

Molecular interactions insights from high-resolution fiber-diffraction structures of polysaccharide solvates

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ABSTRACT: Over the last two decades, we have studied the crystal structures of polysaccharides such as cellulose¹ and chitin². Samples with large crystallite size and high uniaxial orientation yields diffraction data with high spatial resolution. Combined with relatively small unit cells, we could use conventional crystallography approach based on individual diffraction intensities to directly locate missing atoms in the Fourier maps. The use neutron as probe further allowed us to study the hydrogen positions.

Some solvate crystals can be prepared without modifying the integrity of each crystalline fibrils, or grow into relatively large crystallites allowing us to locate the guest molecules at atomic resolution. One such example is the cellulose-amine complexes where ammonia or ethylene diamine molecules spontaneously penetrate into cellulose crystal. The non-hydrogen atoms of both ammonia and ethylene diamine molecule could be directly located in the unit cell from X-ray diffraction data.³ Inspection of the structures shows that the position of nitrogen atom is associated with the primary alcohol O6 of cellulose. Neutron diffraction showed the hydrogen atom between O6 and the nitrogen of ammonia, but hydrogen atoms of ammonia could not be localized. The O6 would be donating hydrogen bond to ammonia, while the hydrogen atoms of ammonia remains highly mobile inside the

structure. Similar structure was observed in the β -chitin/ethylenediamine and α -chitin/hydrazine complexes⁴, in which again the O6 is donating to the amine. Mixing alcohol and amine is highly exothermic since amines are only weakly hydrogen bond donor and strong hydrogen bond acceptor. Thus, accepting hydrogen bond from the primary alcohol would be the driving force for the strong polysaccharide swelling capacity of amines. The secondary alcohols are not involved in hydrogen bond with the amine, probably because their limited degree of freedom does not allow favorable hydrogen bond geometry and compact packing at the same time.

An unexpected structure is the β -chitin dihydrate, in which the inter-molecular hydrogen bond does not exist despite the proximity of the O3 to the ring oxygen O5 of the neighboring residue. All other known structures of cellulose and chitin have the intramolecular hydrogen bond between O3 and O5 which has been considered as a structural constant of cellulose analogues. In the dihydrate the O3 hydroxyl was directed to the water molecule and no hydrogen was found at the proximity of ring oxygen.

High-resolution diffraction data involving other solvents and polysaccharides are emerging.⁵ Challenges for structure determination lie in the larger unit cell size / lower symmetry or disorders in the crystals, but further combination with molecular modeling would lead to extraction of reliable structural information that are key to understand their molecular interactions.

KEY WORDS: Fiber diffraction, cellulose, chitin, molecular interactions

References

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