

Pavelić K., Karminski-Zamola G., *J. Med. Chem.*, 2005, *in press*.

Keywords: intercalators, heterocyclic compounds, DNA binding

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Photooxygenation of Rubrene (5,6,11,12-tetraphenylnaphthacene)

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It is well-known that when polycyclic aromatic hydrocarbons (PAHs) in solution are irradiated by light with their absorption wavelength, they react with molecular oxygen dissolved in solvent to form *endo*-peroxides. This photooxygenation occurs due to 1,4-cycloaddition of singlet oxygen to a PAH molecule in the ground state. When rubrene in benzene solution was irradiated by light, the color of solution gradually changed from reddish orange to colorless. The rubrene peroxide was crystallized from 1,4-dioxane solution and X-ray structure analysis was carried out. A molecular oxygen bonds to 5 and 12 carbon pair of the naphthacene skeleton. Although the naphthacene moiety of rubrene has completely planar structure due to the crystallographic symmetry, that of the peroxide is largely bent at the positions where molecular oxygen binds.

The structure optimization of PAHs including rubrene and their peroxide was performed by applying semi-empirical molecular orbital calculation methods. The optimized structure was coincident with the experimentally determined structure. The photooxygenation reactivity of PAHs including rubrene was well explained by the differences in heats of formation between PAHs and their peroxide.

Keywords: rubrene, photooxygenation, PAH

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Deuterium Isotope Effect on the Crystal Structures of Pyrene: A Lab XRPD Study

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Laboratory XRPD data were collected from capillary samples of perdeuterated pyrene (C₁₆D₁₀) and protonated pyrene (C₁₆H₁₀) in the range $T = 80\text{--}140\text{K}$ [1]. Unit cell volumes were determined by Pawley refinement (*ca.* 120 reflections to 2 Å resolution), yielding:

(i) $V(T) = (0.1511 \pm 0.008672)T + (1001.9 \pm 1.0)$, $r^2 = 0.9743$, for C₁₆D₁₀ (form I);

(ii) $V(T) = (0.1449 \pm 0.006194)T + (1004.8 \pm 0.7)$, $r^2 = 0.9803$, for C₁₆H₁₀ (form I).

A comparison of slopes ($P = 0.553$) and elevations ($P < 0.0001$) within *Prism v4.02* confirmed that whilst the difference between the slopes is not significant, the perdeuterated crystal structure is significantly more compact than its hydrogenous counterpart at any given T . A likewise comparison of form II C₁₆D₁₀ with form II C₁₆H₁₀ produced the same conclusion.

The quality of the XRPD analysis was assessed against a neutron powder diffraction analysis of C₁₆D₁₀ [2]. The principal differences of note are the superior precision of the best-fit parameters, plus the superior goodness of fit, obtained with the neutron analysis, e.g.:

(i) $V(T) = (0.1496 \pm 0.001047)T + (1002.0 \pm 0.2)$, $r^2 = 0.9993$, for C₁₆D₁₀ (form I; HRPD, ISIS Facility, RAL).

[1] Xu X., *Ph.D. Thesis*, University of Strathclyde, Glasgow, UK, 2005. [2] Love S.W., *Ph.D. Thesis*, University of Strathclyde, Glasgow, UK, 1997.

Keywords: pyrene, deuterium effect, powder X-ray diffraction

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Single Crystal and the Third Order non Linear of the Adeninium Dinitrate

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We report the measurement of the degenerate fourth-wave mixing (DFWM) of adeninium dinitrate in aqueous solutions at $\lambda = 532\text{ nm}$ in ps regime with different numbers of π -conjugated bonds. From these measurements, we evaluated the values of the second order hyperpolarizabilities γ , which are about 10^3 larger than the γ value of CS₂. The influence of π -conjugated bonds on the third-order susceptibilities and appropriate figures of merits is discussed. The more important seems to be the possibility of a simultaneous increase of the third-order susceptibilities, together with the decrease of the absorption coefficients that open a possibility of their use as promising materials for laser wavelengths mixing.

In the asymmetric unit of the title compound, C₅H₇N₅²⁺, 2NO₃, the adenine base is diprotonated and cocrystallizes with two nitrate anions. The structure is a layered one, and in each layer all H atoms bonded to O and N atoms are involved in a twodimensional hydrogen-bonding network. Short contacts are observed between parallel layers and ensure the cohesion of the crystals.

Keywords: hydrogen bonding, degenerate four wave mixing, third-order susceptibilities

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In-situ Diffraction Study of C₆₀ Polymerization under High-pressure High-temperature

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Polymerization in C₆₀ has been achieved using photochemical and high-pressure high-temperature (HP-HT) methods [1]. Both polymers have the same 2+2 cycloaddition polymeric bond but their crystal structures are very different. HP-HT polymers are ordered while photopolymers have a disordered fcc structure reflecting a random polymerization [2]. In order to understand the origin of bond order in HP-HT polymers and its absence in photopolymers we have performed in situ diffraction studies at the E.S.R.F. [3]. We have found that the applied anisotropic stress selects the bonding direction, which is crucial to obtain ordered polymeric structures since it avoids geometrical frustration inherent to 2+2 cycloaddition bonds in the fcc monomer lattice. The photochemical method having no symmetry-breaking field leads to a frustrated disordered fcc polymer. The highly anisotropic distribution of polymeric bonds in HP-HT polymers should be at the origin of the elastic anisotropy in the C₆₀-derived amorphous samples and the magnetic anisotropy in 2D-ordered polymerized C₆₀.

[1] Núñez-Regueiro M., Marques L., Hodeau J.L., Béthoux O., Perroux M., *Phys.Rev.Lett.*, 1995, **74**, 278. [2] Putzai T., Ozlányi G., Kamarás K., Gránásy L., Pekker S., *Sol. St. Comm.*, 1999, **111**, 595. [3] Marques L., Mezouar M., Hodeau J.-L., M.Núñez-Regueiro, *Phys.Rev.B*, 2003, **68**, 193408.

Keywords: fullerenes, high-pressure X-ray diffraction, polymerization

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Ortho-halogeno Piedforts

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In an effort to explore Piedfort pairing in a systematic way four 2,4,6-tris(ortho-halogeno-phenoxy)-[1,3,5]-triazine host molecules

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*

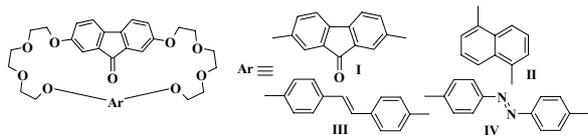
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Crystal Structures of Some Representatives of the Fluorenonocrownophanes

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Four new crownphanes 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 crownphanes 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*

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Crystal Structure of Isosteviol and its Derivatives

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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.

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

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Inclusion Compounds from a Decomposing Host: a Cautionary Tale

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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*

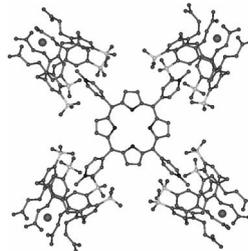
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Design and Crystallographic Characterization of Multi-Porphyrins Complexes

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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-