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Concomitant Polymorphs Exhibiting Differences in the Halogen Bonding Contacts

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The 'halogen bonding' interactions are receiving increasing attention due to their potential applications in crystal engineering and host-guest chemistry [1]. The C-halogen…O bonding is comparable in energy with the conventional H-bonding interactions [2]. Tri-*O*-p-halo-benzoyl-*myo*-inositol 1,3,5-orthoformates (halo = chloro (**1**), bromo (**2**)) produced concomitant polymorphs when crystallized from a number of solvents. Crystals (of **2** from chloroform) of Form I (Triclinic, P $\bar{1}$) were large octahedral blocks whereas Form II (Monoclinic, C2/c) were long, thin whiskers. Although common interactions such as Br…Br and C-H…O exist in both the forms, notable differences were seen in the halogen bonding contacts. Form I makes C-Br…O=C whereas Form II shows C-Br…O-C (orthoformate bridge) contacts. The Br…O distances are less than the sum of their van der Waals radii (3.173 Å in Form I & 3.027 Å in Form II) with better linearity in Form I (C-Br…O 173.8º) than in Form II (163.4º). To examine the propensity of the C-halogen…O contacts with differently hybridized O atoms, a brief survey of CCDC carried out showed better directionality of halogen bonds involving carbonyl oxygen than ether O atoms.

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Keywords: halogen bonding, polymorphism, inositol

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Hydrogen Bonding Study by X-ray Diffraction of Sugars and Aminoacids

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The aim of this work is to study the different types of hydrogen bondings, by X-ray diffraction at room and low temperature, in biologically active molecules such as carbohydrates and aminoacids.

The effort will be mostly focused on sulfonic acids and their derivatives as they are important constituents of living organism found in nature as taurine (2-aminoethanesulfonic acid), homotaurine (3-aminopropanesulfonic acid), cysteic acid or guanidotaurine, and on structurally related sulfoamino carbohydrates and sulfoaminopoliols. All of them posses physiological properties essential for the well-being of various species. Taurine is present in relatively high concentration in the central nervous system and brain, acts as neurotransmitter in retine, and shows cardioprotective activity.

These compounds show zwitterion structure, with electrostatic and hydrogen bonding interaction between the protonated aminogroups and the sulfonate groups, that have been scarcely studied in solid state.

Cooperative hydrogen bonding, three- and four-center hydrogen bonds, and the role of the water molecules in the crystal stability, will be subject of a special study.

The study also involves the structural analysis of these compounds, to stablish their conformational and configurational characteristic unequivocally.

Keywords: sulfonic acids, hydrogen bonds, zwitterions

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X-ray Structure of a Mixed Spiroketal-Xylylene Macrocyclic Receptor

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Difructose Dianhydrides (DFAs) are a family of up to 14 diastereomeric spiroketal disaccharides formed during thermal or acidic treatment of D-fructose-containing food materials, being the major constituents of caramel [1]. Among them, the C_2-symmetric bis-spiro di-β-D-fructopyranose isomer has been shown to exhibit strong metal cation complexing properties [2]. This unique behaviour makes it particularly attractive as building block for the construction of macrocyclic receptors. We have now prepared the first representative of this class of compounds by connecting two DFA motifs by two semirigid *p*-xylylene segments. Although the molecule conserves C_2-symmetry in solution, as seen by NMR, the X-ray structure (data collected at the Daresbury Synchrotron) reveals desymmetrisation in the solid state. The existence of an edge-to-face interaction between the two aromatic rings is probably responsible for this situation. Interestingly, the oxygen atoms involve in cation complexing in the parent spirodisaccharide are inside directed in the macrocycle, therefore showing high promise as ion-encapsulating receptor.

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Keywords: carbohydrate structures, macrocycles, receptor structures

P.06.01.4

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Trisaccharide Crystal Structures from X-ray Powder Diffraction and Solution NMR

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Carbohydrates belong to a large class of molecules that are ubiquitous in nature. Crystallographic information on oligosaccharides is limited due to their inherent difficulty to crystallize and especially to grow as single crystals. The direct-space methods are nowadays commonly used to solve crystal structures from X-ray powder data. Prior to calculations, the elaboration of the molecular model is an issue since carbohydrates are especially difficult to model because of their flexibility, polarity, and specific stereoelectronic effects (i.e. anomeric, exo-anomeric and/or gauche effects). Complementary investigations on carbohydrate conformations could be performed in solution by NMR spectroscopy. NMR techniques constitute a valuable tool for pyranose rings flexibility and glycosidic linkages study, and for the distinction of the multiple conformations that will coexist in solution. In the course of our studies on synthetic pentasaccharides active as antithrombin heparin inhibitors, we have determined the structures and conformations of several oligosaccharide precursors that are isolated as crystallized material without single crystals available. In this contribution, we report the crystal structures of two chemically protected trisaccharides, elucidated using X-ray powder diffraction data. These two trisaccharides being highly flexible, we imagined a method consisting of relieving the computational procedure by introducing geometrical features as deduced from 2D NMR solution studies.

Keywords: structure elucidation, powder diffraction, NMR

P.06.02.1

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Lipid Model Membranes for Drug Interaction Study

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The present work shows a structural study on the process of incorporation of a hydrophobic drug, Ellipticine (ELPT), into lipid model membranes for drug targeting purpose. The ELPT is an alkaloid that showed an anti proliferation activity against several types of tumour cells and against the HIV1 virus. In the context of drug targeting, there are several important processes and parameters to be studied. For instance, the drug loading efficiency into the lipid matrix, the order into the lipid system that encapsulates the drug, the lipid-carrier critical size and stability to transport the drug and the releasing mechanisms. We used the zwitterionic lipid dipalmitoylphosphatidylcholine (DPPC) and some other phopholipids with different size of head and tail and/or different net electronic charge both on a Langmuir monolayer and deposited on a solid substrate. First results appointed toward a strong increase in drug loading efficiency into DPPC lipid systems mixed with charged lipids. However, this increasing in loading efficiency was accompanied by a disturbance in the ordering of the bilayers. To characterize these systems we used Grazing Incidence X Ray Diffraction and also specular X Ray Reflectivity technique with synchrotron radiation at Troika II beamline-ESRF, France and also a rotating anode set-up at State University of Campinas, Brazil to monitor structural changes of loaded and non-loaded lipid systems.

Keywords: lipid mesophases, drug interaction, diffraction

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Crystal Structure of Chocolate from Powder Diffraction Data

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We solved the crystal structure of the β(V)-form of chocolate and cocoa butter (CB). Chocolate is a made from cocoa and sugar in a complicated process. At room temperature it consists of a well-crystallised continuous CB matrix in which fine cocoa powder and sugar particles are dispersed. In good quality consumer chocolate, the CB is crystallised in one of the two highest melting forms, β(V) or β(VI). Poor storage or improper production may result in fat bloom, the whitish layer on chocolate that is commonly associated with the phase transition from β(V) to β(VI). Any CB consists for 75% of three triacylglycerols, SOS (1,3-distearoyl-2-oleoylglycerol), POS (2-O-1-palmitoyl-3-S-glycerol) and POP. In particular SOS is known to play a major role in the β-crystallisation of CB.

The powder patterns of chocolate, CB and SOS are very similar suggesting a close structural relation. Unit cells were obtained with an indexing routine written specially for this purpose by RP. The cells of β(V)-CB and β_2-SOS are very similar and, surprisingly, so are the indexing figures of merit M_{20}. We solved SOS (63 unique non-H atoms), using the programs FOX and ORGANA. After refinement we used this structure as a starting model to solve and refine the structure of β(V)-CB, employing partial occupancies (57%) for the two end-carbon atoms of both stearin chains. Our results show a considerably different packing as postulated earlier. Moreover the crystal structure gives rise to the explanation of the mechanism of the β(V) to β(VI) phase transition of CB. This is supported by the XRD of β-POS.

Keywords: SDPD, chocolate, structure of cocoa butter

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X-ray Analysis as the Important Tool in Controlling Stereoselective Synthesis of Drugs

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Alkaloids form a group of natural heterocyclic compounds exhibiting valuable pharmacological properties: from painkilling and antihypertensive, through antidepressant and antipsychotic to anticancer. Some of them have dangerous narcotic, hallucinogenic and paralysing action. The bioactivity of compound, in great degree, depends on its stereochemical constitution and hence much effort has been made to develop new, bio mimetic methods of stereoselective synthesis of alkaloids and other heterocyclic compounds. Although the results of chemical synthesis are usually widely documented by many physicochemical methods, the final proof for stereochemistry is possible only after crystal structure determination. Here we propose a new method of synthesis using natural amino acids as building blocks which define three-dimensional structures of products. The case of 16 isoquinoline and β-carboline alkaloids and the application of X-ray methods to determine stereochemistry of products serve as an example. Quantum chemical calculations suggest thermodynamically controlled reaction.

Keywords: alkaloids, structure, modelling

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Structures of Cocrystals of Peganole with 6-Brompeganole

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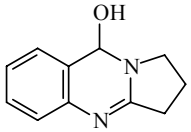
The crystal structures of two polymorphic cocrystals (I, II) of peganole (1) with 6-brompeganole (**2**) have been determined. Both forms are in the monoclinic system with space group of P2(1)/n. Cell parameters of I are a=8.232(4), b=11.768(8), c=10.156(6)Å, β=98.12(4)°, V=974.0(10) Å^3 and II are a=7.995(6) , b=15.501(8), c=8.816(6), β=112.25(5)°, V=1011.2(11) Å^3.

It is interesting to note that asymmetric unit of cell in both case consist of one molecule where this molecule at the same time can be **1** or **2**. Site occupation factors of molecules **1** and **2** are ~0.7 and ~0.3 (in I) and ~0.3 and ~0.7 (in II) respectively.

As well, tests on composition of single crystals by High-Performance Thin-Layer Chromatography (CAMAG, Switzerland) confirms the X-ray results.



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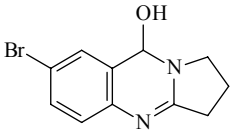

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Keywords: cocrystals, polymorphs, small-molecule single crystals

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Crystal Structures of Fluorescent Bisazomethine Pigments

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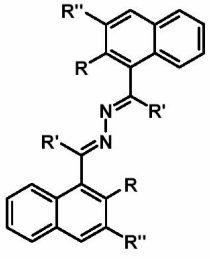
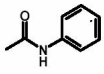
Pigment Yellow 101 (**1**) is a well-known greenish-yellow fluorescent organic pigment. The compounds **1-5** were synthesized and crystallized from DMSO, xylene and CH_3OH/C_2H_5OH mixtures



Compound	1 P.Y.101	2	3	4	5
R	OH	OCH_3	OH	H	OH
R'	H	H	CH_3	H	H
R''	H	H	H	H	
Solid state fluorescence	yes	no	yes	no	yes