

Eight supramolecular assemblies constructed from bis(benzimidazole) and organic acids through strong classical hydrogen bonding and weak noncovalent interactions



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HIGHLIGHTS

- Eight organic acid–base adducts with 3D structure have been prepared and structurally characterized.
- The classical hydrogen bonds in the eight supramolecules containing the OH...bzim synthons have been discussed.
- The secondary interactions in the solid-state packing of the final structure have also been discussed.

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ABSTRACT

Eight crystalline organic acid–base adducts derived from alkane bridged bis(N-benzimidazole) and organic acids (2,4,6-trinitrophenol, p-nitrobenzoic acid, m-nitrobenzoic acid, 3,5-dinitrobenzoic acid, 5-sulfosalicylic acid and oxalic acid) were prepared and characterized by X-ray diffraction analysis, IR, mp, and elemental analysis. Of the eight compounds five are organic salts (**1**, **4**, **6**, **7** and **8**) and the other three (**2**, **3**, and **5**) are cocrystals. In all of the adducts except **1** and **8**, the ratio of the acid and the base is 2:1. All eight supramolecular assemblies involve extensive intermolecular classical hydrogen bonds as well as other noncovalent interactions. The role of weak and strong noncovalent interactions in the crystal packing is ascertained. These weak interactions combined, all the complexes displayed 3D framework structure. The results presented herein indicate that the strength and directionality of the classical N⁺–H...O[−], O–H...O, and O–H...N hydrogen bonds (ionic or neutral) and other nonbonding associations between acids and ditopic benzimidazoles are sufficient to bring about the formation of cocrystals or organic salts.

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1. Introduction

Organic crystals built from acid–base recognition have received considerable attention in the construction of supramolecular architectures [1–7]. One of the important ways is the use of self-organization of discrete molecules through N–H...O, O–H...N, O–H...O, and other weak intermolecular interactions to create 1D–3D frameworks in crystalline solids [8,9].

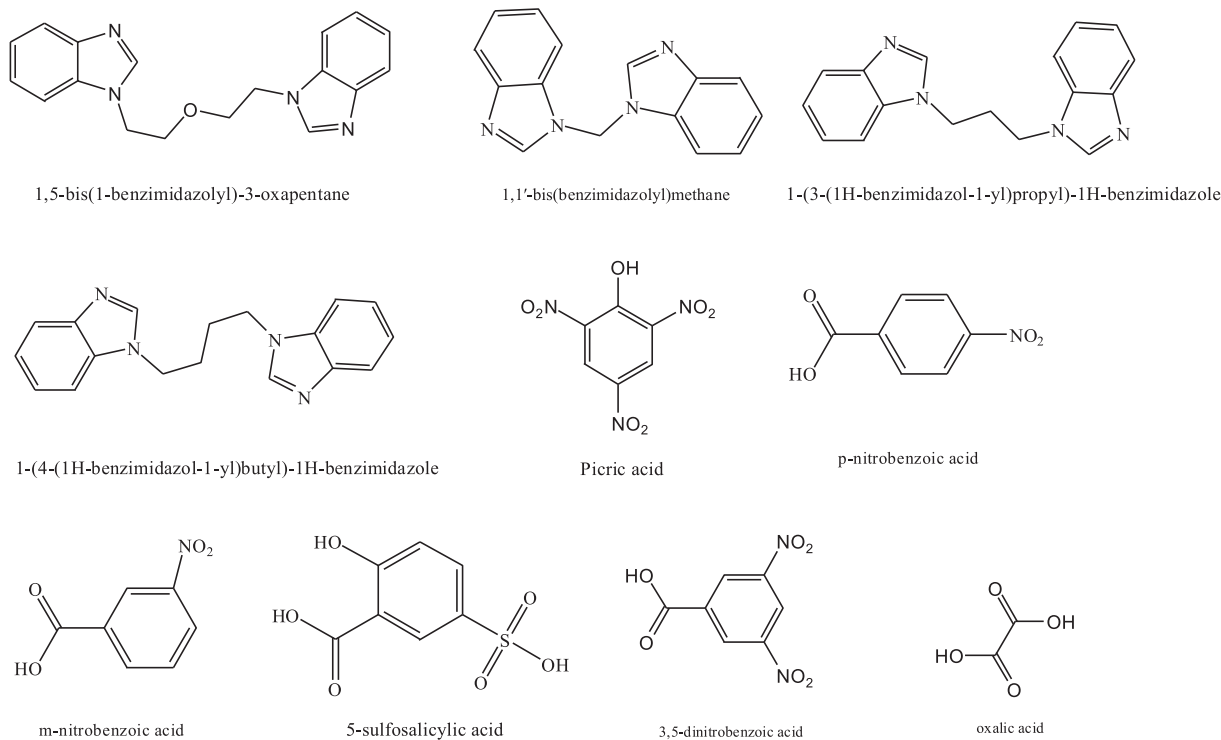
The hydrogen bonding between hydroxyl group of carboxylic acid and heterocyclic N atom has been proved to be a useful and powerful organizing force for the formation of supramolecules. Numerous supramolecular assemblies composed of acids and a

variety of N-containing basic building blocks have been archived recently [10–14]. Imidazole and its derivatives are ubiquitous in biological and biochemical structure and function, which attracted special attention in the construction of some interesting metal–organic frameworks in recent years [15–20]. And also, great efforts have been devoted to the development of organic molecular crystals containing a variety of imidazole derivatives [21–23]. Among these supramolecular architectures, however, only a very few reports described the crystals composed of bridged imidazoles [24–28] (e.g., 1,4-bis[(imidazol-1-yl)methyl]-benzene [24,28], (bis(1-methyl-imidazol-2-yl)methyl)-4-nitroimidazol-2-yl)methylamine [26], etc.).

Following our previous works of acid–base adducts based on bis(imidazole) and carboxylic acids [29,30], herein we report the preparation and crystal structure of eight supramolecular

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Scheme 1. The building blocks discussed in this paper.

compounds assembled through hydrogen bonding interactions between organic acids and bis(benzimidazole). In this study, we got eight organic compounds composed of acids and symmetric ditopic bis-benzimidazol-1-yl compounds (Scheme 1), namely 1,5-bis(1-benzimidazolyl)-3-oxapentane: (2,4,6-trinitrophenol) [(HL1)⁺·(pic⁻), pic⁻ = 2,4,6-trinitrophenolate, L1 = 1,5-bis(1-benzimidazolyl)-3-oxapentane] (**1**), 1,1'-bis(benzimidazolyl)methane: (p-nitrobenzoic acid) [(L2)·(Hnba)₂, L2 = 1,1'-bis(benzimidazolyl)methane, Hnba = p-nitrobenzoic acid] (**2**), 1,1'-bis(benzimidazolyl)methane: (m-nitrobenzoic acid)₂ [(L2)·(Hmba)₂, Hmba = m-nitrobenzoic acid] (**3**), (1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole): (p-nitrobenzoic acid)₂ [(H₂L3)²⁺·(nba⁻)₂, L3 = 1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole, nba⁻ = p-nitrobenzoate] (**4**), 1-(4-(1H-benzimidazol-1-yl)butyl)-1H-benzimidazole: (p-nitrobenzoic acid)₂ [(L4)·(Hnba)₂, L4 = 1-(4-(1H-benzimidazol-1-yl)butyl)-1H-benzimidazole] (**5**), 1,5-bis(1-benzimidazolyl)-3-oxapentane: (3,5-dinitrobenzoic acid)₂: H₂O [(H₂L1)²⁺·(dna⁻)₂·H₂O] (**6**), (1-(4-(1H-benzimidazol-1-yl)butyl)-1H-benzimidazole): (5-sulfosalicylic acid)₂: CH₃OH: 2H₂O [(H₂L4)²⁺·(5-ssa⁻)₂·CH₃OH·2H₂O, 5-ssa⁻ = 5-sulfosalicylate] (**7**), and (1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole): (oxalic acid): 5H₂O [(H₂L3)²⁺·(OA²⁻)·5H₂O] (**8**) (Scheme 2).

2. Experimental section

2.1. Materials and methods

L1–L4 were prepared as described previously [31]. All other reagents were commercially available and used as received. The C, H, N, and S micro-analysis were carried out with a Carlo Erba 1106 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in range 4000–400 cm⁻¹ on a Mattson Alpha-Centauri spectrometer. Melting points of new compounds were recorded on an XT-4 thermal apparatus without correction.

2.2. Preparation of supramolecular compounds

2.2.1. 1,5-Bis(1-benzimidazolyl)-3-oxapentane: (2,4,6-trinitrophenol) [(HL1)⁺·(pic⁻), pic⁻ = 2,4,6-trinitrophenolate], (**1**)

1,5-Bis(1-benzimidazolyl)-3-oxapentane L1 (29 mg, 0.10 mmol) dissolved in 3 mL ethanol. To this solution was added 2,4,6-trinitrophenol (23 mg, 0.1 mmol) in 20 mL methanol. Pale yellow block crystals were isolated after several minutes from the solution at room temperature in air. The crystals were collected and dried in air to give the title compound [(HL1)⁺·(pic⁻)] (**1**), yield 40 mg, 74.70% (Based on L1). m.p. 178–180 °C. Elemental analysis performed on crystals exposed to the atmosphere: Calc. for C₂₄H₂₁N₇O₈ (535.48): C, 53.78; H, 3.92; N, 18.30. Found: C, 53.71; H, 3.87; N, 18.23. Infrared spectrum (KBr disc, cm⁻¹): 3440s(v_{as}(NH)), 3329s(v_s(NH)), 3186m, 2943m, 2886m, 1745m, 1668s, 1612s, 1558s, 1527s(v_{as}(NO₂)), 1476m, 1434m, 1378s, 1321s(v_s(NO₂)), 1264s, 1218m, 1164m, 1080m, 1032m, 978m, 879m, 834m, 791m, 726m, 683m, 632m, 604m.

2.2.2. (1,1'-Bis(benzimidazolyl)methane): (p-nitrobenzoic acid)₂ [(L2)·(Hnba)₂] (**2**)

1,1'-bis(benzimidazolyl)methane L2 (24.8 mg, 0.10 mmol) was dissolved in 5 mL of ethanol. To this solution was added p-nitrobenzoic acid (16.8 mg, 0.1 mmol) in 3 mL ethanol. Colorless block crystals were afforded after several weeks of slow evaporation of the solvent. The crystals were dried in air to give the title compound [(L2)·(Hnba)₂] (**2**), yield 38 mg, 65.2% (Based on L2). m.p. 187–188 °C. Elemental analysis performed on crystals exposed to the atmosphere: Calc. for C₂₉H₂₂N₆O₈ (582.53): C, 59.74; H, 3.78; N, 14.42. Found: C, 59.68; H, 3.74; N, 14.36. Infrared spectrum (KBr disc, cm⁻¹): 3658s(v(OH)), 3089m, 2993m, 2926m, 2486m, 1902m, 1763w, 1648s(v(C=O)), 1620m, 1536s(v_{as}(NO₂)), 1515m, 1486m, 1448m, 1324s(v_s(NO₂)), 1288s(v(C–O)), 1246m, 1202m, 1162m, 1094m, 1006m, 952w, 877w, 831m, 797w, 724m, 654w, 618w.

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