

CRYSTAL STRUCTURES AND HYDROGEN BONDING IN CELLULOSES I α , I β , AND II

James A. Kaduk, BP Chemicals, Naperville IL 60566 and
Paul Langan, Biosciences Division, Los Alamos National Laboratory, Los Alamos NM 87545

Quantum chemical geometry optimizations have been carried out for celluloses I α , I β , and II using density functional plane wave pseudopotential techniques. The resulting improved structural models provide insight into the intra-chain and inter-chain hydrogen bonding (which includes both O-H \cdots O and C-H \cdots O hydrogen bonds) in these three polymorphs. The optimizations have resulted in structures for cellulose I β and cellulose II that are in good agreement with recently-reported high-resolution X-ray fiber diffraction studies. No diffraction structure has been reported yet for cellulose I α , and therefore the structure reported here is an important contribution to our understanding of cellulose. The H-bonding arrangement reported for cellulose I β is also in excellent agreement with recently reported high-resolution neutron fiber diffraction studies. Although the intra-chain H-bonding arrangement reported for cellulose II is in good agreement with recently reported neutron fiber diffraction studies, the inter-chain H-bonding arrangement is not. The H-bonding structure reported for cellulose I α is unique in that it involves an alternation in H-bonding between glucose residues along the cellulose chain. The differences in the H-bonding arrangements observed in the different polymorphs provide important insights into the factors that determine their stability and properties.

Cellulose is probably the most abundant biomacromolecule, and is encountered in the powder diffraction laboratory as the filter paper which has trapped deposits, and also (as microcrystalline cellulose) as the binder in many pharmaceuticals. The increasing use of the Rietveld method for quantitative phase analysis provides the impetus for developing improved structural models for the various forms of cellulose.

The structures presented here have been used to calculate powder diffraction patterns for use in qualitative phase analysis. The powder diffraction pattern calculated for cellulose I β is in good agreement with experimental patterns of filter paper and microcrystalline cellulose. Quantitative analysis of cellulose/sucrose mixtures was complicated by difficulties in preparing accurate mixtures. However, the final agreement between experiment and calculation provide an important proof-of-principle application of the Rietveld method to the analysis of cellulose-containing mixtures.