

porphyrin complexes as sensors of spermine is reported.

[1] a) Di Costanzo L., et al., *Angew. Chem. Int. Ed. Engl.*, 2001, **40**, 4245; b) Moschetto A., et al., *J. Am. Chem. Soc.*, 2002, **124**, 14536.

Keywords: non covalent assembly, porphyrins, sensors

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Strychnine and Brucine Self-Assemblies: Structures and Properties

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Strychnine and brucine self-assemblies play an important role in molecular recognition during racemic resolution by fractional resolution [1]. Different strychnine and brucine self-assemblies are accountable for their "quasi-enantiomeric" behaviour in some cases of racemic resolution [2], [3]. Change of alkaloid self-assemblies can lead to change of recognition sequence of resolved enantiomers [3].

Controlling time of crystallization, they can play an important role for determination of various sizes and topologies water cluster.

Surfaces of the strychnine and brucine self-assemblies have determined their various arrangement of chloride anions, that lead to destruction by redox reaction of only brucine molecules. The brucine sheet determines hydrogen bonds network, where chloride anion is linked to chair water hexamer (similar water-chloride anion structure is observed for ionization of HCl on ice at low temperature leading to formation of polar stratospheric clouds and further to ozone holes). Bilayer sheet of strychnine, which determines helical arrangement of chloride anions and water molecules into channels, preserves strychnine molecules from destruction.

[1] Jacques J., Collet A., Wilen S.H., *Enantiomers, Racemates and Resolutions*, Ed.: Krieger Publishing Company, Malabar, Florida, 1991. [2] Gould R.O., Walkinshaw M.D., *J. Am. Chem. Soc.*, 1984, **106**, 7840. [3] Bialonska A., Ciunik Z., *CrystEngComm.*, 2004, **6**, 276.

Keywords: supramolecular assemblies, recognition molecular, alkaloid structures

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Polymorphism in an Anti-implantation Agent: A Subtle Interplay of Weak Intermolecular Interactions

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Polymorphism is defined as a solid crystalline phase of a given compound resulting from the possibility of at least two crystalline arrangements of that compound in the solid state. Substituted Indol-4-ones are anti-fertility agents and have been used for the inhibition of implantation activity in rats. Polymorphism in 1-(4-fluorophenyl)-3,6,6-trimethyl-2-phenyl-1, 5, 6, 7-tetrahydro-4H-indol-4-one based on solvent variation and the subsequent changes in intermolecular interactions is discussed.

A complete analysis has been made in terms of morphology, Single Crystal Structure, Powder X-Ray diffraction, Non Linear Optical Activity (NLO) and Differential Scanning Calorimetry. Polymorph (P1) crystallizes from a solution in Dichloromethane/Hexane in a monoclinic space group, non-centrosymmetric P2₁ (as plates) whereas the second polymorph (P2) crystallizes from a solution in EtOH/Acetone in a tetragonal space group, centrosymmetric P4₂/n (as blocks).¹ C-H...O and C-H... π intermolecular interactions forming chains stabilize P1 while P2 is stabilized by C-H...O and C-H... π dimers and a not so common F...F intermolecular interaction.

[1] Chopra D., Nagarajan K., Guru Row T.N., *Cryst. Growth & Design*, 2005, in press.

Keywords: polymorphism, intermolecular interactions, NLO

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Morphotropism: A Link between the Similarity and Polymorphism of Organic Crystals

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Kitaigorodskii, in *Organic Chemical Crystallography* (1961) – applied a term "morphotropic step" by the aid of which nonisomorphous crystals of chemically similar molecules may keep their close packing coefficient around 0.6-0.7. However, the essence of the phenomenon remained unanswered. Since 2000, an ongoing analysis of the supramolecular self-assembly of disubstituted cycloalkanes led to the discovery of nine packing patterns built up by hydrogen bonded homo- and heterochiral chains of racemic molecules, associated either antiparallel or parallel array [1]. Since every pattern is represented at least by one crystal structure (solved in Budapest), the chemical similarity and crystallographic properties of these crystals led to a recognition that these distinct patterns, by pairs, mostly differ only by one non-crystallographic turn of motifs forming a pattern, or the whole pattern turns through 180°. A proper definition of the word *morphotropism* helped to identify non-crystallographic turns with the morphotropic steps left unexplained by A.I.K. It has been shown that stereoisomers, in particular, are related by a morphotropic step, which may also play a bridge between isostructural crystals, and occasionally hallmarks the enantiotropic polymorphism of molecules. While a non-crystallographic turn between isostructures and stereoisomers is imaginary, polymorphs are linked by real, solvent mediated turns of the motifs.

[1] Kálmán A., Fábrián L., Argay Gy., Bernáth G. Cs., Gyarmati Zs., *Acta Cryst.*, 2004, **B60**, 755, and references therein.

Keywords: isostructurality, morphotropism, polymorphism

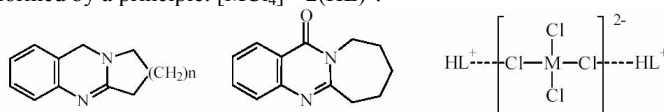
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The Crystal Structural Variety of Tricyclic Quinazoline Salts

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Quinazoline type of alkaloids are widely distributed in plants and induce a wide spectrum of biological activity. Usually they are used in applied medicine in a form of salts. For this reason their structures have practical importance. Hydrochlorides of tricyclic 3,4-dihydroquinazolines (L) easily form complexes with chlorides of metals (M= Zn, Co, Cu). Thus crystallographic independent unit is formed by a principle: $[MCl_4]^{2-} \cdot 2(HL)^+$:



In salt complex of alkaloid (n=3) with ZnCl₄ two polymorphic crystals have been found. Crystallographic independent unit forms a skeleton. Change in geometry of this skeleton can give rise to polymorphism. Hydrochlorides of alkaloids with n=1-3 are dihydrates. Here the aqua-systems are stabilized in crystal by hydrogen and the donor – acceptor interactions.

Similar skeletons form complex chlorides of 2,3-pentamethylen-3,4-dihydroquinazolone-4 with chlorides of metals. But this skeleton includes 3 water molecules. Crystals of hydrochlorides, depending on a crystallization condition, can be hydrates (inclusion 4.5 water molecules). However, these crystals after recrystallization transform into stable hydrochlorides.

Keywords: alkaloid structures, supramolecular assemblies, inclusion phenomena

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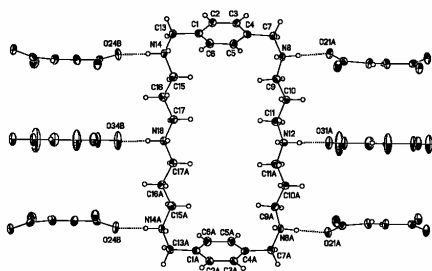
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Macrocyclic Amines and their Adducts with Acids

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Conformations of the macrocyclic amine in the structures of N-methylated derivative (1) and of the adduct with fumaric acid (2) are different. In (2) the cation is hexaprotonated and occupies a special position in a plane of symmetry. The ionic synthon is built from one hexaprotonated macrocyclic cation and six fumaric anions. Each anion is linked to three neighbouring cations and to water molecules by strong hydrogen bonds N⁺-H...O thus generating one-dimensional supramolecular ribbons.



The ionic synthon of (2)

Keywords: macrocyclic amines, fumaric acid adduct of, one-dimensional supramolecular ribbons

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Calix[4]dihydroquinone Units as Building Blocks in Supramolecular Chemistry

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In the last years our group has been exploiting calixarene molecules bearing quinone and hydroquinone moieties to form supramolecular networks based on hydrogen bonds and charge transfer interactions. We have prepared and characterized both proximal and distal calix[4]dihydroquinone derivatives, whose molecular self-assembly properties will be discussed in connection with the molecular structure of the building blocks.

The proximal *p*-*tert*-butylcalix[4]arene dihydroquinone derivative forms cubic crystals by an interesting interplay of H-bond and van der Waals-like interactions and is characterized by the simultaneous existence of water channels and unoccupied lattice voids of ca. 1400 Å³. Interestingly the supramolecular framework is preserved after removal of channel water molecules under vacuum at 50°C [1]. *p*-*H*-1,3-calix[4]arene dihydroquinone presents two polymorph structures: one is formed by alternate layers of crystallographically independent calixarene molecules, the second one is constituted by calixarene self-inclusion trimers connected each other by two water molecules. *p*-*H*-1,2-calix[4]arene dihydroquinone crystallizes in a bilayer type structure.

[1] Tedesco C., Immediata I., Gregoli L., Vitagliano L., Immirzi A., Neri P., submitted.

Keywords: calixarenes, supramolecular assemblies, nanotechnology

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Molecular and Crystal Structure of Crown Ethers Containing Biphenyl Fragment

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X-ray diffraction study of dibenzo-14-crown-4, dibenzo-17-crown-5, dibenzo-20-crown-6 and tetrabenzo-24-crown-8 reveals unexpected independence of conformation of biphenyl fragment from size and conformation of macrocycle. Comparison of geometry of this fragment in isolated biphenyl, its ortho-dimethoxy derivative and crown ethers demonstrates that angle between two aromatic rings is determined by intramolecular repulsion between the oxygen atoms in ortho position of benzene ring and steric interactions of the C-H fragment of aromatic ring and nearest methylene group. Analysis of electron density distribution reveals the presence of numerous intramolecular C-H...O hydrogen bonds which may influence conformation of macrocycle. Crystal packing of crown ethers is determined by competition between trends to parallel arrangements of aromatic rings and aliphatic macrocycles. In the case of dibenzo-14-crown-4 benzene rings form stacks along (1 0 0) direction. Increase of macrocycle size results in parallel arrangement of aliphatic fragments. This leads to formation of cavities and channels in the crystal phase.

Keywords: organic molecular structure, crown ethers, crystal structure analysis

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Experimental and Theoretical Evaluation of N-H...O Hydrogen Bonds in Alkylamine Oxalate Crystals

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Design of new materials possessing interesting structure and properties has become an important area in organic crystal engineering. This strategy is based on existence the hydrogen bond interactions between molecules in crystals [1]. Dicarboxylic acids generally interact through intermolecular hydrogen-bonding to form the linear chains. This is the reason why these molecules has been recently used as new building block in crystal engineering [2].

Due to this development we are interested in studying the hydrogen-bonded supramolecular systems of oxalic acid and alkylamines. Oxalates of *t*-butylamine, *n*-ethylamine, *n*-diethylamine and *n*-ethyldimethylamine has been obtained and characterized by X-ray diffraction method, IR and quantum-mechanical calculations. An examination of the crystal structure of these compounds indicated two distinct types of hydrogen bond patterns, involving linear chains of hydrogen bonded monohydrogen oxalate anions and isolated oxalate anions surrounded by the monoprotonated *t*-butylamine cations. The quantum-mechanical calculations were performed to optimize geometries of complexes linked by N-H...O using the Gaussian 98 suite of programs [3].

[1] Desiraju G.R., *Acc. Chem. Res.*, 2002, **35**, 565. [2] Vaidyanathan R., Natarajan S., Rao C.R.N., *J. Mol. Struct.*, 2002, **608**, 123. [3] Gaussian 98, Revision A.7, Frisch M.J., et. al., *Gaussian, Inc., Pittsburgh PA*, 1998.

Keywords: alkylamine oxalate, hydrogen bonds, ab-initio calculation

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Extended Hydrogen Bond Patterns in Small Molecule Crystal Structures: A CSD Study

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A search algorithm, 3DSEARCH¹, is used to identify extended hydrogen bond patterns in a set of small molecule crystal structures obtained from the Cambridge Structural Database. Searches are performed to identify the frequency of occurrence of various classes of 1-D tape and 2-D sheet motif that are composed of arrangements of strong inter-molecular hydrogen bonds. The 'R2 tape', 'R4 sheet' and the 'R2R6 sheet' patterns are found to be the most common out of the types considered (see Figure 1). An R4 sheet, for example, is composed of hydrogen bond ring motifs that span 4 molecules.