



Seven supramolecular frameworks constructed from combination of hydrogen-bonds and other non-covalent associations between organic acids and bis-imidazoles

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ABSTRACT

Seven crystalline organic acid–base adducts derived from bis(N-imidazolyl) and organic acids (2,4,6-trinitrophenol, p-nitrobenzoic acid, 3,5-dinitrobenzoic acid, oxalic acid, m-phthalic acid, and 1,5-naphthalenedisulfonic acid) were prepared and characterized by X-ray diffraction analysis, IR, mp, and elemental analysis. The seven compounds are all organic salts. In salts **1**, and **3**, the L1 are monoprotonated, while in **4** and **6** the L1 are diprotonated. All supramolecular architectures involve extensive classical hydrogen bonds and C–H···O interactions. The role of weak and strong non-covalent interactions in the crystal packing is analyzed. The complexes displayed 2D–3D framework structures for the synergistic effect of the various non-covalent interactions.

The results presented herein indicate that the strength and directionality of the N–H···N, N–H···O, O–H···O, O–H···N, N–H···S, and O–H···S hydrogen bonds between the organic acids and the ditopic imidazoles are sufficient to bring about the formation of binary organic salts.

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1. Introduction

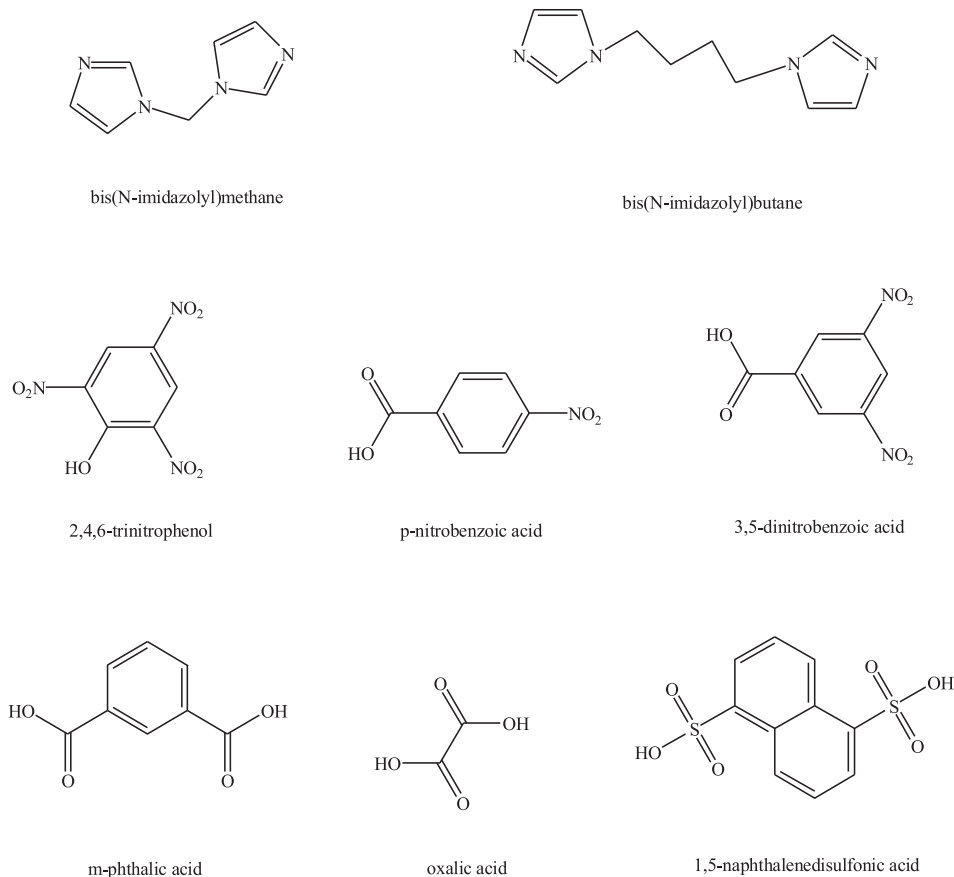
Non-covalent interactions between molecules are weak intermolecular contacts that govern the physicochemical properties of molecular systems in the condensed phase [1]. Non-covalent interactions include classical/non-classical hydrogen bonds, stacking, electro-static, hydrophobic and charge-transfer interactions [2]. Of these interactions hydrogen bond interactions are well-established supramolecular interactions and numerous crystallographic examples are regularly reported [3–6].

Organic acids represent one of the most prevalent functional groups in crystal engineering because they can form persistent supramolecular heterosynthons with a number of different N-containing components [7–11]. In this regard, the most frequently used N-containing moieties with hydrogen-bonding capability are amine (including aromatic amine and aliphatic amine), pyridyl, and azole derivatives [12–20].

Great efforts have been devoted to the development of organic molecular crystals containing a variety of imidazole architectures [21–28]. Following our previous works of acid–base adducts based on bis(imidazole) and carboxylic acids [29,30], herein we report the synthesis and crystal structures of seven supramolecular compounds assembled through the combination of hydrogen bonding and other non-covalent interactions between the organic acids and bis(imidazole). In this study, we got seven compounds composed of organic acids and symmetric ditopic bis-imidazol-1-yl compounds (Scheme 1), namely bis(N-imidazolyl)methane: (2,4,6-trinitrophenol) [(HL1)⁺ · (pic[−]), L1 = bis(N-imidazolyl)methane, pic[−] = picrate] (**1**), (bis(N-imidazolyl)butane): (p-nitrobenzoic acid)₂ [(H₂L2) · (pba)₂, L2 = bis(N-imidazolyl)butane, pba = p-nitrobenzoate] (**2**), bis(N-imidazolyl)methane: (3,5-dinitrobenzoic acid)₃ [(HL1⁺) · (dna[−]) · (Hdna)₂, dna = 3,5-dinitrobenzoate, Hdna = 3,5-dinitrobenzoic acid] (**3**), bis(N-imidazolyl)methane: (oxalic acid)₂ · H₂O [(H₂L1)²⁺ · (Hoa)₂^{2−} · H₂O, Hoa = hydrogen oxalate] (**4**), (bis(N-imidazolyl)butane): (m-phthalic acid) [(HL2) · (Hpta), Hpta = hydrogen m-phthalate] (**5**), (bis(N-imidazolyl)methane)₂: (1,5-naphthalenedisulfonic acid)₂: acetonitrile [(H₂L1)₂ · (npa)₂ · CH₃CN, npa = 1,5-naphthalenedisulfonate] (**6**), and (bis(N-

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Scheme 1. The building blocks discussed in this paper.

imidazolyl)butane): (1,5-naphthalenedisulfonic acid)₂: 2H₂O [(H₂L2)²⁺ · (npa)²⁻ · 2H₂O] (**7**).

2. Experimental section

2.1. Materials and methods

Bis(N-imidazolyl)methane and bis(N-imidazolyl)butane were prepared as described previously [31]. All other reagents were commercially available and used as received. The C, H, N, and S microanalysis 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.

3. Preparation of the supramolecular compounds

3.1. Bis(N-imidazolyl)methane: (2,4,6-trinitrophenol) [(HL1)⁺ · (pic⁻)] (**1**)

Bis(N-imidazolyl)methane (0.0150 g, 0.1 mmol) was dissolved in 1 mL methanol. To this solution was added 2,4,6-trinitrophenol (0.0230 g, 0.1 mmol) in 10 mL methanol. Colorless block crystals were afforded after several days by slow evaporation of the solvent (yield: 0.0250 g, 66.26%, based on L1). mp 108–109 °C. Elemental analysis: Calc. for C₁₃H₁₁N₇O₇ (377.29): C, 41.35; H, 2.92; N, 25.97. Found: C, 41.29; H, 2.86; N, 25.91. Infrared spectrum (KBr disc, cm⁻¹): 3451s(*v*_{as}(NH)), 3334s(*v*_s(NH)), 3090m, 2930m, 2867m, 1664m, 1611m, 1564m, 1526s(*v*_{as}(NO₂)), 1475m, 1431m, 1374m,

1323s(*v*_s(NO₂)), 1270m, 1222m, 1174m, 1098m, 1043m, 987m, 936m, 875m, 828m, 786m, 729m, 677m, 639m, 606m.

3.2. Bis(N-imidazolyl)butane: (p-nitrobenzoic acid)₂ [(H₂L2) · (pba)₂] (**2**)

Bis(N-imidazolyl)butane (0.0190 g, 0.1 mmol) was dissolved in 2 mL ethanol. To this solution was added p-nitrobenzoic acid (0.0170 g, 0.1 mmol) in 4 mL ethanol. Colorless block crystals were afforded after several days by slow evaporation of the solvent (yield: 0.0320 g, 61.01%, based on L2). mp 206–208 °C. Elemental analysis: Calc. for C₂₄H₂₄N₆O₈ (524.49): C, 54.91; H, 4.58; N, 16.02. Found: C, 54.86; H, 4.51; N, 15.95. Infrared spectrum (KBr disc, cm⁻¹): 3426s(*v*_{as}(NH)), 3386s(*v*_s(NH)), 3074 m, 2998m, 2930m, 2864m, 1622m, 1589s(*v*_{as}(COO⁻)), 1534s(*v*_{as}(NO₂)), 1498m, 1449m, 1383s(*v*_s(COO⁻)), 1327s(*v*_s(NO₂)), 1273m, 1225m, 1156m, 1098m, 1032m, 959w, 888w, 836m, 788w, 727m, 666w, 631m, 609w.

3.3. Bis(N-imidazolyl)methane: (3,5-dinitrobenzoic acid)₃ [(HL1)⁺ · (dna⁻) · (Hdna)₂] (**3**)

Bis(N-imidazolyl)methane L1 (0.0148 g, 0.10 mmol) was dissolved in 5 mL of ethanol. To this solution was added 3,5-dinitrobenzoic acid (0.0212 g, 0.1 mmol) in 4 mL methanol. Colorless prisms were afforded after several weeks of slow evaporation of the solvent. The crystals were dried in air to give the title compound [(HL1)⁺ · (dna) · (Hdna)₂] (**3**), yield 0.0360 g, 45.88% (Based on L1). m. p. 166–167 °C. Elemental analysis performed on crystals exposed to the atmosphere: Calc. for C₂₈H₂₀N₁₀O₁₈ (784.54): C, 42.83; H, 2.55; N, 17.84. Found: C, 42.79; H, 2.49; N, 17.78. Infrared

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