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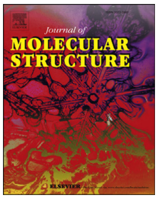

Six hydrogen-bonded supramolecular frameworks assembled from organic acids and p-dimethylaminobenzaldehyde

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ABSTRACT

Cocrystallization of the commonly available organic compound, p-dimethylaminobenzaldehyde, with a series of organic acids gave a total of six molecular adducts with the compositions: p-dimethylaminobenzaldehyde : (3,5-dinitrosalicylic acid) [(L) · (Hdsa), Hdsa = 3,5-dinitrosalicylic acid] **(1)**, p-dimethylaminobenzaldehyde : (3-nitrophthalic acid) [(L) · (3-H_2npa), 3-H_2npa = 3-nitrophthalic acid] **(2)**, p-dimethylaminobenzaldehyde : (4-nitrophthalic acid) [(L) · (4-H_2npa), 4-H_2npa = 4-nitrophthalic acid] **(3)**, p-dimethylaminobenzaldehyde : (1,5-naphthalenedisulfonic acid) : $(NH_3)_2$ [NH_4 · (HL) · (nds^{2-}) · NH_3, nds^- = 1,5-naphthalenedisulfonate] **(4)**, p-dimethylaminobenzaldehyde : (oxalic acid)$_{0.5}$ [(L) · $(H_2oa)_{0.5}$, H_2oa = oxalic acid] **(5)**, and p-dimethylaminobenzaldehyde : (fumaric acid)$_{0.5}$ [(L) · $(H_2fum)_{0.5}$, H_2fum = fumaric acid] **(6)**. The six molecular adducts have been characterized by X-ray diffraction technique, IR, and elemental analysis, and the melting points of all adducts were also reported. And their structural and supramolecular aspects are fully analyzed. Of the six adducts, only **4** is an organic salt and the other five are cocrystals.

The crystal packing is interpreted in terms of the strong classical hydrogen bonds as well as other weak non-classical hydrogen bonds. The different families of non-covalent bonds contribute to the stabilization and expansion of the total high-dimensional (2D–3D) frameworks.

1. Introduction

An efficient strategy in the crystal engineering is to construct supramolecular structures from molecules that are brought together by multiple interactions such as electrostatic forces, hydrogen bonding, lp···π, cation···π, C–H···π, and π···π interactions [1]. Hydrogen bonding system is the main key for the organization of supramolecules from the organic acid and base containing the hydrogen bonding sites [2]. The intramolecular, and intermolecular hydrogen bonds are the driving forces for the construction of the complex self-assembled structures generated by N-containing bronsted bases and the acidic components [3,4].

Organic acids belong to one of the most prevalent functional compounds in crystal engineering because they possess the nice hydrogen bond donor and acceptor with a geometry that self-associates by supramolecular homosynthons of dimer or catemer [5–7]. Furthermore, it is now widely known that organic acids are good candidates for multicomponent crystals since they can form persistent supramolecular heterosynthons with a number of different components including amine, and aromatic nitrogen etc. For instance, much has been documented about the use of organic acid and pyridyl derivatives in the design of supramolecular systems [8–13]. Besides the acidic group, other functional groups such as CH_3, NO_2, and phenol groups are all good groups in forming the organic solids through various non-covalent associations [14]. As an amine derivative, besides the N group, p-dimethylaminobenzaldehyde contains two CH_3, one –CHO, and one phenyl moiety, which can provide more complex nonbonding interactions when it interacted with the acidic compounds. To the best of our knowledge, there were no reports of the organic adducts involving p-dimethylaminobenzaldehyde and organic acids.

In order to understand the interaction fashions p-

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dimethylaminobenzaldehyde have in binding with the organic acids, we began to study the p-dimethylaminobenzaldehyde-acids system, also aiming to find the role the weak non-covalent interactions played in forming the final supramolecular frameworks. Thus, in the following, we will hope to report the preparation and crystal structures of six supramolecular compounds assembled *via* nonbonding interactions between the organic acids and p-dimethylaminobenzaldehyde (L) (Scheme 1). In this study, we got six acid-base adducts composed of organic acids and p-dimethylaminobenzaldehyde, namely p-dimethylaminobenzaldehyde : (3,5-dinitrosalicylic acid) [(L) · (Hdsa), Hdsa = 3,5-dinitrosalicylic acid] **(1)**, p-dimethylaminobenzaldehyde : (3-nitrophthalic acid) [(L) · (3-H_2npa), 3-H_2npa = 3-nitrophthalic acid] **(2)**, p-dimethylaminobenzaldehyde : (4-nitrophthalic acid) [(L) · (4-H_2npa), 4-H_2npa = 4-nitrophthalic acid] **(3)**, p-dimethylaminobenzaldehyde : (1,5-naphthalenedisulfonic acid) : $(NH_3)_2$ [NH_4 · (HL) · (nds^{2-}) · NH_3, nds$^-$ = 1,5-naphthalenedisulfonate] **(4)**, p-dimethylaminobenzaldehyde : (oxalic acid)$_{0.5}$ [(L) · (H_2oa)$_{0.5}$, H_2oa = oxalic acid] **(5)**, and p-dimethylaminobenzaldehyde : (fumaric acid)$_{0.5}$ [(L) · (H_2fum)$_{0.5}$, H_2fum = fumaric acid] **(6)**, respectively (Scheme 2).

2. Experimental section

2.1. Materials and methods

The chemicals and solvents used in this work were of analytical grade commercial products and were used without further purification. The FT-IR spectra were recorded from KBr pellets in range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer, and the IR bands were marked as strong (s), medium (m), and weak (w) at the preparation part. The carbon, hydrogen, nitrogen, and sulfur data were obtained microanalytically on a Perkin–Elmer elemental analyzer (with Model 2400II). The melting points of the new compounds were measured by an XT-4 thermal instrument without correction.

2.2. Preparation of the supramolecular adducts

2.2.1. a. p-dimethylaminobenzaldehyde : (3,5-dinitrosalicylic acid) [(L) · (Hdsa), Hdsa = 3,5-dinitrosalicylic acid] (1)

p-dimethylaminobenzaldehyde (14.9 mg, 0.1 mmol) was dissolved in 2 mL methanol. To this solution was added 3,5-dinitrosalicylic acid (22.8 mg, 0.1 mmol) in 12 mL ethanol. Light yellow block crystals were obtained after ten days by slow evaporation of the solvent, the yield was 24 mg (63.61%, based on L). mp 113–114 °C. Elemental analysis: Calc. for $C_{16}H_{15}N_3O_8$ (377.31): C, 50.89; H, 3.98; N, 11.13. Found: C, 50.85; H, 3.96; N, 11.08. IR (KBr disc, cm^{-1}): 3617s(ν(OH)), 3135m, 3087m, 2979m, 2872w, 1742s, 1693s(ν_{as}(C=O)), 1620m, 1572m, 1529s(ν_{as}(NO_2)), 1488w, 1446m, 1403m, 1359m, 1315s(ν_s(NO_2)), 1284(ν_s(C–O)), 1240m, 1196m, 1154m, 1113m, 1070m, 1026m, 979m, 933m, 890m, 846m, 802m, 760m, 717m, 675m, 636m, 609m.

2.2.2. b. p-Dimethylaminobenzaldehyde : (3-nitrophthalic acid) [(L) · (3-H_2npa), 3-H_2npa = 3-nitrophthalic acid] (2)

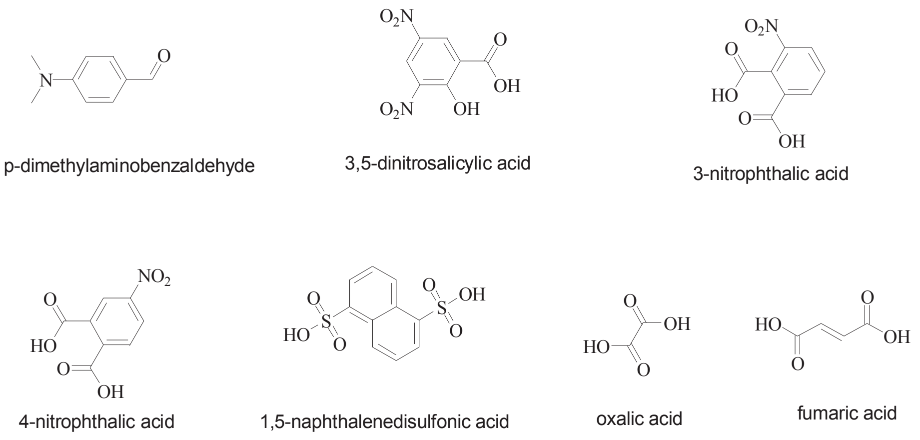
p-dimethylaminobenzaldehyde (14.9 mg, 0.1 mmol) was dissolved in 2 mL methanol. To this solution was added 3-nitrophthalic acid (21.1 mg, 0.10 mmol) in 12 mL methanol. Colorless block crystals were obtained after two weeks by slow evaporation of the solvent, the yield was 30 mg (83.26%, based on L). mp 150–151 °C. Elemental analysis: Calc. for $C_{17}H_{16}N_2O_7$ (360.32): C, 56.62; H, 4.44; N, 7.77. Found: C, 56.55; H, 4.41; N, 7.69. IR (KBr disc, cm^{-1}): 3602s(ν(OH)), 3185m, 3126m, 3081m, 2966m, 2880m, 1722s, 1672s(ν(C=O)), 1620m, 1574m, 1530s(ν_{as}(NO_2)), 1477m, 1436m, 1388m, 1316s(ν_s(NO_2)), 1275s(ν(C–O)), 1233m, 1192m, 1150m, 1108m, 959m, 912m, 866m, 822m, 779m, 734m, 790m, 645m, 612m.

2.2.3. c. p-dimethylaminobenzaldehyde : (4-nitrophthalic acid) [(L) · (npa), npa = 4-nitrophthalic acid] (3)

p-dimethylaminobenzaldehyde (14.9 mg, 0.1 mmol) was dissolved in 2 mL methanol. To this solution was added 4-nitrophthalic acid (21.1 mg, 0.10 mmol) in 15 mL methanol. Colorless block crystals were obtained after 20 days by slow evaporation of the solvent, the yield was 28 mg (77.71%, based on L). mp 127–128 °C. Elemental analysis: Calc. for $C_{17}H_{16}N_2O_7$ (360.32): C, 56.62; H, 4.44; N, 7.77. Found: C, 56.58; H, 4.37; N, 7.71. IR (KBr disc, cm^{-1}): 3547s(ν(OH)), 3170m, 3118m, 3067m, 2964m, 2872m, 1714s, 1667s(ν(C=O)), 1614m, 1568m, 1524s(ν_{as}(NO_2)), 1483m, 1441m, 1400m, 1360m, 1320s(ν_s(NO_2)), 1278s(ν(C–O)), 1231m, 1189m, 1147m, 1105m, 963m, 921m, 876m, 832m, 790m, 746m, 703m, 659m, 621m, 602m.

2.2.4. d. p-dimethylaminobenzaldehyde : (1,5-naphthalenedisulfonic acid) : $(NH_3)_2$ [NH_4 · (HL) · (nds^{2-}) · NH_3, nds$^-$ = 1,5-naphthalenedisulfonate] (4)

p-dimethylaminobenzaldehyde (14.9 mg, 0.1 mmol) and hexamethylenetetramine (14.4 mg, 0.1 mmol) was dissolved in 16 mL methanol. To this solution was added 1,5-naphthalenedisulfonic acid tetrahydrate (36 mg, 0.10 mmol) in 20 mL ethanol. Colorless block crystals were obtained after 16 days by slow evaporation of the solvent, the yield was 33 mg (69.98%, based on L). mp



Scheme 1. Molecular structures of the components mentioned in this work.