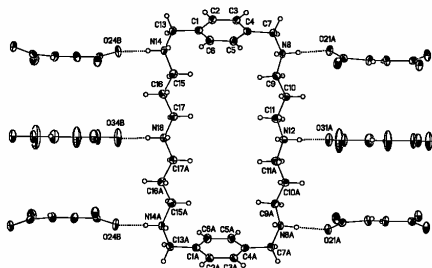


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Conformations of the macrocyclic amine in the structures of N-methylated derivative (1) and of the adduct with fumaric acid (2) are different. In (2) the cation is hexaprotonated and occupies a special position in a plane of symmetry. The ionic synthon 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<sup>+</sup>-H...O thus generating one-dimensional supramolecular ribbons.



The ionic synthon of (2)

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

#### P.06.06.11

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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 Å<sup>3</sup>. 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

#### P.06.06.12

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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

#### P.06.06.13

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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*-ethylidimethylamine 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

#### P.06.06.14

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

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A search algorithm, 3DSEARCH<sup>1</sup>, 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.

Analysis of polymorphic systems shows that extended patterns are conserved between polymorphic forms for 75% of cases studied.

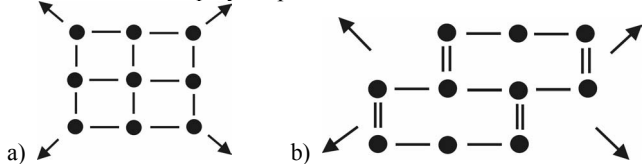


Figure 1. a) An 'R4 sheet' motif. b) An R2R6 sheet motif. Dots represent molecules, lines represent inter-molecular hydrogen bonds. The arrows indicate that these patterns are infinitely repeating in 2D.

[1] Chisholm J. A., Motherwell S., *J. Appl. Cryst.*, 2004, **37**, 311.

**Keywords:** hydrogen bond patterns, hydrogen bonds in organic crystals, database search

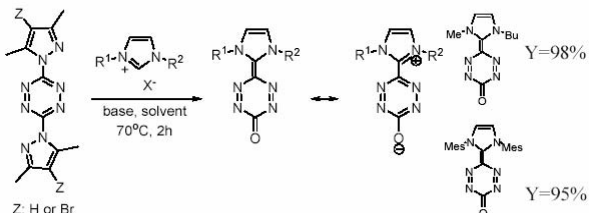
#### P.06.06.15

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#### New Class of Compounds: Quinoidal Tetrazines

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Tetrazine compounds are frequently used in pesticides, pharmaceutical products, explosives etc. Using Arduengo-type carbenes [1] we have prepared and characterized a series of air stable quinoidal tetrazines which represent a new class of compounds.



The surprisingly high torsion angle between the pyrazolyl and tetrazine rings (37-43°) as well as C-C, N-N, and C-O bond distances indicate the quinoidal nature of these compounds without conjugation of the rings. The supramolecular motif of quinoidal tetrazines include stack-like ordering of the molecules. Packing, van der Waals interactions as well as chirality of the compounds when R<sup>1</sup> or R<sup>2</sup> are chiral will be discussed.

Acknowledgements: This work was supported by the Hungarian National Scientific Research Fund (Grants No. OTKA-F047125 and T043365).

[1] Arduengo A., *J. Am. Chem. Soc.*, 1991, **113**, 361.

**Keywords:** crystal packing, chirality, supramolecular chemistry

#### P.06.06.16

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#### Rings, Restraints and Resolving the Superbowl in Crystals

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Determination of the structure of the Superbowl<sup>1</sup> (a fused polycyclic penta-cavitand molecule C<sub>268</sub>H<sub>316</sub>Br<sub>4</sub>O<sub>52</sub>·4EtOH·5CHCl<sub>3</sub>, *MWt* ≈ 5000) presented numerous challenges. Crystals diffracting to 1.25 Å resolution were obtained which, in addition to 35% by volume disordered solvent, were found to be built up from supramolecular assemblies comprising the superbowl molecule holding one chloroform and four ethanol molecules in its interior and four more chloroform molecules lying in smaller non-rigid external cavities. Seventy percent of the non-hydrogen atoms of the superbowl were found by Direct Methods<sup>2</sup>. The model was extended by mapping on a known mono-cavitand structure using the CRYSTALS<sup>3</sup> Regularise/Augment routine to complete the rigid part of the superbowl. Refinement of a mostly isotropic model required application of restraints, first holding geometries to values seen in comparator structures, and later setting chemically equivalent bond lengths to their mean values in the structure. Of special utility in the refinement were the Special Shapes available in CRYSTALS<sup>3</sup> which facilitated modelling the internal chloroform as a combination of fully occupied

sites, fractionally occupied sites, and a ring of electron density accounting for 60% of two disordered chlorine atoms. Only 15 non-H Superbowl atoms are unresolved in the final model *R* = 0.10, *R<sub>w</sub>* = 0.07

[1] Barrett E.S., Irwin J.L., Edwards A.J., Sherburn M.S., *J.A.C.S.*, 2004, 16747-16749. [2] Altomare A., Burla M.C., Camalli M., Cascarano G.L., Giacovazzo C., Guagliardi A., Moliterni A.G.G., Polidori G., Spagna R., *SIR 97, J. Appl. Crystallogr.*, 1999, 115-119 [3] Watkin D.J., Prout C.K., Carruthers J.R., Betteridge P.W., Cooper R.I., *CRYSTALS Issue 11 Chemical Crystallography Laboratory*, Oxford.

**Keywords:** supramolecular assemblies, model building, refinement disorder

#### P.06.06.17

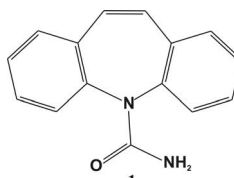
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#### Familial Relationships in Molecular Crystal Structures

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*XPac* is a computer program for the identification of similar "supramolecular constructs" (sub-components of complete crystal structures) of 0-, 1- or 2-dimensionality in different crystal structures of specific molecules (polymorphs) or crystal structures of similar molecules (families) and of 3-dimensionality in isostructural assemblies.

The *XPac* approach is demonstrated using a family of 20 crystal structures of the carbamazepine molecule (**1**) from the CSD, which includes four polymorphic forms, 13 solvates and salt structures. The structural relationships are visualised in a structure family diagram



**Keywords:** software for crystallography, polymorphs, isostructurality

#### P.06.06.18

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#### Supramolecular Synthesis of Caffeine Solvates and Cocrystals

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Caffeine is a biologically active compound, widely used in food and drug industry. Besides a 0.8 hydrate, two anhydrous forms are known<sup>1</sup> which still defy a complete structural determination because of disorder phenomena.<sup>2</sup> We recently carried out a large number of solvent crystallizations where we obtained three new solvates. The solvates are formed with formic acid, acetic acid and methanesulfonic acid. Acetic acid and formic acid solvates lose their solvent readily. The crystal structure analysis of these solvates lead us to design two new, hitherto unknown, caffeine cocrystals in addition to the recently reported ones.<sup>3</sup> This report describes the discovery and structural aspects of these new caffeine solvates and cocrystals. The methanesulfonic acid solvate (monoclinic, *C2/c*) has the highest calculated density (1.594 g cm<sup>-3</sup>) of all the solved cocrystal structures so far. The driving force for the formation of the solvates and cocrystals is presumably an additional hydrogen-bond stabilization by the introduction of an acid group as a hydrogen bond donor for the basic imidazole nitrogen of caffeine by the formation of O-H...N interactions.

[1] Griesser U.J., Szelagiewicz M., Hofmeier U.C., Pitt U., Cianferani S., *J. Therm. Anal. Calorim.*, 1999, **57**, 45, and references therein. [2] Carlucci L., Gavezzotti A., *Chem. Eur. J.*, 2005, **11**, 271, and references therein. [3] Trask A.V., Motherwell W.D.S., Jones W., *J. Cryst. Growth Des.*, 2005, in press.

**Keywords:** caffeine, solvent structure, cocrystals