

water structure.

References

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Keywords: water, nanopipe, nanowire

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H-bonds in andrographolide and related molecules: Neutron diffraction, database and modeling studies

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The biologically active natural product andrographolide has OH and CH₂OH groups at adjacent positions on a decalin ring. Our neutron diffraction study confirms that the OH group is the donor and O(H)CH₂ the acceptor in an intramolecular hydrogen bond (IHB) with H ··· O 1.743(6) Å and O-H ··· O 153.9(5)°, the latter group hydrogen bonding to the OH group of a nearby molecule. A priori this scheme seems preferable since with two rotatable bonds CH₂OH should adapt better than OH to the vagaries of crystal packing. However, an X-ray study of a derivative acetylated at a remote OH group showed the reverse pattern. A CSD search with normalized H atoms for cyclohexane rings with adjacent OH and CH₂OH groups gave 34 matching fragments: 7 with OH ··· O(H)CH₂ ≤ 2.3 Å, 13 with CH₂OH ··· OH ≤ 2.3 Å, the remainder with weaker or no IHB. The former class has 'better' IHB with <H ··· O> 1.82 Å and <O-H ··· O> 142° vs. 1.90 Å and 137°, yet is less numerous. Molecular dynamics suggests a swap to the former when cyclohexane changes to decalin. Cluster analysis with dSNAP classifies mainly IHB type but also substituent location. Work supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under contract DE-AC02-06CH11357, and the Malaysian Ministry of Science, Technology and Innovation (MOSTI) grant no. 02-01-04-SF0089.

Keywords: neutron diffraction, hydrogen bonding, natural products

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Crystal structure of trehalose dihydrate by X-ray and neutron diffraction experiments

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Trehalose is a non-reducing disaccharide that is a frequently synthesized in living organisms as an intracellular protectant or co-protectant against harsh conditions, permitting organisms to survive dehydration or freezing. As this characteristic property is still open to argument, a large number of studies on biopreservation have been performed. However, there are few reports on the crystallographic investigation for trehalose. We have, therefore, tried to determine

both the crystal structure and the electron density distribution (EDD) of trehalose dihydrate using the single-crystal X-ray and neutron diffraction data for understanding of the structural characteristics. The crystal structure of trehalose dihydrate was refined with the data at room temperature. Furthermore, in order to reduce an influence of atomic displacement parameters on the structure refinement, X-ray diffraction intensity has been measured at low temperature. Both the refinement and MEM analysis were performed for obtaining the EDD again. From the results, the covalent bonding was confirmed to exist between the trehalose and the internal water. The EDD, thus obtained, was compared with that calculated using the full-potential linealized augmented plane wave (FLAPW) method.

Keywords: absolute structure determination, electron density distribution, trehalose dihydrate

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Temperature-dependent structural change of trehalose dihydrate and anhydrate crystals

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Thermal analysis method is widely used in order to determine the phase transition temperature for the easier technique, but it is difficult to obtain a detailed information of the temperature. On the other hand, *in-situ* high-temperature powder X-ray diffraction technique is a powerful tool to investigate a detailed structural change. We have, therefore, determined both the crystal structures and the phase transition temperature of trehalose dihydrate and anhydrate crystals using the high-temperature *in situ* powder X-ray diffraction data and the detailed temperature-dependent structural change was investigated. Trehalose anhydrate was obtained by dehydrating from trehalose dihydrate. The melting and crystal-amorphous phase transition peaks of trehalose anhydrate by DSC and TG-DTA were confirmed that it is around 453K. The crystal structure of trehalose anhydrate was refined with the use of powder X-ray diffraction data between 373K and 467K. From this result, trehalose anhydrate have crystal-amorphous phase transition at 461K. For trehalose dihydrate, the same experiment was performed and crystal-amorphous phase transition temperature was confirmed to be around 353K. The structural parameters, i.e. changes of atomic distance in trehalose molecule, were obtained at this temperature. The result, thus obtained, was compared with that calculated using molecular dynamics method.

Keywords: Rietveld structural refinement, *in-situ* powder diffraction, phase transitions

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HTXRD and XRD-DSC study of crystalline-noncrystalline phase transition of sucrose crystals

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Sucrose is one of the most abundant pure organic chemicals in the world and the one most widely known to nonchemists. In recent years, sucrose is reported as a functional material for developing alternative biofuel cells which use biocatalysts to convert energy from sugar into electrical power. However, melting points among sucrose crystals with high purity are occasionally different with each other and the melting points quoted references range from 160°C to 192 °C. Although many researchers have studied the melting point by using differential scanning calorimetry (DSC) or optical microscope, there are few reports on the microscopic observation of the crystalline - noncrystalline phase transition of sucrose. In the present work, using high-temperature X-ray diffraction (HTXRD) and simultaneous instruments for X-ray diffractometry and differential scanning calorimetry (XRD-DSC), we have investigated some possible factors involved in the noncrystallization from the crystalline state under isothermal and non-isothermal conditions. The sucrose from commercial source and its recrystallized one were used. XRD-DSC results showed the occurrence of two peaks around 150 °C and 175°C for recrystallized sucrose at heating rate of 10°C/min, while no significant change in the XRD patterns at the first peak was observed during the heating process. The noncrystallization point moved to high temperature as the rate of heating was increased. The Rietveld analysis of HTXRD data is a key point for understanding the mechanism and kinetics of crystalline – noncrystalline phase transition of sucrose under isothermal condition.

Keywords: sucrose, noncrystallization, kinetics

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Structure of sodium L-malate monohydrate

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An X-ray investigation of the title compound was carried out in order to elucidate unequivocally its molecular conformation in the solid state. The structure of sodium L-malate monohydrate Na₂(C₄H₄O₅).H₂O has been determined at room temperature using single-crystal MoKa diffraction techniques with 2011 measured independent reflections at diffraction angles lower than 30°, and 1096 were considered as observed (2s(I)), giving R= 0.05 in the structure refinements. The structure crystallizes in the monoclinic *P*2₁2₁, Z=4, with unit cell parameters *a*= 6.312(1), *b*= 9.766(1) and *c*= 11.221 Å. The crystal packing is governed by hydrogen bonds. L-malic acid, used as a means for creating two-dimensional anionic networks held together by O-H...O hydrogen bonds, has also been demonstrated to be a suitable anionic building block. We have synthesised a new crystal with an interesting hydrogen bonding network, the L-malate ions are linked together with H-bonds involving carboxylate and OH groups forming infinite helical molecular chains parallel to the *a* direction. These chains, in turn, are interconnected in the *bc* plane via H-bond links to intermediate water molecules.

Keywords: crystal engineering, single-crystal X-ray diffraction, hydrogen bonding

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X-ray structure and hydrogen bonding study of taurine and N-(glucitol-1-yl)taurine

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As a part of our continuing interest in this field we report here the crystal structure by X-ray diffraction of these active molecules, taurine (2-aminoethanesulfonic acid) and their derivative N-(glucitol-1-yl)taurine at low temperature in order to establish their conformational and configurational characteristic unequivocally and also to describe their hydrogen-bonding patterns, as they are important constituents of living organism found in nature. Taurine is one of the lesser-known amino acids, nevertheless it plays a role in the body and is essential to newborns of most mammal species, and it also protects our bodies against damage from radiation, is present in relatively high concentration in the central nervous system and brain, acts as neurotransmitter in retina, and shows cardio protective activity. The stability of these compounds that shown zwitterions structure, with electrostatic and hydrogen bonding interaction between the protonated aminogroups and the sulfonate groups results from a network of hydrogen bonds, which maintain the cohesion in the crystal and have been scarcely studied in solid state.

Keywords: zwitterions, hydrogen bonds, X-ray diffraction

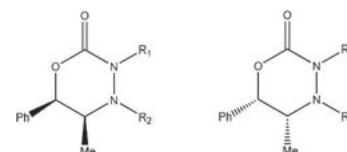
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Binary mixtures of a series of oxa-3,4-diazinan-2-ones

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Structural characterization of a series of 5-methyl-6-phenyl-oxa-3,4-diazinan-2-ones has been carried out. The molecules of interest have been isolated as enantiomerically pure samples. All have two chiral centers, both on the heterocycle in the five and six positions. In addition to structurally characterizing several of the enantiomerically pure samples, various binary mixtures of racemates and pseudoracemates have been prepared, crystallized, and structurally characterized. The likely form of the crystallized products could be mixtures of optically pure crystals, racemic twins, centrosymmetric racemates, pseudo-centrosymmetric racemates, or mixtures of two compounds roughly occupying the same crystallographic positions, where the varying R group appears at half occupancy. For example, (5*R*, 6*S*) 4-isopropyl-5-methyl-6-phenyl-2*H*-1,3,4-oxadiazinan-2-one and (5*S*, 6*R*) 4-isopropyl-5-methyl-6-phenyl-2*H*-1,3,4-oxadiazinan-2-one crystallize individually as isostructural non-centrosymmetric structures in *P*2₁2₁2₁; however, a binary mixture of these two enantiomers crystallize as the racemate in *C*2/*c*.



Keywords: oxadiazinanones, racemates, pseudoracemates