

host scaffolds assembled via O-H...O, N-H...O hydrogen bonds and halogen...halogen, pi-pi stacking interactions based on T-shaped, H-shaped and trigonal tectons have appeared in recent publications from our group [2-4].

[1] Nangia A. in *Nanoporous Materials: Science and Engineering*, Eds. G. Q. Lu and X. S. Zhao, World Scientific, Singapore, 2005, 165-187. [2] Reddy C. M. et al., *CrystEngComm*, 2005, 7, 44-52. [3] Aitipamula S., Nangia A., *Supramol. Chem.*, 2005, 17, 17-25. [4] Saha B. K. et al., *Cryst. Growth Des.*, 2005, 5, ASAP.

**Keywords:** crystal engineering, guest-host structures, thermal analysis

#### MS87.30.4

*Acta Cryst.* (2005). A61, C111

##### Photochemical Reactions in Inclusion Compounds

Tali Lavy, Menahem Kafory, Department of Chemistry, Technion - Israel Institute of Technology, Haifa, Israel. E-mail: lavyt@tx.technion.ac.il

In inclusion compounds the guest molecules occupy space formed by the host molecules. Carrying out photochemical reactions in inclusion compounds proved to be a unique method for the synthesis of a large variety of compounds. The research deals with unimolecular and bimolecular photochemical reactions in inclusion compounds. In a recent publication the effect of the reaction core on the homogeneity/heterogeneity of the reaction was studied. A question arises from this recent study: what happens if the volume of the product is smaller than that of the reactant? Free volumes are not anticipated to exist. Therefore it is expected that the following possibilities will occur: either destruction of the crystal as a result of the collapse of the cavity's walls (heterogeneous reaction) or that some other molecules will occupy the free space. We have encountered for the first time few examples where a photochemical dimerization reaction is taking place in a single crystal of inclusion compound and at the end of the reaction water molecules penetrate into the free space without destruction the crystal lattice. Moreover, at the end of the dimerization, the orientation of the dimer with respect to the host molecules is different than that prior to the reaction. Evidently the dimer is rotating during or after the photoreaction.

The aim of the unimolecular study is to examine to what extent the conformation adopted by N,N disubstituted- $\alpha$ -oxoamides determines its photochemical reaction. We have used different host molecules in order to control the conformation of the guest. It was found that indeed the N,N disubstituted- $\alpha$ -oxoamides show different photochemical behavior which depends on their conformation.

**Keywords:** host-guest complexes, homogeneous reactions, photochemistry

#### MS87.30.5

*Acta Cryst.* (2005). A61, C111

##### Confinement of Gases and Polymers in Van Der Waals Crystals

Piero Sozzani, Department of Materials Science, University of Milano-Bicocca, Milan, Italy. E-mail: piero.sozzani@mater.unimib.it

The exploitation of weak interactions for the fabrication of binary adducts by self-assembly is receiving a great interest. We could obtain high-melting crystalline materials with macromolecules by simple mechanical mixing and grinding of D<sub>3</sub> and D<sub>3h</sub> molecules with linear polyethylene or several polyconjugated oligomers [1]. A number of weak CH... $\pi$  and  $\pi$ ... $\pi$  interactions cooperatively promote the stabilization of the architecture as recognized by solid state 2D MAS NMR. In particular, tris-(*o*-phenylenedioxy)cyclotriphosphazene (TPP) organizes the aromatic paddles parallel to the nanochannels encasing the elongated molecules. The guest hydrogens are subjected to the strong magnetic susceptibility of the surrounding aromatic groups that demonstrate the topology of the guest hydrogen above the  $\pi$ -system. The favorable intermolecular interactions compensate the loss of entropy necessary for constraining the macromolecules to the stretched geometry. However, <sup>2</sup>H NMR and <sup>13</sup>C(T<sub>1</sub>) show diffusional fast spinning motion ( $\tau_c \approx 10^{-10}$ s) about the polymer axis. The exceptional mobility of the polymer chains in the fully aromatic environment creates unique examples of molecular rotors and

gyroscopes stabilized up to 350°C by soft interactions. The anisotropic alignment of polyconjugated molecules is suitable for growing crystal for electronic applications. The same kind of driving forces determine effective enclathration of light molecules and gases and promote absorption properties from the gas phase [2].

[1] Sozzani P., Comotti A., Bracco S., Simonutti R., *Angew. Chem. Int. Ed.*, 2004, 43, 2811. [2] Sozzani P. et al., *Angew. Chem. Int. Ed.*, 2005, 44, 2.

**Keywords:** self-assembly, weak interactions, gas storage

#### MS87.30.6

*Acta Cryst.* (2005). A61, C111

##### Homo- and Heterochirality in Crystal

Rem G. Kostyanovsky, Semenov Institute of Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: kost@chph.ras.ru

In the present communication the methods for the recognition of homo (Ho)- and heterochiral (He) crystals are considered [1], as well as the conditions for the transformations Ho→He or He→Ho crystallization [2], the directed construction of Ho-crystals [3], solid-phase reactions Ho $\leftrightarrow$ He, synthesis of Ho-crystals [4], isomerizations during the formation of the solid phase [5] and the spontaneous resolution of Ho-crystals [6].

On the example of glycoluriles the methodology for the development of chiral drugs via the spontaneous resolution is presented [7].

The differences in physical properties of enantiomers and racemates are demonstrated by distinct differences in ESR spectra of polycrystalline samples of the enantiomers and racemates of nitroxide radicals [8]. Recently it has been found that the enantiomers of a series of compounds are effective organogelators, whereas their racemates do not show that property [9].

For the first time the supramolecular H-bonded catenanes and polycatenated structures in crystals have been synthesized [10].

This works were supported by Russian Academy of Sciences, RFBR (grant nos. 03-03-04010 and 03-03-32019) and INTAS (grant no. 99-00157).

[1] *Mendeleev Commun.*, 2003, 97, 106. [2] *Tetrahedron: Asymmetry*, 2003, 14, 2059. [3] *Mendeleev Commun.*, 2002, 4. [4] *Tetrahedron: Asymmetry*, 2004, 15, 1445. [5] a) *Tetrahedron*, 1982, 38, 549; b) *Tetrahedron*, 1984, 40, 2151. [6] a) *Mendeleev Commun.*, 2000, 16, 83; b) *Mendeleev Commun.*, 2001, 1; c) *Mendeleev Commun.*, 2003, 111; d) *Tetrahedron: Asymmetry*, 2001, 12, 2721. [7] a) *Mendeleev Commun.*, 1998, 231; b) *Mendeleev Commun.*, 2001, 134; c) *Mendeleev Commun.*, 2002, 6. [8] *Mendeleev Commun.*, 2004, 318. [9] *Mendeleev Commun.*, 2005, in press. [10] a) *Tetrahedron: Asymmetry*, 2002, 13, 2697; b) *Mendeleev Commun.*, 2005, in press.

**Keywords:** chirality, solid phase reactions, recognition of chirality

#### MS88 ELECTRONIC EXCITATIONS

*Chairpersons:* John J. Rehr, Keijo Hamalainen

#### MS88.30.1

*Acta Cryst.* (2005). A61, C111-C112

##### Electronic Excitations: What Inelastic X-ray Scattering can Reveal

Winfried Schuelke, Institute of Physics, University of Dortmund, D-44221 Dortmund, Germany. E-mail: schuelke@physik.uni-dortmund.de

A review of inelastic x-ray scattering (IXS) as a method to investigate electronic excitations in solids is presented, where also some aspects of synchrotron radiation based instrumentation are touched. The direct access to the polarizability of electrons in solids by measuring the dynamic structure factor using non-resonant inelastic scattering is stressed. The weight of different terms in the diagrammatic expansion of the proper polarizability can be tested. Special lattice effects on electron correlation as zone boundary collective states, plasmon Fano resonances and the plasmon band structure will be represented, where the role of coherent inelastic x-ray scattering is stressed. The increasing importance of resonant inelastic x-ray scattering (RIXS) is emphasized. It is the sensitivity of this