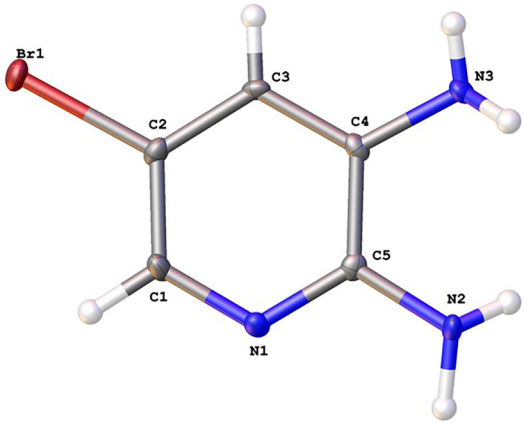
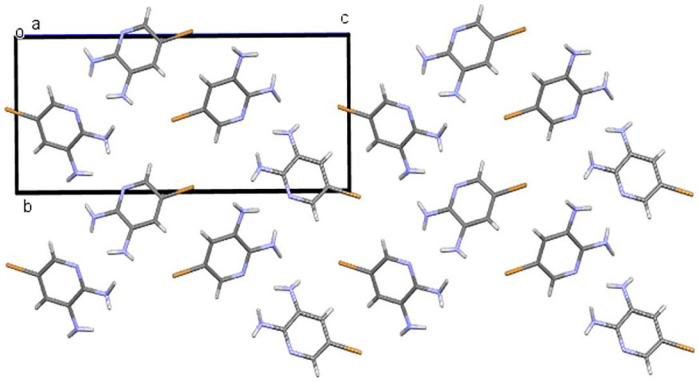
Irina S. Konovalova* and Guido J. Reiss

Crystal and molecular structure of 5-bromopyridine-2,3-diamine





https://doi.org/10.1515/ncrs-2024-0221
Received May 24, 2024; accepted July 15, 2024;
published online July 26, 2024

Abstract

$C_5H_6BrN_3$, orthorhombic, $P2_12_12_1$ (no. 19), a = 3.82640(10) Å, b = 8.7336(2) Å, c = 18.6007(3) Å, V = 621.60(2) Å^3, Z = 4, $R_{gt}(F)$ = 0.0184, wR_{ref} = 0.0473, T = 100(2) K.

CCDC no.: 2370691

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless needle
Size:	0.40 × 0.17 × 0.10 mm
Wavelength:	6.51 mm^{-1}
μ:	Mo $K\alpha$ radiation (0.71073 Å)
Diffractometer, scan mode:	Rigaku Xcalibur, ω
θ_{max}, completeness:	26.0°, >99 %
N $(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	27,820, 1,219, 0.059
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1,197
N(param)$_{refined}$:	106
Programs:	Mercury,[1] CrysAlis^{PRO},[2] Olex2,[3] SHELX[4]

1 Source of material

We thank Professor Sergiy M. Kovalenko (V. N. Karazin Kharkiv National University, Ukraine) for providing some crystals of the title compound.

2 Experimental details

Using Olex2,[3] the structure was solved by with the ShelXT[4] structure solution program. Positions of the hydrogen atoms were located from electron density difference maps and refined by riding models with $U_{iso} = nU_{eq}$ of the carrier atom (n = 1.2).

***Corresponding author: Irina S. Konovalova**, SSI "Institute for Single Crystals" NAS of Ukraine, Nauky Ave., 60, Kharkiv, 61072, Ukraine; and Institut für Anorganische Chemie und Strukturchemie, Lehrstuhl II: Bioanorganische Chemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 1, D-40225, Düsseldorf, Germany, E-mail: ikonovalova0210@gmail.com. https://orcid.org/0000-0001-6245-6642

Guido J. Reiss, Institut für Anorganische Chemie und Strukturchemie, Lehrstuhl II: Bioanorganische Chemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 1, D-40225 Düsseldorf, Germany, E-mail: reissg@hhu.de. https://orcid.org/0000-0002-3004-3955

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.51168 (9)	0.53612 (3)	0.47097 (2)	0.01393 (12)
N1	0.1419 (8)	0.5283 (3)	0.67852 (15)	0.0125 (6)
N2	0.0997 (8)	0.3450 (4)	0.76817 (15)	0.0133 (6)
N3	0.4117 (8)	0.1248 (3)	0.67890 (17)	0.0128 (6)
C1	0.2359 (10)	0.5708 (4)	0.61178 (19)	0.0136 (7)
C2	0.3849 (8)	0.4703 (4)	0.56441 (17)	0.0115 (6)
C3	0.4527 (9)	0.3206 (4)	0.58544 (17)	0.0097 (6)
C4	0.3601 (9)	0.2754 (4)	0.65400 (18)	0.0098 (6)
C5	0.1952 (8)	0.3838 (4)	0.69899 (17)	0.0100 (7)
H1	0.199 (11)	0.677 (5)	0.599 (2)	0.018 (11)*
H2A	0.053 (12)	0.260 (5)	0.776 (2)	0.012 (10)*
H2B	−0.049 (14)	0.418 (6)	0.791 (3)	0.033 (12)*
H3	0.555 (13)	0.259 (5)	0.556 (2)	0.029 (12)*
H3A	0.479 (13)	0.119 (5)	0.724 (2)	0.028 (11)*
H3B	0.552 (13)	0.079 (5)	0.654 (2)	0.020 (12)*

3 Comment

3.1 Introduction

Halogen derivatives of diaminopyridine are of particular interest in medicinal chemistry and organic synthesis due to its potential biological activity and its utility as a building block for the synthesis of more complex molecules.[5] Research into these derivatives is ongoing, as scientists seek to understand their properties and potential applications better. These compounds are integral to the development of new pharmaceuticals, agrochemicals, and advanced materials, offering a wide array of possibilities for innovation in various fields of chemistry and biology.

3.2 Structural comment

The asymmetric unit of the title structure contains one complete molecule (see the figure). The molecular structure of the title compound shows that the molecule is nearly planar with r.m.s deviation from the mean plane of all non-hydrogen atoms of 0.01/Å. Bond lengths are all in the expected ranges[6] and they are similar with bond lengths of 5-chloro-pyridine-2,3-diamine.[7] A more general search in the Cambridge Structural database yielded some related structures that consists of a 5-bromo-pyridine moiety with 2 and 3 positions substituted by an amino group and a halogen substituent, respectively.[8–10]

Both amino groups in the title structure have pyramidal configuration (the sum of valence angles centered on the nitrogen atom are for N2 346.8°, for N3 334.2°) and they can both participate in hydrogen bonds formation as donor and acceptor of proton (see left part of the figure). In the crystal phase molecules of the titled compound form zig–zag columns along the crystallographic *c* axis (see the figure right side) due to the N2–H2A···N1 (H···N 2.32 Å, N–H···N 167°), N2–H2B···N3 (H···N 2.35 Å, N–H···N 167°) and face-to-face stacking interactions.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

Author contributions: All authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This project has received funding through the MSCA4Ukraine project, which is funded by the European Union. Furthermore this study was supported by the Ministry of Innovation, Science and Research of North-Rhine Westphalia; the German Research Foundation (DFG): Xcalibur diffractometer; INST 208/533-1, project no. 162659349.

References

1. Macrae, C. F.; Sovago, I.; Cottrell, S. J.; Galek, P. T. A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G. P.; Stevens, J. S.; Towler, M.; Wood, P. A. Mercury 4.0: From Visualization to Analysis, Design and Prediction. *J. Appl. Crystallogr.* **2020**, *53*, 226–235.
2. *Oxford Diffraction CrysAlis^{PRO} (Version 1.171.41.93a)*; Oxford Diffraction Ltd.: Oxford, UK, 2020.
3. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* **2009**, *42*, 339–341.
4. Sheldrick, G. M. A Short History of SHELX. *Acta Crystallogr.* **2008**, *A64*, 112–122.
5. Sedehizadeh, S.; Keogh, M.; Maddison, P. The Use of Aminopyridines in Neurological Disorders. *Clin. Neuropharmacol.* **2012**, *35*, 191–200.
6. Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. The Cambridge Structural Database. *Acta Crystallogr.* **2016**, *B72*, 171–179.
7. Sulovari, A.; Tanski, J. M. Crystallographic and Spectroscopic Characterization of 5-chloropyridine-2,3-diamine. *Acta Crystallogr.* **2017**, *E73*, 1213–1217.
8. Jiao, Z.-J.; Huang, S.-S.; Li, C.-X.; Diao, Y. P. Crystal Structure of 3,5-dibromopyridin-2-amine, $C_5H_4Br_2N_2$. *Z. Kristallogr. N. Cryst. Struct.* **2012**, *227*, 515–516.
9. Aakeroy, C. B.; Rajbanshi, A.; Li, Z. J.; Desper, J. Mapping Out the Synthetic Landscape for Re-crystallization, Co-crystallization and Salt Formation. *CrystEngComm* **2010**, *12*, 4231–4239.
10. Bunker, K. D.; Sach, N. W.; Nukui, S.; Rheingold, A. L.; Yanovsky, A. 3-amino-5-bromo-2-iodopyridine. *Acta Crystallogr.* **2009**, *E65*, o28.