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Structure of eight molecular salts assembled from noncovalent bonding between carboxylic acids, imidazole, and benzimidazole

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HIGHLIGHTS

- Eight organic salts have been prepared and structurally characterized.
- The hydrogen bonds of the salts have been ascertained.
- The N—H···O and O—H···O hydrogen bonds are the primary forces in these salts.
- The secondary nonbonding interactions also play important role in structure propagation.

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ABSTRACT

Eight organic salts of imidazole/benzimidazole have been prepared with carboxylic acids as 2-methyl-2-phenoxypropanoic acid, α-ketoglutaric acid, 5-nitrosalicylic acid, isophthalic acid, 4-nitro-phthalic acid, and 3,5-dinitrosalicylic acid. The eight crystalline forms reported are proton-transfer compounds of which the crystals and compounds were characterized by X-ray diffraction analysis, IR, mp, and elemental analysis. These structures adopted hetero supramolecular synthons, with the most common $R_2^2(7)$ motif observed at salts **2**, **3**, **5**, **6** and **8**.

Analysis of the crystal packing of **1**–**8** suggests that there are extensive strong N—H···O, and O—H···O hydrogen bonds (charge assisted or neutral) between acid and imidazolyl components in all of the salts. Except the classical hydrogen bonding interactions, the secondary propagating interactions also play important roles in structure extension. This variety, coupled with the varying geometries and number of acidic groups of the acids utilized, has led to the creation of eight supramolecular arrays with 1D–3D structure. The role of weak and strong noncovalent interactions in the crystal packing is analyzed. The results presented herein indicate that the strength and directionality of the N—H···O, and O—H···O hydrogen bonds between acids and imidazole/benzimidazole are sufficient to bring about the formation of organic salts.

Introduction

Crystal engineering using multiple interactions, such as electrostatic forces, hydrogen bonding, cation···π, C—H···π, and π···π interactions, is a constantly growing field of research [1]. Multicomponent crystals and organic acid-base adducts produced via multiple interactions have received considerable attention during the past few years [2,3] not only because of their intriguing structural motifs [4,5] but also for their useful properties and promising applications as functional materials [6,7]. The design and construction of multicomponent supermolecules or supramolecular arrays utilizing noncovalent bonding is a rapidly developing area in supramolecular synthesis. Thus, the supramolecular synthesis successfully exploits hydrogen-bonding and other types of non-covalent interactions in building supramolecular systems [8]. In these non-covalent interactions hydrogen bonds are the most powerful force for generating the supermolecules [9–12].

Because of the ability to form strong and directional hydrogen bonds via the COOH group, carboxylic acids were frequently utilized as building blocks for organic crystal engineering [13–15]. Besides the COOH group, the functional groups such as OH, C=O, NO_2, and phenyl groups are all good groups in forming organic solid through noncovalent interactions [16–21], thus we select some carboxylic acids bearing additional groups such as OH,

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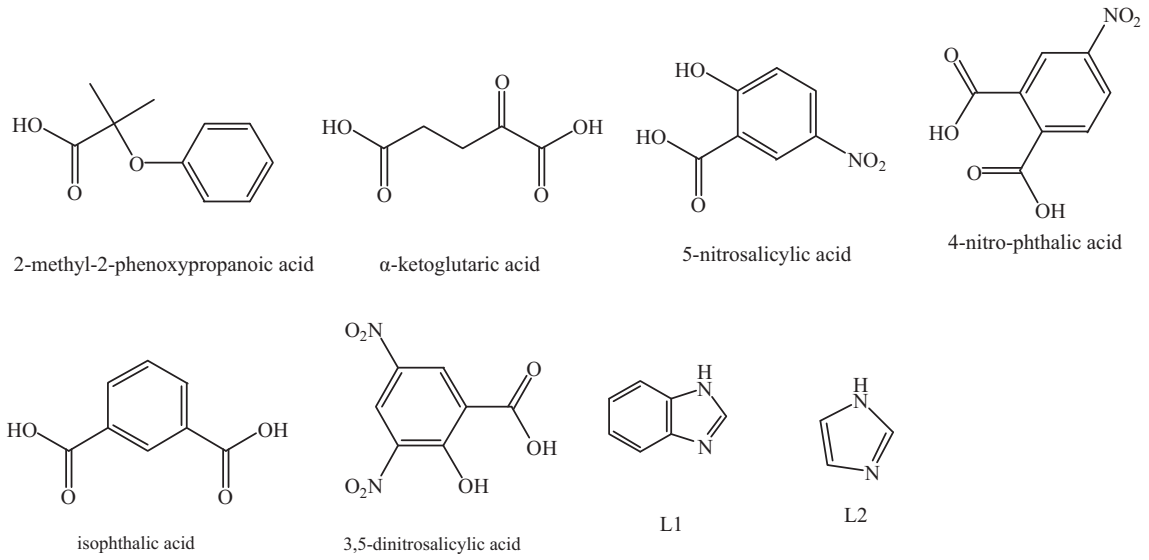

Scheme 1. The building blocks discussed in this paper.

C═O, NO_2, and phenyl groups. A large amount of organic acid-base adducts from carboxylic acids and N-containing basic building blocks have been archived recently [22–26]. Among the N-containing building blocks imidazole/benzimidazole and its derivatives have been widely used [27–34].

Following our previous works of acid-base adducts based on bis(imidazole) and carboxylic acids [35,36], herein we report the synthesis and crystal structure of eight supramolecular compounds assembled via hydrogen bonding interactions between carboxylic acids, imidazole, and benzimidazole. In this study, we got eight salts composed of carboxylic acids and imidazolyl compounds (Scheme 1), namely (benzimidazole): (2-methyl-2-phenoxypropanoic acid): H_2O [$(HL1)^+\cdot(mppa)^-\cdot H_2O$, L1 = benzimidazole, $mppa^-$ = 2-methyl-2-phenoxypropionate] **(1)**, (benzimidazole): (α-ketoglutaric acid) [$(HL1)^+\cdot(kga)^-$], kga^- = α-ketoglutarate] **(2)**, (benzimidazole): (5-nitrosalicylic acid) [$(HL1)^+\cdot(5\text{-}nsa)^-$, $5\text{-}nsa^-$ = 5-nitrosalicylate] **(3)**, (benzimidazole): (isophthalic acid) [$(HL1)^+\cdot(Hmpa)^-$, $Hmpa^-$ = hydrogenisophthalate] **(4)**, (benzimidazole): (4-nitro-phthalic acid) [$(HL1)^+\cdot(Hnpa)^-$, $Hnpa^-$ = 4-nitro-hydrogenphthalate] **(5)**, (imidazole): (4-nitro-phthalic acid) [$(HL2)^+\cdot(Hnpa)^-$, L2 = imidazole] **(6)**, (imidazole): (3,5-dinitrosalicylic acid) [$(HL2)^+\cdot(3,5\text{-}dns)^-$, $3,5\text{-}dns^-$ = 3,5- dinitrosalicylate] **(7)**, and (imidazole): (α-ketoglutaric acid) [$(HL2)^+\cdot(kga)^-$] **(8)** (Scheme 2).

Experimental section

Materials and methods

All reagents were commercially available and used as received. The C, H, and N 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.

Preparation of the salts

*(Benzimidazole): (2-methyl-2-phenoxypropanoic acid): H_2O [$(HL1)^+\cdot(mppa)^-\cdot H_2O$, $mppa^-$ = 2-methyl-2-phenoxypropionate] (**1**)*

Benzimidazole L1 (11.8 mg, 0.1 mmol) was dissolved in 3 ml of methanol. To this solution was added 2-methyl-2-phenoxypropanoic acid (18 mg, 0.1 mmol) in 3 ml methanol. The solution was stirred for a few minutes, then the solution was filtered into a test tube. The solution was left standing at room temperature for several days, colorless block crystals were isolated after slow evaporation of the solution in air. The crystals were dried in air to give the compound [$(HL1)^+\cdot(mppa)^-\cdot H_2O$] (**1**), (yield 28 mg, 88.51%). m.p. 177–178 °C. Elemental analysis performed on crystals exposed to the atmosphere: Calc. for $C_{17}H_{20}N_2O_4\cdot$(316.35): C, 64.48; H, 6.32; N, 8.85. Found: C, 64.41; H, 6.23; N, 8.77. Infrared spectrum (KBr disc, cm^{-1}): 3665s ($\nu(H_2O)$), 3448s(multiple, ν_{as}(NH)), 3362s(ν_s(NH)), 3121m, 2969m, 2883m, 2677m, 2562w, 1869m, 1726m, 1648m, 1620m, 1585s($\nu_{as}(COO^-)$), 1506m, 1454m, 1403m, 1386s($\nu_s(COO^-)$), 1351m, 1287m, 1231m, 1155m, 1030m, 976m, 898m, 824m, 778m, 741m, 701m, 661m, 604m.

*(Benzimidazole): (α-ketoglutaric acid) [$(HL1)^+\cdot(kga)^-$], kga^- = α-ketoglutarate] (**2**)*

Benzimidazole L1 (11.8 mg, 0.1 mmol) was dissolved in 3 ml of methanol. To this solution was added α-ketoglutaric acid (14.6 mg, 0.1 mmol) in 5 ml methanol. The solution was stirred for a few minutes, then the solution was filtered into a test tube. The solution was left standing at room temperature for several days, colorless block crystals were isolated after slow evaporation of the solution in air. The crystals were dried in air to give the compound [$(HL1)^+\cdot(kga)^-$] (**2**), (yield 22 mg, 83.26%). m.p. 136–138 °C. Elemental analysis performed on crystals exposed to the atmosphere: Calc. for $C_{12}H_{12}N_2O_5$ (264.24): C, 54.49; H, 4.54; N, 10.59. Found: C, 54.43; H, 4.48; N, 10.54. Infrared spectrum (KBr disc, cm^{-1}): 3596s(ν(HO)), 3450s (multiple, ν_{as}(NH)), 3365s(ν_s(NH)), 3131m, 2976m, 2885m, 2685m, 2576w, 1876m, 1726m, 1658s, 1616m, 1583s($\nu_{as}(COO^-)$), 1531m, 1475m, 1433m, 1388s($\nu_s(COO^-)$), 1341m, 1279m, 1223m, 1166m, 1088m, 1026m, 874m, 828m, 771m, 712m, 676m, 630m, 603m.

*(Benzimidazole): (5-nitrosalicylic acid) [$(HL1)^+\cdot(5\text{-}nsa)^-$, $5\text{-}nsa^-$ = 5-nitrosalicylate] (**3**)*

Benzimidazole L1 (11.8 mg, 0.1 mmol) was dissolved in 3 ml of water. To this solution was added 5-nitrosalicylic acid (18.3 mg, 0.1 mmol) in 15 ml ethanol. The solution was heated to 60 °C for 2 h. There appeared some precipitate, to this mixture 2 ml DMF was added and heated until the precipitate dissolved completely. Pale yellow block crystals were afforded after several days by slow evaporation of the solvent. The crystals were collected and dried in