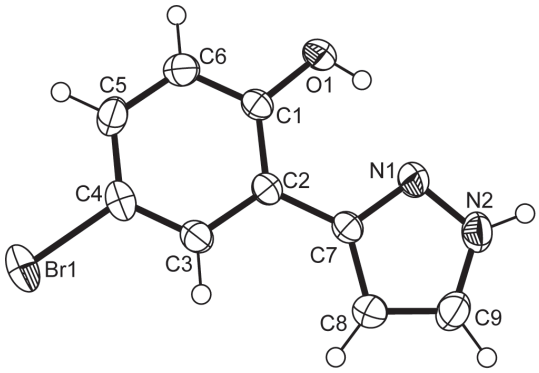
Open Access

Željko K. Jaćimović*, Milica Kosović, Sladjana B. Novaković, Goran A. Bogdanović, Gerald Giester and Vlatko Kastratović

Crystal structure of 4-bromo-2-(1*H*-pyrazol-3-yl) phenol, $C_9H_7BrN_2O$



DOI 10.1515/ncrs-2016-0392
Received December 9, 2016; accepted March 30, 2017; available online April 10, 2017

Abstract

$C_9H_7BrN_2O$, triclinic, $C2/c$ (no. 15), $a = 16.255(3)$ Å, $b = 4.4119(9)$ Å, $c = 25.923(5)$ Å, $\beta = 107.99(3)°$, $V = 1768.2(7)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0450$, $wR_{ref}(F^2) = 0.0960$, $T = 150$ K.

CCDC no.: 1540998

The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

***Corresponding author: Željko K. Jaćimović,** Faculty of Metallurgy and Technology, Džordža Vašingtona bb, University of Montenegro, Podgorica, Montenegro, e-mail: zeljkoj@ac.me
Milica Kosović: Faculty of Metallurgy and Technology, Džordža Vašingtona bb, University of Montenegro, Podgorica, Montenegro
Sladjana B. Novaković and Goran A. Bogdanović: Vinča Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter Physics, University of Belgrade, PO Box 522, 11001 Belgrade, Serbia
Gerald Giester: Institut für Mineralogie und Kristallographie, Universität Wien – Geozentrum, Althanstra&se 14, 1090 Wien, Austria
Vlatko Kastratović: Faculty of Natural Sciences and Mathematics, Džordža Vašingtona bb, University of Montenegro, Podgorica, Montenegro

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.20 × 0.13 × 0.10 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	46.1 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	60°, 96.9 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	12745, 2507, 0.029
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1893
$N(param)_{refined}$:	126
Programs:	Bruker programs [1], SHELX [2]

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

Atom	x	y	z	U_{iso}*/U_{eq}
Br1	0.33374(3)	−0.11067(9)	0.46796(2)	0.05993(16)
N1	0.51366(15)	0.6170(5)	0.31190(9)	0.0341(5)
N2	0.58268(17)	0.8027(6)	0.32665(10)	0.0381(6)
O1	0.39242(14)	0.2440(5)	0.25796(7)	0.0352(4)
C1	0.38214(17)	0.1752(6)	0.30684(9)	0.0269(5)
C2	0.43628(16)	0.2911(6)	0.35612(9)	0.0265(5)
C3	0.42015(18)	0.2016(6)	0.40384(10)	0.0316(6)
H3	0.4552	0.2745	0.4370	0.038*
C4	0.35373(19)	0.0089(7)	0.40245(11)	0.0352(6)
C5	0.29958(19)	−0.1020(7)	0.35372(12)	0.0396(7)
H5	0.2538	−0.2302	0.3530	0.048*
C6	0.31504(19)	−0.0179(7)	0.30627(11)	0.0360(6)
H6	0.2796	−0.0926	0.2733	0.043*
C7	0.50711(17)	0.5008(6)	0.35784(9)	0.0266(5)
C8	0.5726(2)	0.6171(7)	0.40238(11)	0.0395(7)
H8	0.5824	0.5738	0.4389	0.047*
C9	0.6189(2)	0.8075(7)	0.38038(12)	0.0411(7)
H9	0.6670	0.9204	0.3994	0.049*
H2N	0.596(2)	0.902(7)	0.3031(14)	0.043(9)*
H1O	0.430(3)	0.376(9)	0.2628(16)	0.063(13)*

Source of material

4-Bromo-2-(1*H*-pyrazol-3-yl)phenol was purchased from Sigma-Aldrich. The single crystals suitable for the X-ray diffraction experiment were obtained by recrystallization from methanol.

Experimental details

All hydrogen atoms were identified in a difference Fourier map. The aromatic hydrogen atoms were placed at geometrically idealized positions with C—H distances set to 0.93 Å and U_{iso} values set to $1.2U_{eq}$ of the parent C atom. Hydrogen atoms attached to the pyrazole N and phenol O atoms were refined isotropically.

Comment

Pyrazole and its derivatives represent one of the most important classes of organic heterocyclic compounds, with an unusual wide range of biological activities. Many pyrazole derivatives have been reported to possess antimicrobal, anti-inflammatory, analgesic, anticancer activities as well as the fungicidal and pesticidal activities [3, 4]. In addition, due to significant complexation abilities, pyrazole based ligands found applications as extraction reagents for metal ions [5]. Different pyrazole based ligands are used in the synthesis of complexes with the pronounced magnetic properties and also as building blocks of metal organic frameworks [6]. As part of our ongoing research on the synthesis, physico-chemical and structural properties of the pyrazole based coordination compounds [7, 8] herein we report the crystal structure of the title compound.

The title pyrazole derivative contains one independent molecule in the asymmetric unit. The bond lengths and angles of the phenyl-pyrazole core are consistent with those in similar molecules [9–23]. The dihedral angle between the pyrazole and phenyl ring is 8.6(2)° and reflects a nearly planar geometry of the molecule. The planar conformation is stabilized by the intramolecular hydrogen bond formed between the phenol hydroxy group and the pyrazole nitrogen [O1—H1···N1: O—H 0.83(4), H···N 1.87(4), O···N 2.615(3) Å, O—H···N = 148(4)°]. This intramolecular hydrogen bond is the main structural property of different 3{5}-(2′-hydroxyaryl)pyrazoles and it ensures the co-planarity of the phenyl-pyrazole fragment in the various intramolecular environments [9–23]. The presence of this intramolecular N—H···O hydrogen bond is related to the photostability of some hydroxyarylpyrazoles and their ability to act as UV stabilizers [9]. In the crystal packing, the strongest intermolecular hydrogen bond formed between the pyrazole N—H donor and the phenol O-acceptor [N2—H2n···O1^{i}: N—H 0.85(4), N···O 3.051(3), H···O 2.22(4) Å, N—H···O 165(3)°, (i) −x + 1, +y + 1, −z + 1/2], links the molecules along the *b* axis. This arrangement is supported by weak O—H···N interactions [O1—H1o···N1^{ii}: O—H 0.83(4), O···N 3.165(3), H···N 2.61(5), O—H···N 126(4)°, (ii) −x + 1, +y, −z + 1/2] and π-π contacts between parallelly arranged molecular planes (interplanar distance of 3.423 Å).

Acknowledgements: G. A. B. and S. B. N. thank the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support (Project No. 172014 and 172035). Ž. K. J. and M. K. thank the Ministry of Science of the Republic of Montenegro for financial support - National project.

References

1. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, (2009).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Khan, M. F.; Alam, M. M.; Verma, G.; Akhtar, W.; Akhter, M.; Shaquiquzzaman, M.: The therapeutic voyage of pyrazole and its analogs: a review. Eur. J. Med. Chem. **120** (2016) 170–201.
4. Alam, J.; Alam, O.; Alam, P.; Naim, M. J.: A review on pyrazole chemical entity and biological activity. Internat. J. Pharm. Sci. Res. **6** (2015) 1433–1442.
5. Attayibat, A.; Radi, S.; Lekchiri, Y.; Ramdani, A.; Hacht, B.; Bacquet, M.; Willai, S.; Morcellet M.: New functionalised C,C-bipyrazoles. Synthesis and cation binding properties. J. Chem. Res. **10** (2006) 655–657.
6. Pettinari, C.; Tabacaru, A.; Galli, S.: Coordination polymers and metal-organic frameworks based on poly(pyrazole)-containing ligands. Coord. Chem. Rev. **307** (2016) 1–31.
7. Jaćimović, Ž. K.; Leovac; V. M.; Tomić, Z. D. Z.: Crystal structure of hexakis(μ_2-chloro)-μ_4-oxo-tetrakis((3,5-dimethylpyrazole)copper(II)) ethanol tetrasolvate, $Cu_4OCl_6(C_5H_8N_2)_4 \cdot 4C_2H_5OH$· Z. Kristallogr. – NCS **222** (2007) 246–248.
8. Jaćimović, Ž. K.; Gieste; G.; Kosović, M.; Bogdanović, G. A.; Novaković, S. B.; Leovac, V. M.; Latinović, N.; Holló, B. B.; Mészáros Szécsényi, K.: Pyrazole-type complexes with Ni(II) and Cu(II) Solvent exchange reactions in coordination compounds. J. Therm. Anal. Calorim. **127** (2017) 1501–1509.
9. Catalan, J.; Fabero, F.; Claramunt, R. M.; Santa Maria, M. D.; Foces-Foces, M.; de la, C.; Cano, F. H.; Martinez-Ripoll, M.; Elguero, J.; Sastre, R.: New ultraviolet stabilizers: 3- and 5-(2′-hydroxypheny1)pyrazoles. J. Am. Chem. Soc. **114** (1992) 5039–5048.
10. Jeyakanthan, J.; Velmurugan, D.; Selvi, S.; Perumal, P. T.: 1-(2,4-Dinitrophenyl)-3-(2-hydroxyphenyl)-4-methyl-1*H*-pyrazole. Acta Crystallogr. **C55** (1999) 1926–1928.
11. Pinto, D. C. G. A.; Silva, A. M. S.; Cavaleiro, J. A. S.; Foces-Foces, C.; Llamaz-Saiz, A. L.; Jagerovic, N.; Elguero, J.: Synthesis and molecular structure of 3-(2-benzyloxy-6-hydroxyphenyl)-5-styrylpyrazoles. Reaction of 2-styrylchromones and hydrazine hydrate. Tetrahedron **55** (1999) 10187–10200.
12. Zhang, Z.; Wang, F.-W.; Wang, S.-Q.; Ge, F.; Zhao, B.-X.; Miao, J.-Y.: A highly sensitive fluorescent probe based on simple pyrazoline for Zn^{2+} in living neuron cells. Org. Biomol. Chem. **10** (2012) 8640–8644.
13. Ronson, T. K.; Adams, H.; Ward, M. D.: Bis-bidentate bridging ligands containing two *N,O*-chelating pyrazolyl-phenolate units; double helical complexes with Co(II), Cu(II) and Zn(II). Inorg. Chim. Acta **358** (2005) 1943–1954.

14. Huang, S.; Ying, H.; Hu, Y.: One-pot synthesis of 1,3,5-triarylpyrazoles. J. Heterocycl. Chem. **50** (2013) 478–483.
15. Zats, G. M.; Arora, H.; Lavi, R.; Yufit, D.; Benisvy, L.: Phenolate and phenoxyl radical complexes of Cu(II) and Co(III), bearing a new redox active *N,O*-phenol-pyrazole ligand. Dalton Trans. **40** (2011) 10889–10896.
16. Patel, U. H.; Gandhi, S. A.; Barot, V. M.; Varma, N. V. S.: 1-[3-(2-Benzoyloxy-6-hydroxy-4-methylphenyl)-5-[3,5-bis (trifluoromethyl)phenyl]-4,5-dihydro-1*H*-pyrazol-1-yl]propane-1-one. Acta Crystallogr. **E69** (2013) o840.
17. Yunus, U.; Kauser, R.; Bhatti, M. H.; Zia-ul-Haq, M.; Wong, W.-Y.: Synthesis, spectroscopic characterisation and X-ray analysis of regioisomeric 1,3,5-trisubstituted pyrazoles. J. Mol. Struct. **995** (2011) 173–180.
18. Hua, S.; Wua, G.; Xua, C.; Donga, J.; Gaob Q.: A new fluorescent chemosensor for Fe^{3+} based upon 2,5-diphenylfuran and 8-hydroxyquinoline. J. Photochem. Photobiol. A: Chem. **270** (2013) 37–42.
19. Lokhande, P.; Hasanzadeh, K. H.; Khaledi, A. H. M.: 3-(3-Chloro-2-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde. Acta Crystallogr. **E67** (2011) o2736.
20. Das, A.; Gieb, K.; Krupskaya, Y.; Demeshko, S.; Dechert, S.; Klingeler, R.; Kataev, V.; Buchner, B.; Muller, P.; Meyer, F.: A new family of 1D exchange biased heterometal single-molecule magnets: observation of pronounced quantum tunneling steps in the hysteresis loops of quasi-linear $\{Mn_2Ni_3\}$ clusters. J. Am. Chem. Soc. **133** (2011) 3433–3443.
21. Li, Y.-X.; Wang, Y.-Z.: 2-[1-(4,6-Dimethoxypyrimidin-2-yl)-1*H* -pyrazol-3-yl]phenol. Acta Crystallogr. **E63** (2007) o873.
22. Craig, G. A.; Barrios, L. A.; Costa, J. S.; Roubeau, O.; Ruiz, E.; Teat, S. J.; Wilson, C. C.; Thomas, L.; Aromi, G.: Synthesis of a novel heptacoordinated Fe(III) dinuclear complex: experimental and theoretical study of the magnetic properties. Dalton Trans. **39** (2010) 4874–4881.
23. Busch, M.; Cayir, M.; Nieger, M.; Thiel, W. R.; Brase, S.: Roadmap towards novel n-heterocyclic[2.2]paracyclophanes. Eur. J. Org. Chem. (2013) 6108–6123.