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Short Note

Bis(pyrazol-1-yl)methane-4,4′-dicarboxylic Acid

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Abstract: The molecular structure of bis(pyrazol-1-yl)methane-4,4′-dicarboxylic acid (H_2bpmdc) was determined by single crystal X-Ray diffraction analysis. The compound crystallizes in a monoclinic crystal system; the unit cell contains four formula units. The molecules of H_2bpmdc are linked into zig-zag chains by intermolecular carboxyl–carboxyl hydrogen bonds. Other types of supramolecular interactions, namely, CH···N and CH···O short contacts, CH–π interactions and carbonyl–carbonyl interactions were detected in the crystal structure.

Keywords: bis(pyrazol-1-yl)methane-4,4′-dicarboxylic acid; dicarboxylic acid; crystal structure; hydrogen bond; intermolecular interactions

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1. Introduction

Dicarboxylic acids are important supramolecular synthons for metal–organic frameworks [1,2], hydrogen-bonded networks [3], organogels [4], deep eutectic solvents [5] and other applications [6]. Pyrazole-4-carboxylic acid and its derivatives have demonstrated potent biological activity [7,8]; they were also used for construction of highly porous metal–organic frameworks [9]. Dicarboxylic acids derived from bis(pyrazol-1-yl)methane have been less explored, but were successfully employed as building blocks for metal–organic frameworks with luminescent properties [10,11], gas separation capability [12], and single metal site catalysts [13,14].

Recently, we have developed a universal approach for the synthesis of a new series of bis(pyrazol-1-yl)alkane-4,4′-dicarboxylic acids starting from the commercially available pyrazole-4-carboxylic acid [15]. Taking into account the potential of these compounds as supramolecular building block, biologically active substances, monomers for polyesters and polyamides, we have studied the crystal structure and supramolecular analysis of N-heterocyclic compound titled bis(pyrazol-1-yl)methane-4,4′-dicarboxylic acid (H_2bpmdc). This dicarboxylic acid was synthesized recently in our group and was characterized by NMR and IR spectroscopy, thermal and elemental analyses [15]; however, its crystal structure determination has not been performed yet.

2. Results and Discussion

The molecular structure of H_2bpmdc is shown in Figure 1. The compound crystallizes in a monoclinic crystal system, space group C2/c. The asymmetric unit consists of a half of the molecule and the unit cell contains four formula units. The angle between the planes of two pyrazole rings is 81.24(8)°, while the angle N1-C5-N1 is closer to tetrahedral (111.3(8)°). The neighboring molecules are involved in intermolecular hydrogen bonding via the carboxylic groups (Figure 2), the D-H distance, d(O2-H2) = 0.87(1) Å, A-H distance d(O1-H2) = 1.79(1) Å and D-H-A angle (O2-H2-O1) is 177(1)°. The interatomic distance d(O1-O2) = 2.655(1) Å is in the range typical for a carboxyl–carboxyl cyclic dimer motif [16].

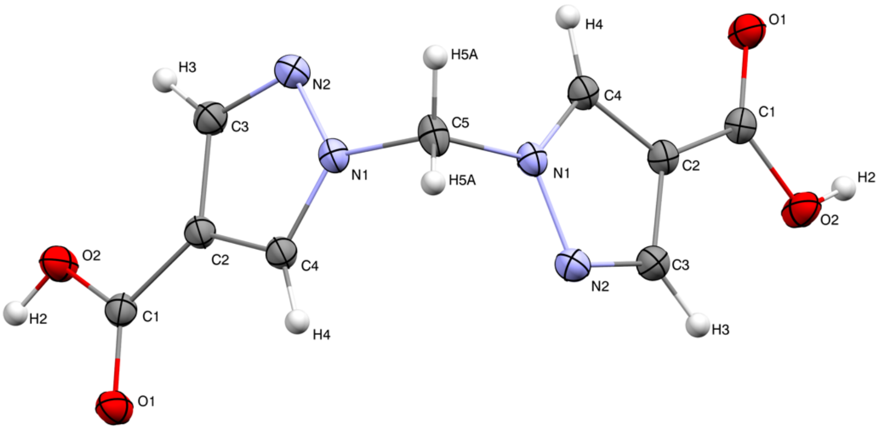


Figure 1. Molecular structure of H_2bpmdc; thermal ellipsoids are drawn at the 50% probability level.

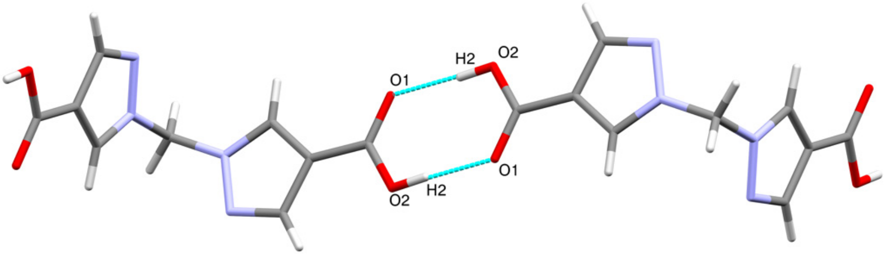
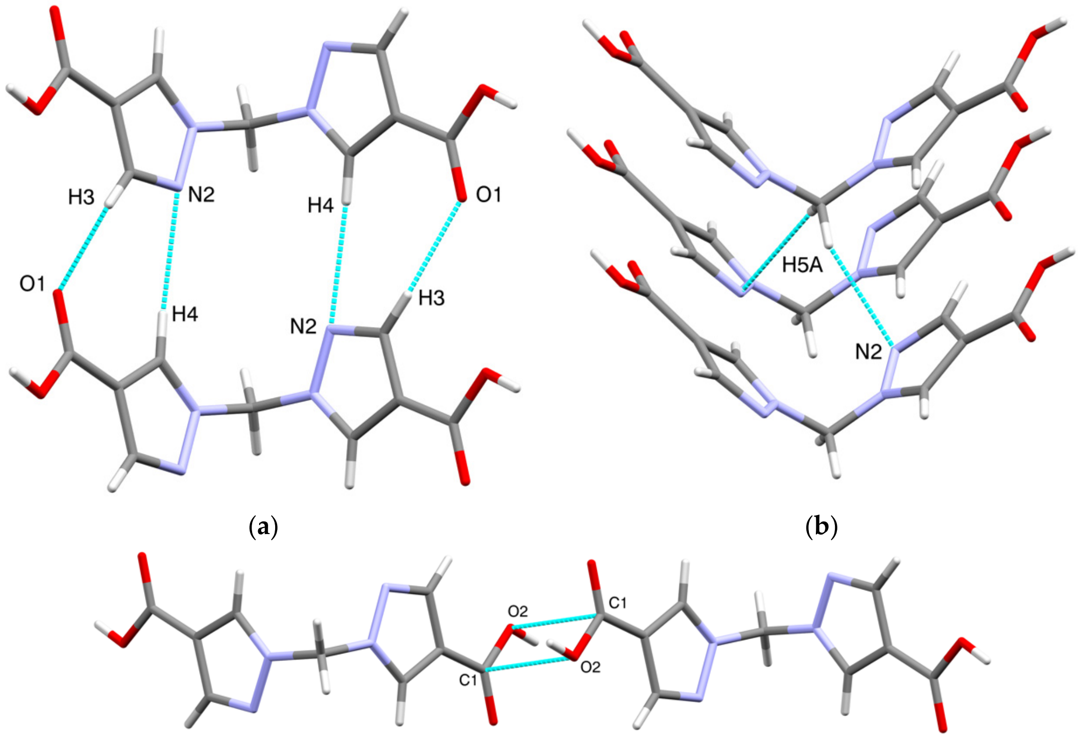


Figure 2. Hydrogen-bonded carboxyl–carboxyl cyclic dimers between H_2bpmdc molecules.

Other types of intermolecular interactions include CH$\cdots$N and CH$\cdots$O short contacts (Figure 3a) with the distances of 2.62(1) and 2.88(1) Å, correspondingly, CH–π interactions between CH_2 groups and pyrazole rings (d(N2-H5A) = 2.716(7) Å, Figure 3b) and carbonyl–carbonyl interactions, d(C1-O2) = 3.170(1) A (Figure 3c). Hydrogen bonds link the H_2bpmdc molecules into zig-zag chains oriented along the crystallographic axis *c*, while the above-mentioned interactions join the chains into supramolecular stacks along the axis *b* (Figure 4). Selected geometric parameters of H_2bpmdc are listed in Table 1.

Table 1. Selected geometric parameters of the molecular structure of H_2bpmdc.

Bond	d, Å	Angle	θ, °
O1—C1	1.2280 (12)	C4—N1—N2	112.94 (8)
O2—C1	1.3187 (11)	C4—N1—C5	127.88 (7)
N1—C4	1.3500 (12)	N2—N1—C5	118.65 (7)
N1—N2	1.3683 (11)	C3—N2—N1	104.25 (8)
N1—C5	1.4497 (10)	O1—C1—O2	124.15 (9)
N2—C3	1.3267 (12)	O1—C1—C2	123.49 (9)
C1—C2	1.4627 (13)	O2—C1—C2	112.36 (8)
C2—C4	1.3830 (12)	C4—C2—C3	105.11 (8)
C2—C3	1.4150 (13)	C4—C2—C1	128.28 (9)
		C3—C2—C1	126.59 (9)
		N2—C3—C2	111.58 (8)
		N1—C4—C2	106.10 (8)
		$N1^i$—C5—N1	111.34 (11)



(**a**) (**b**)

(**c**)

Figure 3. Intermolecular interactions in the crystal structure of H_2bpmdc: (**a**) short contacts CH···N and CH···O; (**b**) CH–π interactions; (**c**) carbonyl–carbonyl interactions.

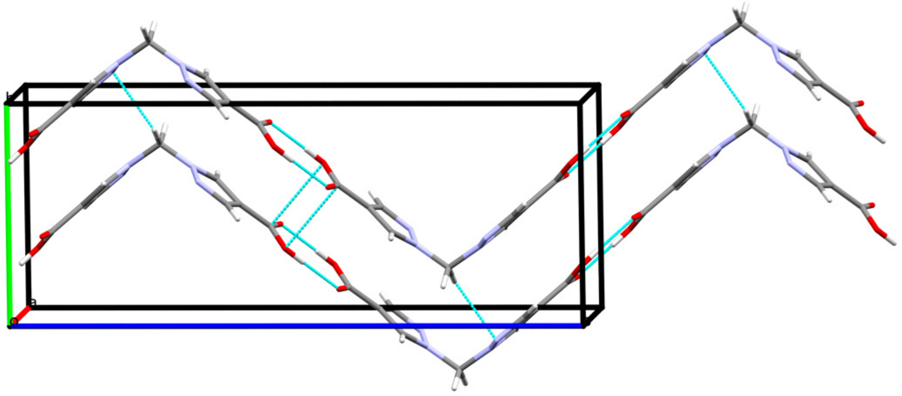


Figure 4. Hydrogen-bonded chains of H_2bpmdc molecules.

3. Materials and Methods

Bis(pyrazol-1-yl)methane-4,4′-dicarboxylic acid (H_2bpmdc) was synthesized as described previously [15] and recrystallized from water to give single crystals suitable for X-ray crystal structure determination.

Single crystal XRD data for H_2bpmdc were collected with a Bruker D8 Venture diffractometer with a CMOS PHOTON III detector and IμS 3.0 source (mirror optics, $\lambda(\mathrm{MoK}\alpha) = 0.71073$Å). The φ- and ω-scan techniques were employed to measure intensities. The crystal structure was solved using the SHELXT [17] and was refined using SHELXL [18] programs with OLEX2 GUI [19]. Atomic displacement parameters for non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and treated as a mixture of independent and constrained refinement.

Crystal Data for $C_9H_8N_4O_4$ (M = 236.19 g/mol): monoclinic, space group $C2/c$, $a = 5.7619(7)$, $b = 8.0578(11)$, $c = 20.806(2)$ Å, $\beta = 90.370(4)^\circ$, $V = 966.0(2)$ Å^3, $Z = 4$, $T = 150(2)$ K, $\mu(\mathrm{MoK}\alpha) = 0.12\ \mathrm{mm}^{-1}$, $D_{calc} = 1.624\ \mathrm{g/cm}^3$, 9866 reflections measured

($3.92° \leq 2\Theta \leq 33.16°$), 1406 unique ($R_{int}$ = 0.045, R_{sigma} = 0.039). The final R_1 was 0.0393 ($I > 2\sigma(I)$) and wR_2 was 0.110 (all data).

Full crystallographic information (as CIF file) along with CheckCIF report are given in the supplementary materials.

Supplementary Materials: The following are available online. Crystallographic information file (CIF) and CheckCIF report for compound H_2bpmdc.

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Data Availability Statement: CCDC 2118484 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center at http://www.ccdc.cam.ac.uk/data_request/cif (last accessed 18 November 2021).

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