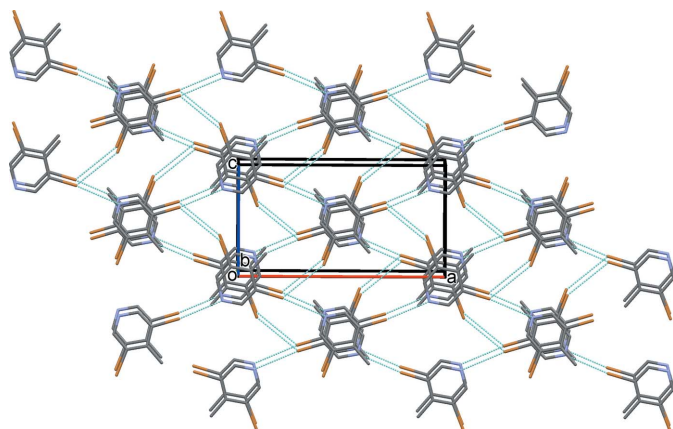


Figure 2
The crystal packing of the title compound, viewed along the *b* axis. The Br...N and Br...Br interactions are shown as dashed lines.

Table 1
Experimental details.

Crystal data	
Chemical formula	C ₆ H ₅ Br ₂ N
<i>M_r</i>	250.91
Crystal system, space group	Orthorhombic, <i>Pnma</i>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.178 (3), 6.9187 (18), 7.6407 (12)
<i>V</i> (Å ³)	749.5 (3)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	10.72
Crystal size (mm)	0.11 × 0.10 × 0.08
Data collection	
Diffractometer	Oxford Diffraction Xcalibur Eos
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Oxford Diffraction, 2013)
<i>T_{min}</i> , <i>T_{max}</i>	0.566, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	3138, 1228, 650
<i>R_{int}</i>	0.049
(sin θ/λ) _{max} (Å ⁻¹)	0.756
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.051, 0.125, 1.02
No. of reflections	1289
No. of parameters	55
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.72, −0.83

Computer programs: *CrysAlis PRO* (Oxford Diffraction, 2013), *SIR97* (Altomare *et al.*, 1999), *Mercury* (Macrae *et al.*, 2008), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

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full crystallographic data

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3,5-Dibromo-4-methylpyridine

Crystal data

$C_6H_5Br_2N$

$M_r = 250.91$

Orthorhombic, *Pnma*

$a = 14.178$ (3) Å

$b = 6.9187$ (18) Å

$c = 7.6407$ (12) Å

$V = 749.5$ (3) Å³

$Z = 4$

$F(000) = 472$

$D_x = 2.224$ Mg m⁻³

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

Cell parameters from 659 reflections

$\theta = 4.1$ – 31.1°

$\mu = 10.72$ mm⁻¹

$T = 293$ K

Prism, colourless

$0.11 \times 0.10 \times 0.08$ mm

Data collection

Oxford Diffraction Xcalibur Eos
diffractometer

Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator

Detector resolution: 8.0226 pixels mm⁻¹

CCD rotation images, thin slices ω scans

Absorption correction: multi-scan

(CrysAlis PRO; Oxford Diffraction, 2013)

$T_{\min} = 0.566$, $T_{\max} = 1.000$

3138 measured reflections

1228 independent reflections

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

$R_{\text{int}} = 0.049$

$\theta_{\max} = 32.5^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -17 \rightarrow 20$

$k = -8 \rightarrow 9$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.051$

$wR(F^2) = 0.125$

$S = 1.02$

1289 reflections

55 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

$w = 1/[\sigma^2(F_o^2) + (0.0347P)^2 + 0.0979P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.72$ e Å⁻³

$\Delta\rho_{\min} = -0.83$ 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Br3	1.21026 (6)	0.25	0.84557 (11)	0.0563 (3)	
Br5	0.91081 (6)	0.25	1.35326 (10)	0.0573 (3)	
N1	0.9215 (5)	0.25	0.8206 (8)	0.0470 (16)	
C4	1.0582 (5)	0.25	1.0898 (9)	0.0364 (15)	
C41	1.1284 (5)	0.25	1.2406 (9)	0.0467 (18)	
H41A	1.0949	0.25	1.3497	0.07*	
H41B	1.1674	0.3633	1.2335	0.07*	0.5
H41C	1.1674	0.1367	1.2335	0.07*	0.5
C5	0.9601 (5)	0.25	1.1226 (9)	0.0369 (16)	
C6	0.8968 (5)	0.25	0.9855 (11)	0.0476 (19)	
H6	0.8327	0.25	1.0119	0.057*	
C2	1.0145 (5)	0.25	0.7880 (9)	0.0411 (16)	
H2	1.0344	0.25	0.6721	0.049*	
C3	1.0811 (5)	0.25	0.9163 (9)	0.0345 (15)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br3	0.0359 (5)	0.0897 (6)	0.0432 (5)	0	0.0061 (4)	0
Br5	0.0448 (5)	0.0912 (6)	0.0361 (4)	0	0.0069 (4)	0
N1	0.051 (4)	0.067 (4)	0.024 (3)	0	-0.006 (3)	0
C4	0.034 (4)	0.051 (4)	0.025 (3)	0	-0.005 (3)	0
C41	0.032 (4)	0.075 (5)	0.033 (3)	0	-0.011 (3)	0
C5	0.030 (4)	0.047 (4)	0.034 (3)	0	-0.003 (3)	0
C6	0.038 (4)	0.058 (4)	0.047 (4)	0	-0.017 (4)	0
C2	0.041 (4)	0.052 (4)	0.030 (3)	0	0.001 (3)	0
C3	0.026 (4)	0.044 (3)	0.033 (4)	0	0.009 (3)	0

Geometric parameters (\AA , $^\circ$)

Br3—C3	1.909 (7)	C4—C5	1.414 (9)
Br5—C5	1.896 (7)	C4—C41	1.522 (9)
N1—C6	1.308 (9)	C5—C6	1.380 (9)
N1—C2	1.342 (9)	C2—C3	1.362 (10)
C4—C3	1.365 (8)		
C6—N1—C2	116.2 (6)	C4—C5—Br5	121.9 (5)
C3—C4—C5	114.0 (6)	N1—C6—C5	123.9 (7)
C3—C4—C41	125.4 (7)	N1—C2—C3	123.3 (7)
C5—C4—C41	120.6 (7)	C2—C3—C4	122.3 (7)
C6—C5—C4	120.4 (7)	C2—C3—Br3	117.5 (6)
C6—C5—Br5	117.8 (6)	C4—C3—Br3	120.2 (6)
C6—N1—C2—C3	0.00	C2—C3—C4—C41	180.00
C2—N1—C6—C5	0.00	C3—C4—C5—Br5	180.00

N1—C2—C3—Br3	180.00	C3—C4—C5—C6	0.00
N1—C2—C3—C4	0.00	C41—C4—C5—Br5	0.00
Br3—C3—C4—C5	180.00	C41—C4—C5—C6	180.00
Br3—C3—C4—C41	0.00	Br5—C5—C6—N1	180.00
C2—C3—C4—C5	0.00	C4—C5—C6—N1	0.00
