

were synthesized and their crystal structures were determined. Unexpectedly all such molecules form interlocked *Piedfort*-associates. Thus the two superposed molecules of a *Piedfort*-unit serve as supramolecular *synthon*[1]. We can also clearly see *intramolecular halogen-halogen interactions* which are developed at the external surface of the *Piedfort*-pair.

The effect of the halogen atom on the *Piedfort* stacking distances and the dimensions of the halogen *synthon* will be described in details. The authors acknowledge *Hungarian Scientific Research Fund* (OTKA grants T042642).

[1] Czugler M., Weber E., Párkányi L., Korkas P.P., Bombicz P., *Chem. Eur. J.*, 2003, **9**, 3741-3747.

Keywords: *Piedfort association, halogen-halogen interaction, supramolecular chemistry*

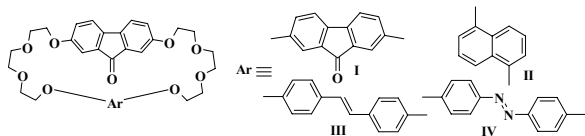
P.06.06.2

Acta Cryst. (2005). A61, C283

Crystal Structures of Some Representatives of the Fluorenonocrownophanes

Mark Botoshansky^a, Yurii Simonov^b, Marina Fonari^b, Nikolay Lukyanenko^c, Tatiana Kirichenko^c, Alexander Lyapunov^c, ^a*Department of Chemistry Technion-Israel Institute of Technology, Haifa, Israel.* ^b*Institute of Applied Physics Academy of Sciences of Moldova.* ^c*Department of Fine Organic Synthesis A. V. Bogatsky Physico-Chemical Institute National Academy of Sciences of Ukraine.* E-mail: botoshan@technion.ac.il

Four new crownophanes containing the 2,7-dioxyfluorenone fragment, bridged with another aromatic units (I – IV) via triethylene glycol residues were synthesized as the perspective complexing agents for the metal and organic cations [1-2].



The molecular geometry of crownophanes and their packing in crystals are governed by the combination of intra- and intermolecular C–H...O hydrogen-bonding, C–H... π and π – π stacking interaction that provide the T-shape for all but bisfluorenone crownophane (Ar = I) which exhibits the antiparallel alignment of the fluorenone units in the centrosymmetric molecule. The incorporation of fluorenone building block in crownophane molecule ensures the advantages, such as strong hydrogen bonding of the substrate, often dominating in the processes of molecular recognition. Fluorenone and its derivatives have good luminescence properties that are important for the development of sensitive fluorescence-based chemosensors.

[1] Lukyanenko N.G., Kirichenko T.I., Lyapunov A.Yu., Mazepa A.V., Simonov Yu.A., Fonari M.S., Botoshansky M.M., *Chem. Eur. J.*, 2005, **11**, 262. [2] Lukyanenko N.G., Kirichenko T.I., Lyapunov A.Yu., Kulygina C.Yu., Simonov Yu.A., Fonari M.S., Botoshansky M.M., *Tet. Lett.*, 2004, **45**, 2927.

Keywords: *crown compounds, macrocycles, intermolecular interactions*

P.06.06.3

Acta Cryst. (2005). A61, C283

Crystal Structure of Isosteviol and its Derivatives

Dmitry Beskrovnyy, Aidar Gubaidullin, Igor Litvinov, A.E. Arbusov *Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Kazan, Russia.* E-mail: b_d_v@iopc.knc.ru

Crystal structure determination of 33 derivatives of plant terpenoid isosteviol and its molecular complexes with small molecules were performed. It was analyzed a molecular geometry and intermolecular interactions in the crystal, and types of crystalline packing. The absolute configuration of chiral centers of the molecule of isosteviol was established.

Shown that for single framework isosteviol derivatives, solvates, or complexes of including are got only at presence of not modified acid group.

For bis-framework derivatives – «tweezers» structures, built on

the type «head to head», molecular complexes is not observed, while in crystals of structures, having type of buildings «head to tail» even at short connecting bridge, received solvates with small molecules.

It was established that molecular complexes of isosteviol with small aromatic molecules (benzene, toluene, aniline, dimethylaniline, naphthalene, etc.) are isostructural in the space group $P4_32_12$. The supramolecular structure of these complexes is a double spiral around an axis of fourth order; branches, which formed by hydrogen bonded molecules of isosteviol. Molecules of aromatic «guests» are located in the same areas of crystal, but differently oriented for molecules of isosteviol. Shown that forming of complexes with technical mixtures of nitroanilines and toluene runs regioselective.

Work is supported by RFBR (grants 01-03-32188, 01-03-32190, 02-03-06020, 02-03-32280)

Keywords: *absolute configuration, crystal and molecular structure, hydrogen bonds in organic crystals*

P.06.06.4

Acta Cryst. (2005). A61, C283

Inclusion Compounds from a Decomposing Host: a Cautionary Tale

Gaëlle Ramon^{1,2}, Mino R. Caira², Anthony W. Coleman¹, Luigi R. Nassimbeni², Benjamin Taljaard³, ¹*IBCP, CNRS-UMR 5086, Lyon, France.* ²*Chemistry Dept, UCT, South Africa.* ³*Chemistry Dept, UPE, South Africa.* E-mail: ramon@science.uct.ac.za

5-Naphthalen-1-yl-5H-dibenzo[a,d]cyclohepten-5-ol (1) has been synthesised from bromo-naphthalene and 5H-Dibenzo[a,d]cyclohepten-5-one (2). Analysis (IR, NMR, TLC) showed the product to be pure. It was stored in a dark bottle in an inert atmosphere. However, when recrystallised from EtOH, we found that the crystal structure contained 1, 2 and a dimer of 2 (referred as 3). Upon recrystallisation from toluene, we obtained a crystal containing 1 and 2, while from hot DMSO we obtained different crystals of 1·DMSO and 3.

When recrystallised from either pyridine or 1,4-dioxane, we obtained crystals of the respective solvates, and we employed the dioxane solvate in order to purify the mixture of the contaminated host which contains 1 + 2 + 3.

Pure 1 was obtained by desorption of its dioxane inclusion compound, and allowed us to estimate that it is present in 59% quantity in the original mixture.

Keywords: *supramolecular assemblies, host-guest structures, inclusion complexes*

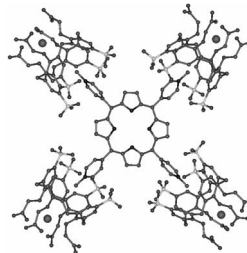
P.06.06.5

Acta Cryst. (2005). A61, C283-C284

Design and Crystallographic Characterization of Multi-Porphyrins Complexes

Lucio Randaccio^a, Rita De Zorzi^a, Luigi Di Costanzo^a, Silvano Geremia^a, Rosaria Lauceri^b, Roberto Purrello^b, ^a*Dipartimento di Scienze Chimiche, Università di Trieste, Italy.* ^b*Dipartimento di Scienze Chimiche, Università di Catania, Italy.* E-mail: randaccio@units.it.

The interactions of the tetracationic *meso*-tetrakis(4-N-methylpyridyl)porphyrin (H₂T4) and its metallo-derivatives (MT4) with the octa-anionic form (at neutral pH) of 5,11,17,23-tetrakisulfonato-25,26,27,28-tetrakis(hydroxycarbonylmethoxy)calix[4]arene (C₄TsTc) leads to a series of complex species whose stoichiometry and



porphyrin sequence can be easily tuned. X-ray solid state and solution studies suggest a picture where a central 1:4 (porphyrin to calixarene) unit (Figure) serves as template for obtaining more complex species. The latter arise by step-wise addition of porphyrin molecules above and below the plane of the 1:4 core, allowing to tune the species stoichiometry up to 7:4

[1]. Structural results, reported here strongly suggest that the interactions between the anionic calixarenes and cationic porphyrins are not significantly influenced by the presence of tetra-coordinated metals in the porphyrin core. Finally, an application of the homo-

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

P.06.06.6

Acta Cryst. (2005). A61, C284

Strychnine and Brucine Self-Assemblies: Structures and Properties

Agata Bialonska, Zbigniew Ciunik, Faculty of Chemistry, University of Wrocław, Wrocław, Poland. E-mail: bialonsk@wcheto.chem.uni.wroc.pl

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

P.06.06.7

Acta Cryst. (2005). A61, C284

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

Deepak Chopra^a, K. Nagarajan^b, Tayur. N. Guru Row^a, *Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560012*. ^bHikal Limited, Bannerghatta Road, Bangalore-560076. E-mail: deepak@sscu.iisc.ernet.in

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

P.06.06.8

Acta Cryst. (2005). A61, C284

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

Alajos Kálmán, Institute of Structural Chemistry, HAS Budapest, Hungary. E-mail: akalman@chemres.hu

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., Fábán L., Argay Gy., Bernáth G. Cs., Gyarmati Zs., *Acta Cryst.*, 2004, **B60**, 755, and references therein.

Keywords: isostructurality, morphotropism, polymorphism

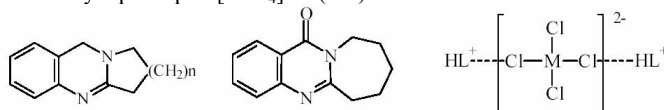
P.06.06.9

Acta Cryst. (2005). A61, C284

The Crystal Structural Variety of Tricyclic Quinazoline Salts

Bahodir Tashkhodjaev, Akmal Tojiboev, Kambarali K.Turgunov, Khusnuddin M.Shakhidoyatov, *S.Yunusov Institute of Chemistry of Plant Substances, Tashkent, Uzbekistan*. E-mail: rentgen@uzsci.net

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

P.06.06.10

Acta Cryst. (2005). A61, C284-C285

Macrocyclic Amines and their Adducts with Acids

Teresa Borowiak^a, Grzegorz Dutkiewicz^a, Maciej Kubicki^a, Marek Pietraszkiewicz^b, Oksana Pietraszkiewicz^b, Rainer Mattes^c, *a*Faculty of