

resp. The crystal structures of compounds **1-4** were determined by single crystal X-ray structure analysis. Compound **5** was determined from scratch by X-ray powder diffraction.

From the crystal structures it is not evident why the compounds **1**, **3**, and **5** are fluorescent but **2** and **4** are not. Thus extensive quantum mechanical calculations have been made and the reason for the fluorescence quenching of **2** and **4** was finally found [1].

[1] Dreuw A., Wachtveitl J., Brüning J., Schmidt M. U., *in preparation*.

Keywords: organic pigments, crystal structures, fluorescence

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Structure of 19-Hydroxyneohopane

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Several fused multicyclic natural product ring systems, especially those that are saturated or nearly saturated, are poorly represented in the Cambridge Structural Database of crystallographic determinations of organic compounds.

19-hydroxyneohopane, $C_{30}H_{48}O$, is one such compound consisting of a five fused ring system (rings 1 to 4 containing six carbons and ring 5 containing five carbons) with two double bonds trans across the 2-3 ring junction. The compound was obtained from the rhizome of *Davallia solida* Sw and crystallizes in the monoclinic space group, $P2_1$, with two molecules in a cell of dimensions: $a = 12.587(3)$, $b = 7.558(3)$, $c = 13.620(3)$ Å, and $\beta = 102.68(3)^\circ$ at $T = 113(2)$ K.

Crystal Data: $C_{30}H_{48}O$, $MW = 424.68$, clear colorless plate crystal, $0.50 \times 0.50 \times 0.02$ mm, monoclinic, $P2_1$, $a = 12.587(3)$, $b = 7.558(3)$, $c = 13.620(3)$ Å, $\beta = 102.68(3)^\circ$, $V = 1264.10$, $Z = 2$ $T = 113(2)$ K, $d_{calc} = 1.116$ Mg m^{-3} , $\mu = 0.48$ mm $^{-1}$, $CuK\alpha$ radiation, $F(000) = 472$, $\sin\theta/\lambda_{max} = 0.545$ Å $^{-1}$, $R_{int} = 0.0688$, 3876 unique data, 3404 observed $F_o > 4\sigma(F_o)$, $R_I = 0.0737$, $goof = 1.126$.

Keywords: fused ring system, natural product, hopane

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X-ray Investigations of Bicyclic α -methylene- δ -valerolactones

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The α -methylene- δ -valerolactones moiety is present in various biologically active natural compounds, e.g. vernolepin, vernomenin, pentalenolactone *E*, teucrum lactone, artemisitene and crassin. However, work on isolation and synthesis of new α -methylene- δ -valerolactones has not led to a significant number of crystal structure investigations. A search of the CSD (version 5.26) shows that system in which δ -valerolactone ring is condensed with the cyclohexane moiety along the individual $C_\delta-C_\gamma$ single bond is unique among crystal structures examined to date. Investigated compounds represent a novel group of the optically active α -methylene- δ -valerolactones synthesized in a highly stereoselective Michael reaction. Recently we reported crystal structures of two compounds *i.e.* the 3-methylene-2-oxohexahydrochromene-4a-carboxylic acid ethyl ester [1] and the 4-methyl-3-methylene-octahydro-chromen-2-one [2]. The six following crystal structures will be shown in detail. In all compounds the δ -valerolactone rings adopt a half-chair conformation. The highly polar character of the carbonyl group hinders π electron density delocalization within the $O=C-C=C$ moiety. In the crystal, molecular conformation is stabilized by attractive interactions between the oppositely charged atoms. The mechanism of interactions has been investigated using NBO theory at the $MP2/6-31+G(d,p)$ level.

[1] Krawczyk H., Śliwiński M., Wolf W.M., Bodalski R., *Synlett*, 2004, 1995.

[2] Krawczyk H., Śliwiński M., Wolf W.M., *Acta Cryst.*, 2004, C60, o897.

Keywords: δ -valerolactone, crystal structure, NBO

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Conformation of Dioxaphosphopin Ring – Structures of 6-Substituted Benzo and Dibenzo [d,f] [1,3,2] Dioxaphosphopin 6-oxide (I) and Sulphide (II)

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The hetro cyclic form of organophosphorous compounds containing phosphoryl unit with suitable substitution exhibits significant physiological activity and they have unique multifaceted applications. Structural studies of organophosphorous compounds have gained considerable importance recently because of their use as insecticides, anti-cancer agents, lubricating oil additives and polymer stabilizers. As part of our continuing investigations on this molecules, we have investigated the structures of 6-substituted benzo and dibenzo [d,f] [1,3,2] dioxaphosphopin 6-oxide and sulphide to know the dependence of substituents on the conformation and geometrical parameters of dioxaphosphopin hetro ring. compound (I): $C_{15}H_{15}O_4P$, colourless crystals grown from methanol are Monoclinic $P2_1/c$ with $a = 9.441(1)$; $b = 15.202(2)$ and $c = 9.746(1)$ Å; $\beta = 95.8(2)^\circ$; $V = 1391.5(3)$ Å 3 ; $Z = 4$; $F(000) = 608$; $\rho_c = 1.385$ g cm^{-3} ; $\mu(Mo K\alpha) = 2.08$ cm^{-1} ; $R = 4.96$ and $R_w = 0.1157$ for 2457 unique reflections. compound (II): $C_{18}H_{11}O_3Cl_2P$ S, colourless crystals obtained from 2-propanol, Monoclinic $P2_1/n$ with $a = 10.816(6)$; $b = 13.615(8)$ and $c = 12.321(7)$ Å; $\beta = 99.6(9)^\circ$; $V = 1789.5(2)$ Å 3 ; $\rho_c = 1.519$ g cm^{-3} ; $Z = 4$; $F(000) = 832$; $\lambda(Mo K\alpha) = 0.71073$ Å; $R = 0.048$ and $R_w = 0.130$ for 2410 unique reflections. based on intensity data collected on Bruker Smart Apex diffractometer using Monochromated $MoK\alpha$ radiation, structures were solved by the direct methods and refined by full-matrix least squares methods. The seven membered dioxaphosphopin ring exhibits a pseudo-chair form for the former where as a distorted boat like conformation for the later. This is evident for the structural changes with different substituents fused to the hetro ring and also attached to the phosphorous.

Keywords: organophosphorous compounds, conformation of dioxaphosphopin ring, seven membered hetro ring

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N-isopropylamidino-substituted Derivatives of Benzo[b]thiophene-2-carboxanilides and Benzo[b]thieno[2,3-c]quinolones: DNA Binding by Intercalation

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Recently, we published syntheses, characterization and antitumor evaluation of series of cyano- and *N*-isopropylamidino-substituted derivatives of benzo[b]thiophene-2-carboxanilides and benzo[b]thieno[2,3-c]quinolones [1]. Aromatic surface of such aromatic compounds, usually built of three or more condensed aromatic units, is more than large enough for intercalation with the DNA. On the other hand, organic cations (*i.e.* amidinium cation) are known to bind in the DNA minor groove showing various biological activities, especially anticancer properties. The X-ray crystal structure study of 4'-carbomethoxy *N*-phenyl-3-chlorobenzo[b]thiophene-2-carboxamide and *N*-[4'-(*N'*-isopropylamidino)-phenyl]-3-chlorobenzo[b]thiophene-2-carboxamide hydrochloride is undertaken in order to compare their sterical properties with some classical intercalators and to give an answer if insertion between basepairs of DNA/RNA is possible.

[1] Jarak I., Kralj M., Šuman L., Pavlović G., Dogan J., Piantanida I., Žinić M.,

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-tetraphenylnaphthalene)

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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 naphthalene skeleton. Although the naphthalene 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 $T = 80$ – 140 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 $\lambda = 532$ 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