Salt or co-crystal ambivalent systems

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The acid-base equilibrium in the solid state is difficult to grasp and even more difficult to predict. Organic molecules in multicomponent materials can crystallize in their neutral forms (as in co-crystals) or as protonated or deprotonated ions (in salts). There are also many structures where one component can be present in both these forms (e.g., barbituric acid cytosine water <1:1^- /1^+:1/2> [1]). For such systems, structure prediction calculations or even conventional nomenclature may be very challenging. The ultimate distinction of such forms is based on locating of all hydrogen atoms, for example, by neutron diffraction or NMR studies. In some cases, however, it is possible to distinguish neutral and ionic forms by their different spectroscopic (UV-Vis, IR) characteristics.

Here we present two systems, two pairs of organic compounds that can form a crystal structure either as a salt or as a co-crystal. We show the synthetic approach yielding both types of compounds (salt or co-crystal) as well as structural and spectroscopic characteristics that demonstrate the presence of certain forms (ionic or neutral). The investigations are supported by Hirshfeld surfaces [2], NCI calculations [3] and electron density topological analysis [4]. We also applied the name system proposed by us [1] to all products for easier identification.

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