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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

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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

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Lipid Model Membranes for Drug Interaction Study

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