



Structural insights into salts and a salt polymorph of nitrogen containing small organic molecules

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ABSTRACT

Three salts and a salt polymorph were synthesized from N-heterocyclic aromatics and their complementary acids. The salts were obtained by solvent assisted grinding (SAG) method and their structure was obtained by X-ray diffraction method. The crystal packing for all salts is primarily stabilized via $N^+ - H \cdots O^-$, $N^+ - H \cdots O$, $N - H \cdots O^-$, $O - H \cdots O^-$, $O - H \cdots O$, and $N - H \cdots N$ hydrogen bonds. Thermal stability was characterized by differential scanning calorimetry and thermo-gravimetric analysis and the salt formation on account of bulk-grinding was confirmed by powder X-ray diffraction. The significant red-shift in the IR stretching frequency of hydroxyl and carboxyl functional groups depict the importance of intra and intermolecular hydrogen bonds.

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1. Introduction

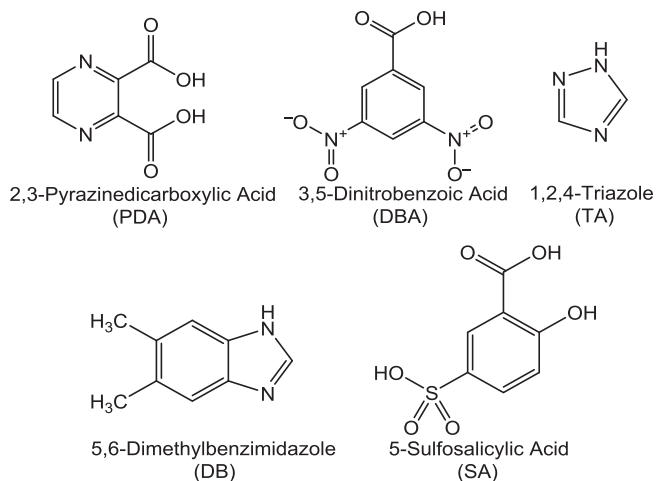
Organic co-crystals/salts and hydrates have gained significant interest in pharmaceutical industry and in molecular electronics [1,2]. Co-crystallization is a periodic three-dimensional self-assembling between molecules which is spontaneous and proceeds through a series of molecular recognition process. This process may be considered to be stabilized by the mutual interactions which can be either strong or weak in nature [3,4]. The co-crystallization method provides a path for the synthesis of desirable cocrystal/salt-based material because of the vast opportunity to tune the structural architecture using the principles of crystal engineering [5]. This has contributed extensively towards the understanding of the molecular geometry and different inter/intramolecular interactions which control crystal packing in co-crystals/salts. The scheme is so chosen that it allows to analyse the role and influence of weak interactions like $C - H \cdots O$, $C - H \cdots \pi$, $\pi \cdots \pi$, $lp \cdots \pi$ etc. in the presence of strong $N - H \cdots O$, $O - H \cdots O$, $N - H \cdots N$, and $O - H \cdots N$ hydrogen bonds in co-crystals/salts [6]. The strategy for designing

salts is based on non-covalent interactions (namely hydrogen bonding and van der Waals interactions) between donor and acceptor atoms present in the molecules. The formation of salt wherein the proton is completely transferred from the donor to the acceptor is of extreme interest on account of the conducting properties associated with such migration at long range in crystalline solids. This is of potential application in fuel cells, sensors and other areas [7–9].

Herein, we present the formation of three salts and a salt polymorph. These salts are prepared by Solvent Assisted Grinding method which is environmentally benign, cost effective, and easy to handle. The nitrogenous organic molecules that we have chosen for synthesis of salts are 1, 2, 4-triazole (TA) and 5, 6-dimethylbenzimidazole (DB) [Scheme 1] [10–15]. Due to presence of different hydrogen bonding sites, we have selected some complementary carboxylic acids, namely 2, 3-pyrazinedicarboxylic acid (PDA), 3, 5-dinitrobenzoic acid (DBA), 5-sulfosalicylic acid (SA) as potential cofomer for the synthesis of salts [Scheme 1]. The resulting products were reflected as new salts PDA-TA, DBA-DB-Form-1, DBA-DB-Form-2, and SA-DB, which were structurally characterized by single crystal X-ray diffraction (SCXRD), and also confirmed by a careful comparison of the powder X-ray diffraction (PXRD) patterns of the bulk salt with the simulated pattern,

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Scheme 1. The molecular structure of N-heterocyclic bases and acid cofomers employed in this study.

obtained from SCXRD data. This was further characterized by the observation of the melting characteristics obtained from differential scanning calorimetry (DSC).

2. Experimental section

2.1. Preparation of salts

All the parent compounds, whose molecular structures are drawn above in Scheme-1 for the study of salts were purchased from Sigma Aldrich. The salts were obtained by performing solvent assisted grinding, also known as liquid assisted grinding, through mechanical grinding of the two components (N-heterocyclic bases and acidic cofomers) using agate mortar and pestle. Initial experiments have been performed by taking 1:1 stoichiometric ratio of the solid components corresponding to the formation of salts. Grinding was carried out for a total time period of ~30–40 min with dropwise addition of MeOH solvent during each period of 10 min interval. The resulting powder was air dried and crystallized using HPLC grade solvent MeOH in 5.0 ml beakers and then kept at room temperature (~25 °C) for crystallization. The DBA-DB salt obtained from grinding experiments with MeOH which gave form-2 [DBA-DB bulk salt confirmed by PXRD] whereas, on consequent crystallization at room temperature (24 °C) in solvent acetone, crystals of form-1 were obtained. The resulting crystals were characterized structurally using SCXRD and the observed stoichiometric ratio corresponds to the stoichiometry of the starting materials. The powdered salts obtained after grinding in the corresponding stoichiometric ratio were used to perform further characterization (DSC, TGA, IR, and PXRD). The experimental powder patterns obtained from all powdered samples and the simulated PXRD patterns obtained from the data collected on the single crystals matched with each other.

2.2. Single crystal X-Ray diffraction (SCXRD)

X-ray diffraction data for all the obtained salts were collected on a Bruker APEX II Kappa CCD single crystal diffractometer equipped with a graphite monochromator (Mo K α radiation, $\lambda = 0.71073$ Å) at 100 K. Unit cell measurements, data collection, integration, scaling, and adsorption corrections were processed using Bruker APEX II software [16]. The data were corrected for absorption by the multiscan method implemented in SADABS [17]. The salt structures

were solved by direct methods implemented in SHELXS-97 [18] and refined with full-matrix least squares method using SHELXS-2014 [19], present in the programme suite WinGX [20]. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms bound to carbon, oxygen, and nitrogen were placed at their idealized positions [X-ray distances] where the residual electron density was observed during refinement. Intermolecular interactions were analysed using PARST [21] and PLATON [22]. The packing diagrams of all salts were analysed using Mercury 3.6 software [23].

2.3. Powder X-ray diffraction (PXRD)

PXRD patterns of all salts were collected on a PANalytical Empyrean X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å). Bulk powder of each sample was packed in a silica sample holder and measured by a continuous scan between 5 and 50° in 2θ with step size of 0.013103°. PXRD profile fitting refinement was performed with JANA 2006 [24] for all the three-bulk salts with the lattice parameters obtained from SCXRD.

3. Results and discussion

All the salts obtained show unique diffraction pattern in comparison to the starting material and are shown in Fig. 1. The experimental PXRD pattern of the formation of new solid phases has been confirmed by matching PXRD pattern with simulated SCXRD. However, the bulk PXRD pattern of DBA-DB has been confirmed by matching PXRD pattern with DBA-DB-Form-2 (SCXRD) simulated. Moreover, the profile fitting results also suggests that the bulk powder is mainly present as salts [ESI F-1].

Differential Scanning Calorimetry measures [ESI S-1] the melting point (MP) and/or decomposition temperature with the desired accuracy for a solid compound. The heating and cooling of all four salts in DSC are shown in Fig. 2 between the temperature range 50–365 °C and the melting temperature of all the salts and the parent components are given in ESI T-3. The DSC thermogram of the PDA-TA salt showed an endotherm at 170 °C which is also in between the melting points corresponding to the two parent components [The MP of PDA at 188 °C and MP of TA at 120 °C]. The DBA-DB salts exhibit a sharp melting endotherm at 214 °C (Form 1) and 213 °C (Form 2) which are also thermally more stable than its individual parent components [The MP of DBA at 205 °C and MP of DB at 202 °C]. The SA-DB salt showed two small endotherms at 214 °C and 237 °C before complete melting at 327 °C which indicates the existence of possible phase transition (to be investigated in a future study) before melting. The melting endotherm at higher temperature shows the high thermal stability of SA-DB over its parent components. The salt SA-DB does not exhibit any solidification peak during the cooling run of DSC and this was confirmed by TGA analysis. The TGA curve is showing significant mass loss during melting of the sample due to decomposition or vaporization [ESI F-2]. Moreover, the FT-IR spectroscopy is a useful technique to characterize and distinguish salts from its parent compounds [ESI S-2, F-3].

The packing diagram illustrates the presence of strong (N⁺–H \cdots O[−], N⁺–H \cdots O, N–H \cdots O[−], O–H \cdots O[−], O–H \cdots O, and N–H \cdots N hydrogen bonds) and weak interactions (C–H \cdots O, C–H \cdots O[−], C–H \cdots π , $\pi\cdots\pi$, $lp\cdots\pi$ etc.) present in the crystal which significantly influences the formation of crystals. All the packing interactions with their respective symmetry, distance and angles are provided in ESI T-2. The ORTEP of the asymmetric unit of all the obtained salts with intra- and intermolecular interactions are shown in Fig. 3.

The 1:2 salt of PDA-TA crystallizes in a centrosymmetric monoclinic space group $P2_1/c$ with $Z=4$ (ESI T-1). In the

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