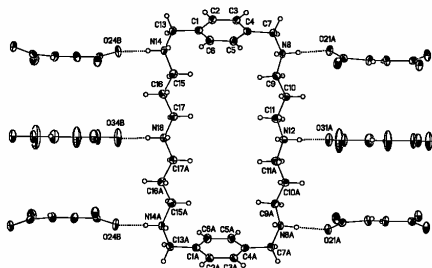


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Conformations of the macrocyclic amine in the structures of N-methylated derivative (1) and of the adduct with fumaric acid (2) are different. In (2) the cation is hexaprotonated and occupies a special position in a plane of symmetry. The ionic synthon 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

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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.