



Crystal polymorphism of sodium benzene-1,3-dicarboxy-5-sulfonate monohydrate

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ABSTRACT

Two different crystal forms of sodium 5-sulfoisophthalate monohydrate have been found and structurally characterized by X-ray diffraction and FT-IR spectroscopic methods. Polymorph **I** is monoclinic, $P2_1/n$, and polymorph **II** is triclinic, $P1$. The analysis of the crystal structures reveals that the connectivity patterns in both polymorphs are different. Two of the sulfonate oxygen atoms (sites) interchange their function and are used to accept two hydrogen bonds in the first polymorph or to donate two bonds toward the metal ion in the second polymorph. Consequently the hydrogen-bonded anionic subnetwork reduces from two-dimensional in **I** to one-dimensional in **II**. The FT-IR spectra correlate well with the structural peculiarities of the crystals and reflect the variation of hydrogen-bonded networks in them.

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1. Introduction

Crystal polymorphism reflects the ability of the same molecular aggregate (salt, cocrystal, solvate) to crystallize in more than one crystal structure [1,2]. This phenomenon deserves special consideration in solid-state chemistry research, since distinct polymorphic forms usually display different physical and chemical properties, which might have serious implications on their material function as dyes, pigments, explosives, agrochemicals, food additives, etc. [3]. On the other hand, supramolecular isomerism, defined as the existence of more than one type of network superstructure for the same molecular building blocks in polymeric network structures, is closely related to polymorphism in crystalline solids [4]. In many cases supramolecular isomerism is effected by the same molecular components that generate different supramolecular synthons and can be considered as synonymous with polymorphism. In this context polymorphism is particularly important and ubiquitous in pharmaceuticals and is treated with special care by the pharmaceutical industry since the bioavailability and the physical properties (melting point, solubility, density, conductivity, dissolution rate, etc.) of the drugs crucially depend upon the crystal packing [5,6]. While the above phenomena are receiving increasing attention from a scientific perspective [7–12] the relationship between crystal nucleation, crystal growth, supramolecular isomerism and crystal polymorphism still represents a fundamental scientific challenge [13,14].

Study of crystal structures of polymorphic forms can provide a valuable information about preferences and compromises between intermolecular interactions and packing forces, competing for structure formation in different environmental conditions. Deep understanding of these interrelations is crucial to crystal design and synthesis of novel materials. Recently, the inorganic–organic hybrids have gained special attention due to their applicable properties like porosity, catalytic activity, ion exchange, luminescence, optical non-linearity, conductivity, magnetism, and spin-transition behavior [15]. An unlimited number of coordination compounds with different functionalities can be prepared considering the chemical nature and the electronic properties of the metal ions, their coordination geometry and preferences toward specific ligand sites. The role of linkers between the metal centers in these compounds is usually played by a multifunctional organic ligands, able to adopt variable coordination modes and bind more than one metal center. However, such compounds are characterized by enhanced competition between the ligand's functional sites for hydrogen bonding and/or coordination bond formation, which may lead to crystal polymorphism. Even so, the conditions, that affect the formation of a particular polymorph, are still a result of a serendipity rather than a completely controlled process. While polymorphism in organic substances has been studied for long time [14,16–18], the interest in the analogous behavior of inorganic and metalloorganic materials has arisen more recently [19–22]. The significance of hydrogen bonding and its variability in polymorphic organic crystal structures has been demonstrated by Allen [23]. Detailed structural comparisons revealed that a large majority of hydrogen bonds are persisting in moving from one polymorphic form to another and are energetically crucial to

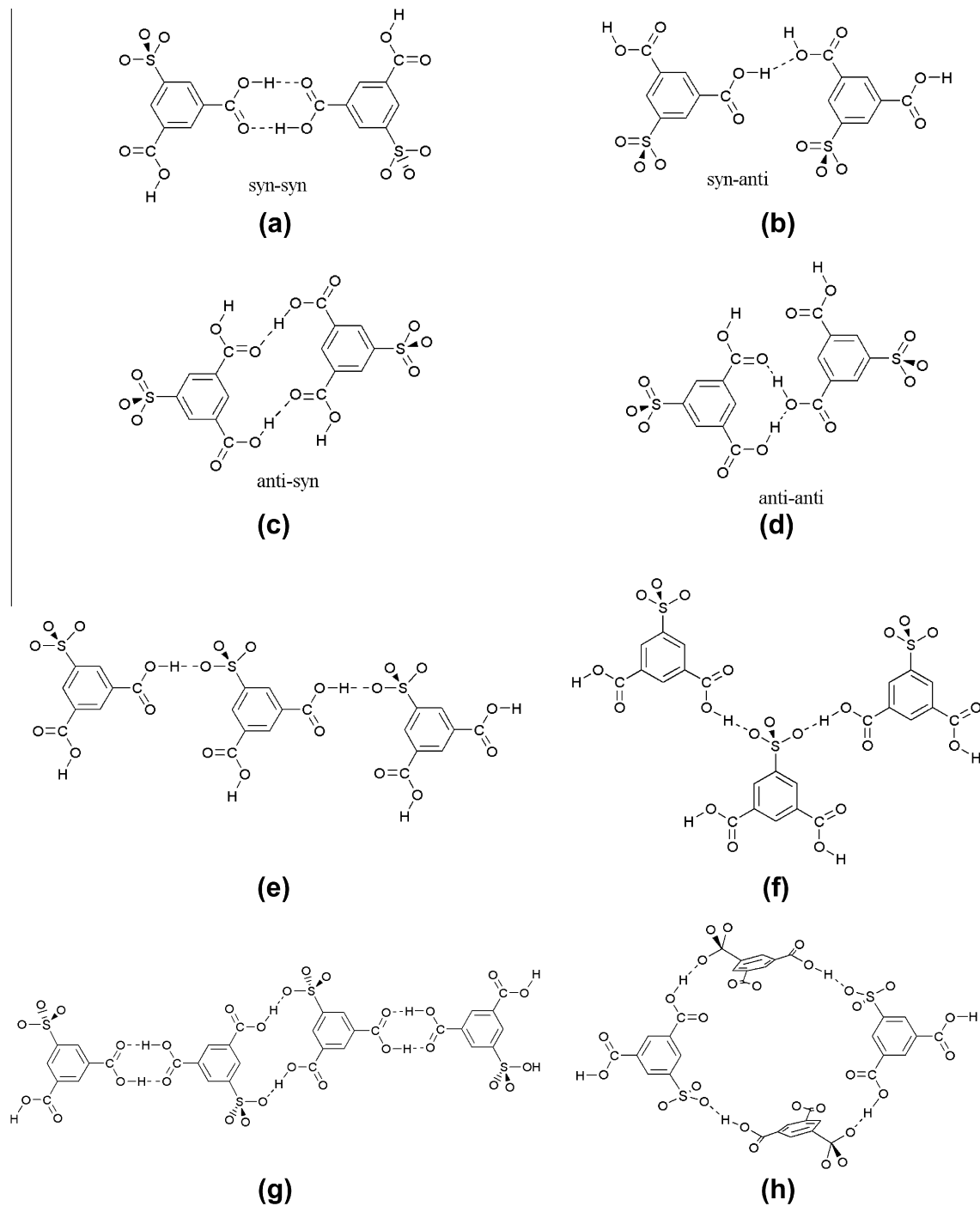
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structural stability. However, the proportion of the persistent hydrogen bonds decreases with the amount of hydrogen bond present, which implies the competition between donors and acceptors as another crucial factor. Only 6% [13 structures out of 882 polymorphic structures from the Cambridge Structural Database (CSD, Version 5.31)] [24] were shown to display completely different hydrogen bonding (i.e. no persistent hydrogen bonding between pair of polymorphs) and they were predominantly structures, in which two acceptor groups compete for a lone donor.

The 5-sulfoisophthalic acid is broadly used as ligand to construct transition metal coordination polymers [25,26]. The topology of the functional groups allows for variable connectivity

patterns within the same composition rate, which may lead to supramolecular isomerism and structural polymorphism. Nonetheless, the crystal structure of the acid itself is not known, and the reported structure of hydronium sulfoisophthalate [27] is strongly disordered. For reasons of a low stability issued from the very low pK_a of the sulfonic group, 5-sulfoisophthalic acid is commercially available as sodium salt. The deficiency of hydrogen bond donors in the monoanion makes the functional groups very competitive for hydrogen-bond formation. On the other hand the sulfonate and carboxylic oxygen atoms potentially act as electron donors to the sodium ion forming flexible metallosupramolecular networks. Some of the possible carboxylic-carboxylic and carbox-



Scheme 1. Possible hydrogen-bonded motifs and connectivity patterns of 5-sulfoisophthalic acid monoanion.

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