

**MS24-P3** Design of Crystal  $Z'=2$  Structures: Obtaining, Search for Polymorphs. Olga Lodochnikova, A.E. Arbutov  
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Within our preceding work, a rich experimental material on the crystallization of compounds with  $Z'=2$  was collected. A series of structurally similar compounds being stably crystallized with  $Z'=2$  was obtained, the causes of that phenomenon were analyzed. Various methods using different crystal growth rates and different solvents were tested, which, in some cases, helped detect polymorphs with different  $Z'$ . In some cases, the formation of  $Z'>1$  structure results from the too fast crystal nucleus growth rate – we found this in a new  $Z' = 3$  crystal modification of methimazole (MIMT, 1-methyl-3H-imidazole-2-thione). In slow MIMT depositing, a known triclinic  $Z'=2$  modification is produced; in very fast solvent evaporating, we found some traces of monoclinic  $Z' = 3$  modification. In the triclinic modification, two independent molecules form a dimer through NH ... S hydrogen bonds, the mutual arrangement of molecules being nearly perpendicular, while similar dimer associates are planar in a monoclinic structures. Two 3-pyrroline-2-one-based sulfide modifications ( $Z'=2$  and  $Z'=1$ ) represent an example of fast and slow crystallization, respectively; in a  $Z'=2$  structure, stronger hydrogen bonds are found, while packing is less dense. Very interesting and nontrivial results were obtained for a number of chiral (enantiopure) structures. The symmetric-synthon-chiral-fragment-type  $Z'=2$  chiral structures were developed. Thus, three structurally similar, noncentrosymmetric (chiral)  $Z'=2$  structures were obtained, which represent a rare example of associates fully asymmetric both in the crystal and in the solution and in gas phase due to their specific construction: the cocrystal of diastereomeric  $\beta$ -hydroxy sulfoxides and the relevant crystal of  $\beta$ -hydroxysulfone based on natural (-) $\beta$ -pinene. In both cases, a  $\beta$ -hydroxysulfoxide (sulfone) fragment associated through S=O ... HO interactions with the identical fragment of opposite configuration serves as a centrosymmetric supramolecular synthon, the pinene skeleton of a natural configuration being present as a “side” chiral fragment. The sulfur atoms of isomeric sulfoxides initially had the opposite chirality, while the sulfur atom within the sulfone group was stereochemically transformed during forming a dimer, namely – two independent molecules are involved in forming hydrogen bonds by different oxygen atoms: *pro-S* and *pro-R*. That is, the sulfone sulfur atom in the pseudosymmetric dimer actually becomes stereogenic again (with different configurations for molecules A and B); and thus independent molecules in the sulfone dimer represent two different diastereomeric forms. Three structurally similar  $Z'=2$  crystal structures based on hybrid pyridinoidhydrazone-fragment-containing isosteviol compounds were obtained, as well. Tetracyclic skeleton conformations are identical in molecules A and B, while the independent molecules' pyridinoidhydrazone fragment is in mirror-symmetric conformations. Through these conformational shifts, a local pseudosymmetry element, the glide plane, is formed in the crystal. Chiral diterpene fragment cannot perform such a symmetry operation, which causes the inclusion of the “extra” molecule into the cell.

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**Keywords:** polymorphs;  $Z'=2$  structures; asymmetric dimer

**MS24-P4** The Exhibition of Isomorphism in Alkylammonium Halides with Rac-1,1'-Bi-2-naphthol  
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Although, the unit cell dimensions of both 1:1 complexes of hexadecyltrimethylammonium bromide and chloride adducts of rac-1,1'-Bi-2-naphthol (hereafter, 16TAB/BNP) and 16TAC/BNP, respectively) are different from each other, the pattern of host-guest interactions as well as packing pattern observed are similar to each other, and the replacement of the halide ion from Cl to Br does not change the molecular arrangement and hydrogen bonding network of the host and guest molecules. The monovalent halogen atoms differing only in size or volume do not develop different intermolecular hydrogen bonding network and the size or volume of the halide anions hardly effect any change in molecular packing. Consequently, functional isomorphism simultaneously occurs. The rigid and large naphthol moieties of BNP molecule seem to play significant role to generation of functional isomorphism in the 16TAB/BNP and 16TAC/BNP crystal complexes. The arrangement of the rigid naphthol moieties also play significant role in formation of C-H... $\pi$  interactions, hydrophobic interactions as well as common hydrogen bonding network that stabilize the crystal structures.

**Keywords:** hydrogen bonding, supramolecular chemistry, isomorphous structures