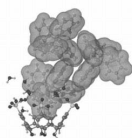


P.06.06.19*Acta Cryst.* (2005). **A61**, C287**Exploiting Phenyl Embraces and π -stacking in the Assembly of Supramolecular Arrays of Tetraphenylphosphonium and *p*-sulfonatocalix[n]arene (n=4,6,8)**Alexandre N. Sobolev, Mohamed Makha, Colin L. Raston, Allan H. White, *Chemistry, M313, School of Biomedical and Chemical Sciences, University of Western Australia, Crawley, WA 6009, Australia*. E-mail: ans@chem.uwa.edu.au

The interactions between Ph_4P^+ cations and *p*-sulfonatocalix-*n*arene anions offer the possibility of building up new materials based on interactions between the anions and cations beyond their electrostatic attraction, such as the possibility of a phenyl ring of the cation residing in the cavity of the calixarene. In developing this concept, we have embarked on a systematic study of the ability of the Ph_4P^+ -*p*-sulfonatocalix-*n*arene system to generate extensive self-assembled arrays. We report herein the formation of materials built up from Ph_4P^+ cations and different sizes calix-*n*arenes with *n* = 4 (see Figure), *n* = 6 and *n* = 8.

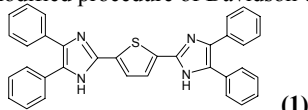


[1] Makha M., Raston C. L., Sobolev A. N., White A. H., *Chem. Commun.*, 2004, **9**, 1066. [2] Makha M., Raston C. L., Sobolev A. N., White A. H., *Chem. Commun.*, 2005, *in press*.

Keywords: calixarene complexes, crystal engineering, self-assembly molecular chemistry

P.06.07.1*Acta Cryst.* (2005). **A61**, C287**Chromotropism of Imidazole, 2,2'-(2,5-thiophenediyl)bis[4,5-diphenyl]**Natalya Fridman, Menahem Kaftory, Shammai Speiser, *Department of Chemistry Technion - Israel Institute of Technology, Haifa 32000, Israel*. E-mail: fridmann@tx.technion.ac.il

We have prepared new doublelophineimidazole derivative, Imidazole, 2,2'-(2,5-thiophene-diyl)bis[4,5-diphenyl] (**1**), according to slightly modified procedure of Davidson et al. [1].



(**1**) shows solvatochromism, halochromism and photochromism in solution and tribochromism, photochromism and thermochromism in the solid state. We have measured the absorption and the fluorescence spectra of (**1**) in aprotic solvent MeCN at different pH. We have measured the absorption and the fluorescence spectra of (**1**) with different periods of irradiation time in neutral MeCN solution and in basic MeCN solution. It was shown that the fluorescence intensity decreases with increasing irradiation time for both solutions.

When (**1**) was triturated in mortar, the light green colour turned to dark green irreversibly. It was found that (**1**) crystallized as inclusion compound in two different colours: yellow and green, depending on the guest molecules. Crystallization of (**1**) from MeCN:Acetone (10:1) yields long solvate yellow needles with the ratio of host-guest (1:2 MeCN:2 H₂O). Crystallization of (**1**) from dry MeCN yields large solvate green prisms with the ratio of host-guest (1:2). When the yellow crystals were allowed to stand at room temperature, the yellow needles lost two molecules of water and gradually turned into green needles. The spectroscopic behavior of (**1**) in solutions of different pH, before and after irradiation, the packing pattern of two different inclusion compounds of (**1**) are presented.

[1] Davidson D., Weiss M., Jelling M., *J. Org. Chem.*, 1937, **2**, 319.

Keywords: colour, conjugate compounds, X-ray structure

P.06.07.2*Acta Cryst.* (2005). **A61**, C287**Selective Enclathration of Picolines**Kirsten C. Corin^a, Susan A. Bourne^a, Luigi R. Nassimbeni^a, Fumio

Toda^b, ^a*Department of Chemistry, University of Cape Town, Cape Town, South Africa.* ^b*Department of Chemistry, Faculty of Science, Okayama University of Science, Okayama, Japan.* E-mail: kirsten@science.uct.ac.za

The host 1,1,2,2-tetraphenyl-1,2-ethane diol has been employed to separate the isomers 2-picoline (2-pic), 3-picoline (3-pic), and 4-picoline (4-pic) by selective enclathration. The crystal structures are all stabilized by (host)-O-H...N(guest) hydrogen bonds.

For any pair of guests, competition experiments were carried out by setting up vials containing the host and mixtures of the guests such that the mole fraction of a given guest varied systematically from 0 to 1. This was also done for all three guests simultaneously. The crystals obtained were analyzed by gas chromatography to give the relative amounts of each guest incorporated within the crystal. The experiments show that enclathration preferentially takes place in the order 4-pic > 3-pic > 2-pic.

The effect of adding a "neutral" (non-competitive) solvent was investigated. The effect of benzene and methanol as "neutral" solvents shows that the former is incorporated as a guest in the 4-pic structure, and enhances the enclathration of 4-pic over 3-pic. Methanol displays no such effect.

[1] Dohi K., Tanaka K., Toda F., *J. Chem. Soc. Jpn., Chem. Ind. Chem.*, 1986, **7**, 927.

Keywords: inclusion compounds, selectivity, separation

P.06.07.3*Acta Cryst.* (2005). **A61**, C287**Anisotropy in the Photodimerization of 9-Acetylanthracene in Inclusion Compound**Irena Zouev, M. Kaftory, *Department of Chemistry Technion - Israel Institute of Technology, Haifa 2000, Israel*. E-mail: charisha@technion.ac.il

Besides their intrinsic and basic scientific significance, organic solid-state photoreactions are attractive for a variety of reasons. They are useful as a means for synthesizing novel products that may be very difficult, if not impossible, to prepare by other means. The advantage of these reactions is that they are friendly to the environment.

Solid-state photochemical reactions are highly dependent on the geometry of the reacting compound and its product. An important advantage in the understanding of the reaction mechanism, the course of the reaction, and the reaction control factors lies in the ability to follow the geometrical changes during the reaction.

In inclusion compounds, the guest molecules occupy space formed by the host molecules. If the host molecules provide topochemical conditions required for bimolecular reactions and the guest molecules are photochemically active, regio- and stereo-selective reactions are anticipated.

Photochemical [4 + 4] dimerization reaction of 9-acetylanthracene inclusion compound was studied using the chromophore absorption spectra tail irradiation method[1]. X-ray diffraction data was collected after irradiation for different periods of time. The interesting finding is that only one of the two crystallographic independent pairs of 9-acetylanthracene undergo solid state photodimerization to ca. 40% conversion to the head-to-tail dimer without destruction of the single crystallinity nature.

[1] Enkelman V., Wegner G., *J. Am. Chem. Soc.*, 1993, **115**, 10390.

Keywords: inclusion compounds, photochemistry, topochemistry

P.06.07.4*Acta Cryst.* (2005). **A61**, C287-C288**Temperature Dependent Selectivity of Inclusion**Lidiya Yu. Izotova^a, D.M. Ashurov^a, B.T. Ibragimov^a, E. Weber^b, S.A. Talipov^a, ^a*Institute of Bioorganic Chemistry, Tashkent, Uzbekistan.* ^b*Institute of Organic Chemistry of Technical University Bergakademie, Freiberg, Germany.* E-mail: ckrystal@uzsci.net

Trans-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (DEDA) is a versatile host, capable to form inclusion complexes with both polar and non polar solvents[1]. At the room temperature

this compound is crystallized from solutions in acetophenone as a host-guest complex with a ratio 2:3. In the crystal structure DEDA molecules form infinite chains in a direction [01-1] through a pair of centrosymmetric hydrogen bonds. The acetophenone molecules are situated inside different channels formed at stacking of these chains and running along [100] and [0-11] directions.

At decreasing of crystallization temperature until 5°C from the same solution DEDA crystallizes as new complex - hydrate with 1:3 host-guest ratio. In the crystal structure one carboxylic group of DEDA molecules is connected via centrosymmetric H-bonding with the carboxylic group of the other host molecule, while other carboxylic group is deprotonated giving rise to a network of intermolecular H-bonds associating with one ion of hydroxonium (H_3O^+) and two molecules of water. The structure may be described as intercalate type complex with strict separation of the hydrophobic and hydrophilic areas.

L.I. is grateful to NATO Reintegration Grant (Rig.Ref. 980768) for scholarship.

[1] Weber E., Csöregi I., Ahrendt J., Finge S., Czugler M., *J. Org. Chem.*, 1988, **53**, 5831-5839.

Keywords: versatile host, host-guest complex, intercalate

P.06.07.5

Acta Cryst. (2005). A61, C288

Different Building Modes of α -Cyclodextrin/Monoalkyl Amphiphile Complexes

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In this study, the impact of the length of the guest molecule alkyl chain and the crystallization conditions on the structural parameters of α -cyclodextrin (α -CD)/monoalkyl complexes was determined. Several procedures to crystallize those complexes were developed for different alkylalcohols as model guest molecules, as a function of temperature. Three different crystalline structures were identified depending on the alkyl chain length, using synchrotron X-ray diffraction (LURE, Orsay, France). In all cases, complexes crystallize in channel-type structures, where α -CD molecules are stacked like coins in a roll and the alkyl chain of the guest compound is embedded in the tubular cavity of the α -CDs. However, depending on the length of the chains and the crystallization conditions, the channels are organized differently. C_6 - C_8 chains give rise to a pseudo-hexagonal lattice, a packing mode already observed for polyiodide complexes [1]. C_{10} - C_{12} chains crystallize in a triclinic pseudo-monoclinic C2 lattice, while longer chains up to C_{18} form hexagonal crystals with R3 symmetry. These two novel crystal structures are described. Understanding these structures opens new routes to nanotube formation through amphiphile-driven crystallization of cyclodextrin templates.

[1] Noltemeyer M., Saenger W., *J. Am. Chem. Soc.*, 1980, **102**, 8, 2710.

Keywords: cyclodextrin, nanotubes, supramolecular assembly

P.06.07.6

Acta Cryst. (2005). A61, C288

Inclusion Compounds of Isomeric Xanthenol Hosts with Aniline

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Two isomeric xanthenol host compounds have been found to form inclusion compounds with aniline. These hosts are H1 = 9-(4-methoxyphenyl)-9H-xanthen-9-ol and H2 = 9-(3-methoxyphenyl)-9H-xanthen-9-ol. We have elucidated the structures of the inclusion compounds and determined their kinetics of desolvation. H1•½aniline crystallises in the triclinic space group $P\bar{1}$ with the host in general positions and the aniline guest on a centre of symmetry. H2•aniline

was solved successfully in the monoclinic space group $P2_1/c$ with both the host and guest molecules in general positions. For H1•½aniline there is (Host)—OH•••O—(Host) hydrogen bonding whereas in H2•aniline (Host)—OH•••N—(Guest) hydrogen bonding occurs. We have correlated the structures with the thermal stabilities of the compounds.

Keywords: isomeric hosts, aniline, desolvation

P.06.07.7

Acta Cryst. (2005). A61, C288

Structural Features of Some Schiff Base Disulfide Compounds

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Schiff bases bearing imine N and anionic S atoms constitute an important class of polydentate ligands and their metal complexes have previously been used as models for biological systems. The molecule and crystal structure of a new synthesized disulfide compound [$\text{C}_{30}\text{H}_{22}\text{F}_6\text{N}_2\text{O}_2\text{S}_2$] has been undertaken with a view to obtaining accurate structural parameters of interest in disulfide compounds. Crystal data: $M=620.62$, Triclinic, $a=7.639(2)\text{Å}$, $b=8.526(8)\text{Å}$, $c=23.349(5)\text{Å}$, $\alpha=89.04(4)^\circ$, $\beta=89.99(2)^\circ$, $\gamma=63.41(4)^\circ$, $V=1359.6(9)\text{Å}^3$, $P\bar{1}$, $R=0.0538$, $R_w=0.0944$. The structure was solved by direct methods and refined by least squares on F_{obs}^2 by using SHELX-97.

In the second phase of the study, structural results have been compared with the values found in our previous studies related at least four Schiff base disulfides [1-4]. The molecular conformation around central S-S bond has been affected by trifluoromethyl groups in the molecule. High electronegativity in the CF_3 groups has been cause to conformational changes in the torsion angle of C-S-S-C [$77.8(4)^\circ$]. Two strong intramolecular hydrogen bonds [O-H•••N, O•••N: 2.612(9) and 2.612(8)Å] have been observed and cause to increasing of the planarity in the main parts of the molecule.

[1] İde S., Öztaş G., Ancin N., Tüzün M., *Acta Cryst.*, 1997, **C53**, 376-378. [2] Özbey S., Temel A., Ancin N., Öztaş S.G., Tüzün M., *Z. Kristallogr.*, 1998, **213**, 207-208. [3] Candan M.M., İde S., Kendi E., Öztaş G., Ancin N., *Spectroscopy Letters*, 1998, **31(4)**, 891-900. [4] İde S., Ancin N., Öztaş S.G., Tüzün M., *Pharm. Acta. Helv.*, 1998, **72**, 291-294.

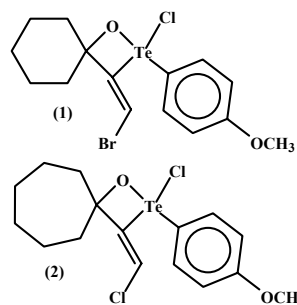
Keywords: Schiff base, disulfides, crystal structure

P.06.07.8

Acta Cryst. (2005). A61, C288-C289

Structural Studies of Human Cathepsin B Inhibitors: Telluroxetanes

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The inhibition of cathepsin B has been postulated to be directly responsible for the abrogation of the invasion process in several tumor cells lines [1], and, as it was shown that AS-101 [2], a Te^{IV} compound, was a cathepsin B inhibitor, compounds (1) and (2) were synthesized and studied.

In both compounds, if intra and two intermolecular secondary bonds and the electron lone pair are considered, then the Te^{IV} is coordinated in a ψ -pentagonal bipyramidal fashion. The secondary interactions join the molecules in chains of centrosymmetric dimers. These compounds, have higher second-order rate constants for the inactivation of cathepsin B, than that of AS-101. Moreover, the compound with a cyclohexane ring is 20-fold more active than (2) and 4-fold than (1), so that it can be