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Crystal structure of (*E*)-4-bromo-*N*-(pyridin-2-ylmethylene)aniline, C₁₂H₉BrN₂

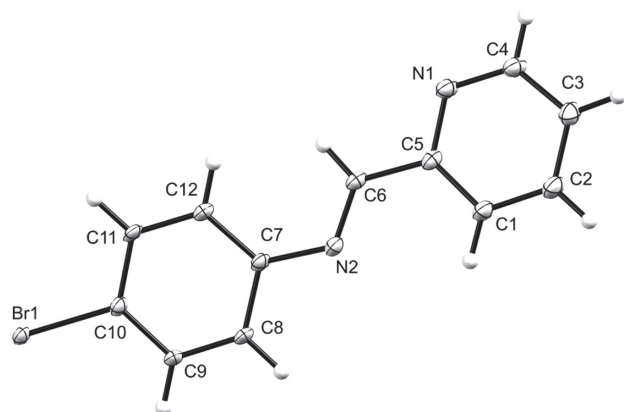


Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.29 × 0.21 × 0.14 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	3.98 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART APEX-II, φ and ω
θ_{\max} , completeness:	28.5°, 98%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	25389, 2527, 0.066
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2166
$N(\text{param})_{\text{refined}}$:	136
Programs:	Bruker [1], SHELX [2, 3], Mercury [4]

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Abstract

C₁₂H₉BrN₂, monoclinic, $P2_1/c$ (no. 14), $a = 19.2197(12)$ Å, $b = 4.8579(3)$ Å, $c = 11.4679(9)$ Å, $\beta = 106.880(4)^\circ$, $V = 1024.60(12)$ Å³, $Z = 4$, $R_g(F) = 0.0449$, $wR_{\text{ref}}(F^2) = 0.1257$, $T = 100(2)$ 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

An ethanolic solution of 2-pyridinecarboxaldehyde (1.07 g, 10 mmol) was added to a solution of 4-bromoaniline (1.72 g, 10 mmol) in ethanol and the solution was refluxed for 6 hours. The reaction mixture was then cooled to room temperature and MgSO₄ was added to remove excess water.

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.04566(2)	1.42267(7)	0.35506(3)	0.01610(14)
N1	0.38153(17)	0.0788(7)	0.6529(3)	0.0209(7)
N2	0.25245(17)	0.5885(6)	0.6725(3)	0.0184(6)
C1	0.3501(2)	0.2097(8)	0.8336(3)	0.0227(7)
H1	0.322357	0.323049	0.870810	0.027*
C2	0.3990(2)	0.0194(10)	0.9019(3)	0.0263(8)
H2	0.405417	0.000766	0.986784	0.032*
C3	0.4387(2)	−0.1440(9)	0.8442(3)	0.0240(8)
H3	0.471805	−0.279112	0.888065	0.029*
C4	0.4281(2)	−0.1026(8)	0.7204(3)	0.0223(8)
H4	0.455978	−0.210746	0.681273	0.027*
C5	0.34250(18)	0.2314(8)	0.7095(3)	0.0179(7)
C6	0.29112(19)	0.4255(7)	0.6300(3)	0.0173(7)
H6	0.286731	0.429397	0.545340	0.021*
C7	0.20549(18)	0.7756(7)	0.5917(3)	0.0163(6)
C8	0.1497(2)	0.8906(8)	0.6324(3)	0.0176(7)
H8	0.145246	0.839072	0.709781	0.021*
C9	0.10111(19)	1.0775(7)	0.5619(3)	0.0166(7)
H9	0.062235	1.147986	0.588680	0.020*
C10	0.11014(18)	1.1601(8)	0.4516(3)	0.0161(6)
C11	0.1658(2)	1.0554(7)	0.4098(3)	0.0163(7)
H11	0.171249	1.113686	0.333830	0.020*
C12	0.21327(19)	0.8651(8)	0.4805(3)	0.0183(7)
H12	0.251765	0.794142	0.452846	0.022*

The MgSO₄ was filtered off and the filtrate was dried overnight under reduced pressure. This gave an off-white powder (1.92 g, 73%). Mp: 69–69.4 °C. Crystals were grown through a slow evaporation of an ethanol solution at 25 °C.

Experimental details

The structure was solved by the direct method using the *SHELXS* [2] program and refined. The visual crystal structure information was performed using *Mercury* [4] system software. All hydrogen atoms were placed in idealized positions and refined in riding models with U_{iso} assigned the values of 1.2 times those of their parent atoms and the distances of C—H were constrained to 0.95 Å for all the aromatic H atoms.

Comment

Schiff bases were described by Hugo Schiff in 1864 as a condensation reaction of imines and aldehydes. Their ease of synthesis, ability to coordinate to various metals with different oxidation states and influence the way a metal reacts in various catalytic transformations has led to remarkable use of these *N,N'*-bidentate ligands. Ligand design has enabled chemists to explore the steric and electronic properties of these ligands on various catalytic platforms [5–7]. Metal complexes of these pyridyl imine ligands have been found to perform various catalytic transformations such as alcohol oxidation [8] and transfer hydrogenation of ketones [9].

The asymmetric unit has one molecular unit of the title compound (cf. the figure). The compound exhibits an *E* conformation around the N2=C6 bond which is comparable to related compounds in literature [10–14]. The analogous compound with a methyl group instead of the bromo substituent forms an isotypic structure [15]. The dihedral angle between the phenyl and pyridyl moieties was measured to be 19.2°, whilst all bond parameters appear normal. The crystal packing contains intermolecular C10—Br1ⁱ⋯Cg_{phenyl}ⁱ interactions crystal packing with Br1ⁱ⋯Cg_{phenyl}ⁱ distance of 3.601(2) Å and C10—Br1ⁱ⋯Cg_{phenyl}ⁱ angle of 89.97(1)° (symmetry code: (i) = $x, 1 + y, z$). Short Br1ⁱ⋯Br1^{ii,iii} contacts (symmetry codes: (ii) = $-x, -1/2 + y, 1/2 - z$; (iii) = $-x, 1/2 + y, 1/2 - z$) with distances of 3.5115(6) Å were also observed. The two types of intermolecular interactions observed in the crystal packing link together neighboring molecules to form a one dimensional supramolecular structure which propagates along the crystallographic *b* axis.

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