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Dicarboxylic acids, $HOOC–(CH2)_n–COOH$, are interesting compounds from the structural point of view [1]. A very long one-dimensional chain can be obtained through hydrogen bond formation at both ends of the molecule. These compounds configure layered structures in the solid state, as well as most of the polymorphic phases of long-chain compounds, such as *n*-alkanes, *n*-alcohols, and *n*-fatty acids. Dicarboxylic acids exhibit interesting thermal properties and a high enthalpy of melting that make them potential candidates for their use in the field of thermal protection and energy storage.

Dimorphism was prevalent in odd carbon members of dicarboxylic acids while one form is only present for even members: α form $P2_1/c$ with Z=4 and β form C2/c with Z=4. High-quality x-ray powder diffraction analyses of pentadecanedioic acid ($C_{15}H_{28}O_4$) have been carried as a function of temperature. A new form, called γ has been observed just before melting: γ form C2/c with Z=4 at 383K.

The packing arrangement of the carboxyl groups at both end of the chain is different in the three forms. From the structural point of view for γ form the distance interlayer is intermediate between α and β distances. Crystal structure of the pentadecanedioic acid is presented.

The carboxyl's group in α form shows two different angles with middle plain of the chain. The packing arrangement of α and γ forms are radically different even if the molecular conformation are *cis* in both cases.

A reversible transition from β form to γ form was observed before melting. Slurry experiments indicate that β is the most stable form at room temperature.

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Keywords: Polymorphism, hydrogen bonds, dicarboxylic acids

FA4-MS35-P08

Polymorphism as an Obstacle for the Applicability of Methoxy-substituted Distyrylpyrazines.

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Distyrylpyrazines (DSPs) are a promising class of organic semiconductors because of their superior electronic properties, such as a highly efficient emission of light and a high electron affinity [1]. Since the supramolecular structure is of great importance when rationalizing and tuning these interesting properties for the materials' use in devices such as organic LEDs, five methoxy-substituted distyrylpyrazines were synthesized and their solid-state structures were investigated; (*E*,*E*)-2,5-bis[2-(4-methoxyphenyl)ethenyl]pyrazine has already been subjected to a synchrotron study by Scaccianoce *et al*. [2]. For (*E*,*E*)-2,5-bis[2-(3,4-dimethoxyphenyl)ethenyl]-pyrazine, (*E*,*E*)-2,5-bis[2-(3,4,5-methoxyphenyl)ethenyl]pyrazine and (*E*,*E*)-2,5-bis[2-(2,4,6-methoxyphenyl)ethenyl]pyrazine suitable crystals were grown and their supramolecular structures were analyzed. The methoxy groups are responsible for the majority of the interactions that determine the crystal packing – mostly through mutual weak hydrogen bonds and CH…π interactions – although the pyrazine moiety also acts as an acceptor of weak hydrogen bonds and is involved in π...π interactions. The structures are compared mutually as well as to their distyrylbenzene counterparts. For each of the two former compounds, two polymorphs have been found. One polymorph of (*E*,*E*)-2,5-bis[2-(3,4,5-methoxyphenyl)-ethenyl]pyrazine proved to be light sensitive and turned out to be a good candidate for a solid-state polymerization reaction.

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Keywords: organic semiconductors, crystal packing, polymorphism

FA4-MS35-P09

Conformational flexibility of chlorpropamide molecule can generate new polymorph.

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Polimorphism of drugs is of utmost importance both for pharmaceutical industry and medicine. Various molecules behave in polymorphs in different ways. For example, polymorphs of sulphathiazole differ in the framework of hydrogen bonds between molecules with similar conformations [1]. In chlorpropamide polymorphs, on the contrary, the hydrogen bonds are very similar, but the molecules have different conformations [2, 3]. There is a correlation between conformation of of chlorpropamide molecule in a polymorph and its density.

We found a new phase transition of the high-temperature ε-chlorpropamide (metastable under normal conditions) into a new polymorph on cooling [4]. The transition is reversible. Structure of the new polymorph was solved from the single-crystal X-ray diffraction data. Space group symmetry of the polymorphs is the same, but the conformation of the molecule changes, resulting in the step-wise change in the density of chlorpropamide. Surprisingly, X-ray powder diffraction pattern of the new polymorph turned out to be nearly identical to that of stable α-chlorpropamide in the range of small angles.

Comparing the structures of chlorpropamide polymorphs, we came to the conclusion that the new polymorph is a transient point in the irreversible transition ε → α. The state is frozen because at low temperatures molecules cannot change their conformation completely, so that every second molecular ribbon would be inverted, to give the α-form. Only the alkyl tails of the molecules turn at about 180°, but the molecular packing of the initial ε-form is preserved. Probably, this is an example of a new general mechanism, when the freezing of one or several degrees of freedom in conformational movement of a molecule can induce polymorphic transition into a new metastable form.

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Keywords: phase transitions in solids, drug polymorphism, low-temperature structure

FA4-MS35-P10

Unprecedented solid-state chemical reaction – from($C_3N_2H_5)_3SbBr_6{\cdot}H_2O$ to $(C_3N_2H_5)_5Sb_2Br_{11}$; polimorphism of substrate and products.

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A novel organic-inorganic hybrid material, tris(imidazolium) hexabromoantimonate(III) hydrate, $(C_3N_2H_5)_3SbBr_6{\cdot}H_2O$ (abbreviated as TIBA) undergoes an unprecedented in situ solid-state chemical reaction above 328 K:

$$2(C_3N_2H_5)_3SbBr_6 \cdot H_2O_{(S)} \rightarrow (C_3N_2H_5)_5Sb_2Br_{11(S)} + (C_3N_2H_5)Br_{(S)} + H_2O_{(L)}$$

that leads to multiphase crystallites dominated by ferroelectric $(C_3N_2H_5)_5Sb_2Br_{11}$.

The room temperatutre structure of TIBA consists of discrete SbB_6^- anions, disordered imidazolium cations, and water molecules forming a 3D array of hydrogen bonds. The solid-state chemical reaction leads from $[SbBr_6]^{3-}$ to $[Sb_2Br_{11}]^{5-}$ chemical stoichiometry of anions. The creation of ferroelectric[1] crystallites – $(C_3N_2H_5)_5Sb_2Br_{11}$ – in an “annealed” sample of $(C_3N_2H_5)_3SbBr_6{\cdot}H_2O$ is confirmed by X-ray diffraction phase analysis, dielectric spectroscopy, and pyroelectric measurements. The dielectric response of the electric permittivity and the critical slowing down of the process observed near 140 K in the “annealed” sample of TIBA are treated as a “fingerprint” of a neat $(C_3N_2H_5)_5Sb_2Br_{11}$ ferroelectric. Furthermore, TIBA undergoes isostructural discontinuous phase transition at 212/221 K (cooling-heating) ($P2_1/c \leftrightarrow P2_1/c$). The phase transition mechanism is characterized by two contributions: an order-disorder (cationic substructure) and a displacive one (water molecules).

Crystal structure of two polimorphs of second product of reaction: $(C_3N_2H_5)Br$ that crystallizes from water solution below 273 K are also presented along with the order-disorder phase transition mechanism.

[1] A. Piecha, A. Pietraszko, G. Bator, R. Jakubas *J. Sol. State Chem.* 2008, 181, 1155-1166

Keywords: ferroelectric, halogenoantimonates(III), phase transitions

FA4-MS35-P11

Topotactic phase transformation of 4H-$Cu_yTa_{1.10}S_2$ into 4H-$Ta_{1.10}S_2$.

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Tantalum forms a series of polytypic ternary sulfides of general composition $Cu_yTa_{1+x}S_2$.[1,2] The layered-type phases are good electronic and ionic conductors. The mobile Cu ions (y) and excess Ta (x) are inserted in spatially separated van der Waals gaps of a layered TaS_2 host structure the type of which depends upon x, y and T. Oxidative deintercalation of Cu with iodine affords new polymorphs of $Ta_{1+x}S_2$. The new polymorphs differ from those accessible from the elements at temperatures above 1250 K by higher order staging, i.e. excess Ta (x) is not found in all van der Waals gaps what confers lubricant-like properties to these Ta-rich disulfides. Such polytypes can be classified by a code nN in which n counts the number of TaS_2 slabs in the repeat unit and N refers to the lattice symmetry, e.g., H for hexagonal. Here, we present the structure of a ternary 4H polytype that - upon progressive deintercalation of Cu at ambient temperature - topotactically transforms into a differing 4H polytype. The transition is reflected in divergent X-ray diffractograms showing an offset of the reflections and a drastic change in the intensity modulation of h0l zonal reflections. Structural features of the two polymorphs derived from the distinctive intensity modulations are highlighted and discussed in the light of known polymorphs. Electronic and mechanistic aspects of the transformation are discussed.

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Keywords: transition metal dichalcogenides, polytypes, topotactic phase transformation

FA4-MS35-P12

Elucidation of Crystallization Processes – The Polymorphism of Nifedipine.

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The crystallization process of the polymorphic compound nifedipine (4-(2-nitrophenyl)-2,6-dimethyl-3,5-dicarbomethoxy-1,4-dihydropyridine, $C_{17}H_{18}N_2O_6$) using different solvents was investigated *in situ* by X-ray diffraction and Raman spectroscopy. In medical treatments, nifedipine acts as dihydropyridine calcium antagonist. Despite the pharmaceutical importance, the wide use of the substance, as well as knowledge of its polymorphism, the crystal structures of most of the nifedipine polymorphs still remain unknown. To investigate the formation of intermediate phases, which are kinetically favored and formed preferentially under fast evaporation conditions, an acoustic levitator was employed as sample environment for the combination of time-resolved X-