Journal of Molecular Structure 1039 (2013) 144–152

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Structure of four molecular salts assembled from noncovalent associations between carboxylic acids and aromatic bases containing benzimidazole moiety

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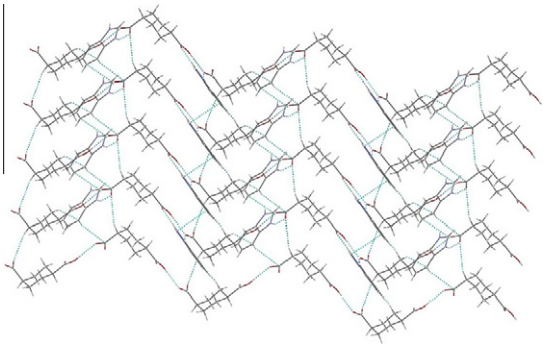
HIGHLIGHTS

- Four supramolecular compounds with 3D structure have been prepared and characterized.
- The noncovalent interaction between benzimidazole moiety and carboxylic acids have been analyzed.
- The N—H···O/O—H···O hydrogen bond is the primary force in a family of structures containing the OH···im synthons.
- The CH—O associations have also been discussed.

GRAPHICAL ABSTRACT

Due to the weak noncovalent interactions, the compounds displayed 3D framework structure.



ARTICLE INFO

Article history:
Received 10 May 2012
Received in revised form 11 December 2012
Accepted 7 January 2013
Available online 27 January 2013

Keywords:
Crystal structure
3D framework
Hydrogen bonds
Carboxylic acid
Benzimidazole derivatives

ABSTRACT

Single crystal X-ray diffraction has enabled the elucidation of four examples of benzimidazole-acid salts, novel contributions to the extensive research into the occurrence of benzimidazole-acid compound motifs in organic salts. In their place are a series of motifs in which extensive strong classical N—H···O/O—H···O hydrogen bonds (ionic or neutral) combine with other nonconventional weaker interactions. This variety, coupled with the varying geometries and number of acidic groups of the acids employed, has led to the creation of four supramolecular arrays with 3D network structure.

All salts were formed in solution and obtained by the slow evaporation technique. 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 (ionic or neutral) between acids and benzimidazole derivatives are sufficient to bring about the formation of organic salts.

1. Introduction

Multicomponent crystals and organic acid_base complexes have received considerable attention over the past few years [1,2] not only because of their intriguing structural motifs [3,4] but also for their useful properties and promising applications as functional materials [5,6]. The design and construction of multi-component 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 noncovalent interactions, in building supramolecular systems [7]. Of these interactions hydrogen bond interactions are the most powerful organizing force for the formation of supermolecules [8–11].

Because of the predictable supramolecular properties and the ability to form strong and directional hydrogen bonds, carboxylic acids were frequently chosen as building blocks for crystal

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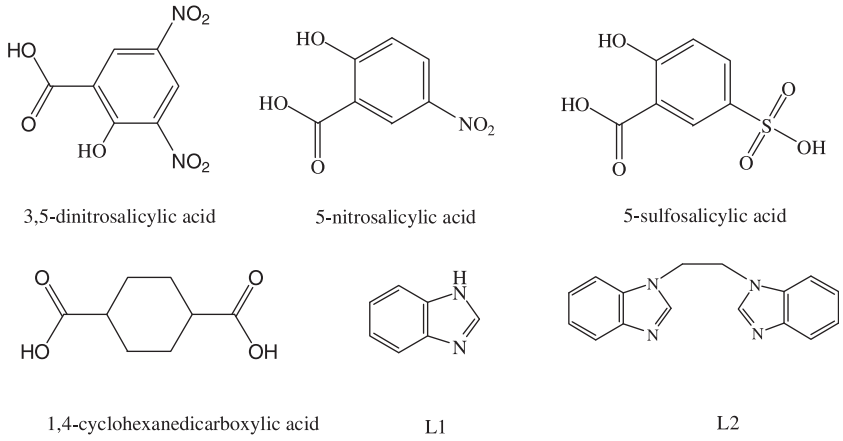
http://dx.doi.org/10.1016/j.molstruc.2013.01.016



Scheme 1. The building blocks discussed in this paper.

engineering [12–14]. Numerous organic acid_base compounds from carboxylic acids and a variety of N-containing basic building blocks have been documented recently [15–19].

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 [20–25]. And also, great efforts have been devoted to the development of organic molecular crystals containing a variety of imidazole architectures [26–28]. Among these supramolecular architectures, however, only a very few reports described the crystals composed of imidazoles [29–33] (e.g., 1,4-bis[(imidazol-1-yl)methyl]-benzene [29,33], (bis(1-methyl-imidazol-2-yl)methyl)-4-nitroimidazol-2-yl)methyl)amine [31], etc.).

Following our previous works of acid–base adducts based on bis(imidazole) and dicarboxylic acid [34,35], herein we report the synthesis and crystal structure of four supramolecular compounds assembled via hydrogen bonding interactions between carboxylic acids and benzimidazole or its derivative. In this study, we got four organic compounds composed of carboxylic acids and benzimidazolyl compounds (Scheme 1), namely (benzimidazole):(3,5-dinitrosalicylic acid) [$(HL1^+)\cdot(3,5\text{-}dns^-)$, L1 = benzimidazole, $3,5\text{-}dns^-$ = 3,5-dinitrosalicylate] **(1)**, $(benzimidazole)_2$:(5-nitrosalicylic acid) $[(HL1)^+(L1)\cdot(5\text{-}nsa^-)$, $5\text{-}nsa^-$ = 5-nitrosalicylate] (**2**), (benzimidazole):1-(2-(1H-benzimidazol-1-yl)ethyl)-1H-benzimidazole:(5-sulfosalicylic acid):$4H_2O$ $[(HL1^+)_2\cdot(H_2L2)^{2+}\cdot(5\text{-}ssa^{2-})_2\cdot 4H_2O$, L2 = 1-(2-(1H-benzimidazol-1-yl)ethyl)-1H-benzimidazole, $5\text{-}ssa^{2-}$ = 5-sulfosalicylate] **(3)**, and (benzimidazole):(1,4-cyclohexanedicarboxylic acid) $[(HL1^+)\cdot(HChda^-)$, $HChda^-$ = hydrogen 1,4-cyclohexanedicarboxylate], **(4)** (Scheme 2).

2. Experimental section

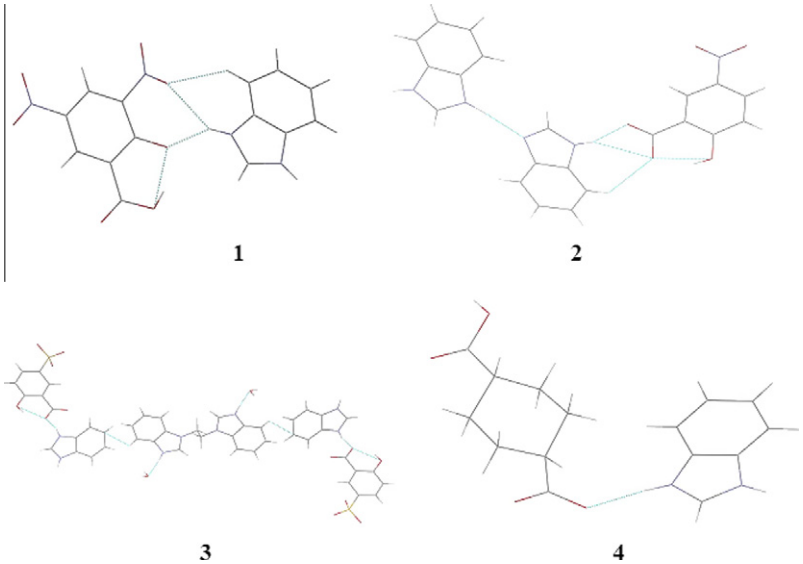
2.1. Materials and methods

L2 was prepared as described previously [36]. 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.

2.2. Preparation of the salts

2.2.1. (Benzimidazole):(3,5-dinitrosalicylic acid) $[(HL1^+)\cdot(3,5\text{-}dns^-)]$ (*1*)

Benzimidazole L1 (11.8 mg, 0.1 mmol) was dissolved in 3 mL of methanol. To this solution was added 3,5-dinitrosalicylic acid



Scheme 2. The four compounds described in this paper, **1**–**4**.