Quantum Chemical Studies of α-, β- and γ-Cyclodextrin Monomers and Dimers

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Cyclodextrin (CD), a cyclic oligosaccharide produced from starch, is an interesting host molecule because of its ability to form inclusion complexes with a variety of guest molecules as well as self-assembled clusters, i.e., dimer, trimer, tetramer and so on. Many computational calculations of CDs and CD complexes have been previously reported. However, high-level quantum chemical calculations have been limited due to their large system size and conformational degrees of freedom.

In this work we report the structures and intra-/inter-molecular interactions in conformers of CDs and CD dimers using quantum chemical methodologies. The geometries of α-, β- and γ-cyclodextrin and their dimers are optimized and harmonic vibrational frequencies of these optimized structures are calculated using the B3LYP and ωB97XD density functionals with the 6-31G(d,p) basis set. Initially, the geometry optimizations were performed from the X-ray structures. Subsequently, the conformers with a homodromic hydrogen bonding network and C_n symmetry ($n = 6, 7, 8$ for the α-, β- and γ-cyclodextrin, respectively) were optimized. The resulting isomers were grouped into families which lie close in energy. For example, there are four low energy conformers of α-cyclodextrin with C_6 symmetry that are almost isoenergetic. Dimer structures were constructed from the low energy monomer isomers and accurate estimates of the dimer binding energies are obtained.