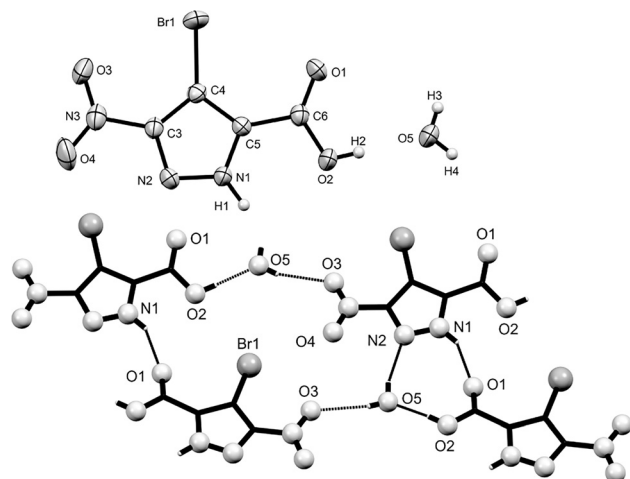


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# Crystal structure of 4-bromo-3-nitro-1*H*-pyrazole-5-carboxylic acid monohydrate, C<sub>4</sub>H<sub>2</sub>N<sub>3</sub>BrO<sub>4</sub>·H<sub>2</sub>O



**Table 1:** Data collection and handling.

Crystal:	Stick, colorless
Size:	0.15 × 0.10 × 0.10 mm
Wavelength:	Mo K $\alpha$ radiation (0.71073 Å)
$\mu$ :	5.08 mm <sup>-1</sup>
Diffractometer, scan mode:	Bruker APEX-II, $\varphi$ and $\omega$ -scans
$\theta_{\max}$ , completeness:	26.4°, >99%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	16034, 1646, 0.048
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 1323
$N(\text{param})_{\text{refined}}$ :	126
Programs:	Bruker programs [1], SHELX [2], Mercury [3], PLATON [4], WinGX [5, 6]

<https://doi.org/10.1515/ncrs-2023-0199>

Received April 24, 2023; accepted June 14, 2023;  
published online July 5, 2023

## Abstract

C<sub>4</sub>H<sub>2</sub>N<sub>3</sub>BrO<sub>4</sub>·H<sub>2</sub>O, monoclinic,  $P2_1/c$  (no. 14),  $a = 7.177(2)$  Å,  $b = 10.999(3)$  Å,  $c = 10.414(3)$  Å,  $\beta = 100.145(11)^\circ$ ,  $V = 809.3(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_{\text{gt}}(F) = 0.0379$ ,  $wR_{\text{ref}}(F^2) = 0.0714$ ,  $T = 200$  K

CCDC no.: 2269769

## 1 Source of materials

4-bromo-3-nitro-1*H*-pyrazole-5-carboxylic acid (L) was dissolved in a warm ethanol and added to a warm ethanol

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## 2 Experimental details

The N-bound H atom were positioned geometrically and included as riding atom with  $U_{\text{iso}}(\text{H})$  set to  $1.2U_{\text{eq}}(\text{N})$ . The H atom of the hydroxyl group was allowed to rotate around the C–O bond, with O–H distance refined to best fit the experimental electron density (HFIX 148 in the SHELX program suite [2], with  $U_{\text{iso}}(\text{H})$  set to  $1.5U_{\text{eq}}(\text{O})$ . Hydrogen atoms from water were located from a difference-Fourier map and their positions were refined with  $U_{\text{iso}}(\text{H})$  set to  $1.5U_{\text{eq}}(\text{O})$  (Tables 1 and 2).

## 3 Comment

The pyrazoles possess many biological and pharmaceutical properties [7]. They also have interesting coordination properties [8]. Important use of pyrazole complexes is in the extraction of metal ions [9]. Pyrazoles are also important for the synthesis of metal-organic frameworks [10]. Supramolecular aspect is important for understanding of the pyrazoles chemistries [11]. Main driving force for self-assembly of pyrazolyl molecules are hydrogen bonds [12]. Pyrazolyl molecules crystallize in a variety of motifs

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
Br1	0.20057 (6)	0.88241 (3)	0.49285 (4)	0.04232 (15)
O1	0.4727(4)	0.8378(2)	0.7732(3)	0.0384(7)
O2	0.5981(4)	0.6531(2)	0.8218(3)	0.0395(7)
H2	0.652(6)	0.686(2)	0.885(4)	0.059*
O3	0.0057(5)	0.7041(3)	0.2786(3)	0.0559(9)
O4	0.0196(5)	0.5080(3)	0.2865(3)	0.0541(9)
N1	0.3681(4)	0.5500(3)	0.6203(3)	0.0284(7)
H1	0.4333	0.4994	0.6764	0.034*
N2	0.2571(4)	0.5140(3)	0.5108(3)	0.0299(7)
N3	0.0609(5)	0.6083(3)	0.3309(3)	0.0366(8)
C3	0.1877(5)	0.6175(3)	0.4560(3)	0.0276(8)
C4	0.2516(5)	0.7195(3)	0.5292(3)	0.0264(8)
C5	0.3709(5)	0.6720(3)	0.6368(3)	0.0257(8)
C6	0.4857(5)	0.7309(3)	0.7511(3)	0.0290(8)
O5	0.7550(5)	0.7563(3)	1.0365(3)	0.0442(8)
H3	0.765(7)	0.827(5)	1.037(5)	0.066*
H4	0.822(7)	0.731(5)	1.090(5)	0.066*

determined by N–H··N hydrogen bonds [13]. Capacity for nonbonding interaction of substituents additionally influences the aggregation of pyrazole derivatives [14]. Halogen bonding can be competitive to hydrogen bonding [15]. Both interactions are possible in the halogenated pyrazoles. As a continuation of our previous work [16–19] we report molecular and crystal structure of 4-bromo-3-nitro-1H-pyrazole-5-carboxylic acid monohydrate. Title pyrazolyl compound (L) exhibits high capacity for non-covalent bonding. COOH, N–H··O/N [20], NO<sub>2</sub> [21] and Br [22] can form hydrogen bonds. Br atoms can form Br··Br contacts of non-covalent nature [23]. The ORTEP diagram in the upper part of the figure depicts asymmetric unit and atom labeling. Hydrogen bonds N1–H1··O1<sup>i</sup> = 1.94 Å/151°, O2–H2··O5<sup>ii</sup> = 1.80 Å/174°, O5–H3··N2<sup>iii</sup> = 2.12 Å/165° and O5–H4··O3<sup>iv</sup> = 2.18 Å/163° form layers of molecules, depicted in the lower part of the figure (symmetry codes: i = 1 – x, 1/2 + y, 1/2 – z; ii = x, 1/2 – y, –1/2 + z; iii = 1 – x, 1 – y, 1 – z; iv = –1 + x, 1/2 – y, –1/2 + z). There are no significant intermolecular contacts between the layers. Two strong acceptors of hydrogen bonds, O<sub>4</sub> and Br, do not take part in the non-covalent contacts. Also, there are no Br··Br interactions. In the related molecules, 4-bromo-3,5-diphenylpyrazole [24], 3(5)-phenyl-4-bromo-5(3)-methylpyrazole and 5-phenyl-4-bromo-3-methylpyrazole [25] Br is at the same position, relative to NH, as in L. As opposed to the title structure, in both [24, 25], Br··Br contacts of type I are present [26]. Search of CSD gave one pyrazole derivative with NO<sub>2</sub> and COOH in the same stereochemical relations as in L. It is 3,4-dinitro-1H-pyrazole-

5-carboxylic acid monohydrate (L1) [27]. L and L1 differ in the substituent at position C<sub>4</sub>, Br in L and NO<sub>2</sub> in L1. Like in the L, N–H··O, O–H··N and O–H··O interactions, play essential roles in the assembly of molecules in the solid state of L1. In both L1 and L2 the substituent at C<sub>4</sub> is not involved in the assembly of molecules.

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

**Research funding:** None declared.

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

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