Atomic and molecular clusters: designer materials for the nanoworld

The scientific community at present seems to be obsessed with nanomaterials and the ways they open up for miniaturization of devices. While the preparation of nanomaterials per se does not seem to be that difficult, their characterization and utilization in meaningful ways poses a challenge to scientists as well as technologists. Nanomaterials can be prepared either by the bottom up or by the top down approach. The latter approach has been known for long. The former approach has become possible due to developments in ultrahigh vacuum, molecular beam and laser techniques. A theoretician finds it easier to follow the bottom up approach as a logical extension of building atoms from fundamental particles and molecules from atoms. One can use atoms and molecules as building blocks and form supramolecules that constitute nanomaterials.

The discovery of fullerenes opened up ways of constructing large atomic clusters of various shapes and sizes and research has been going on for the last two decades in discovering similar cage structures and modifying the known cage structures to yield materials with different characteristics. While the covalent bonds linking the atoms in these large clusters provide them the stability, they also make these structures rigid. Hydrogen bonded molecular clusters, on the other hand, have the required stability and also the flexibility for modification.

The interaction between two water molecules is perhaps the classic example of a hydrogen bond in which a hydrogen atom that is covalently bonded to one electronegative atom like oxygen is (hydrogen) bonded with another electronegative atom. As more and more water molecules are added, a pattern emerges. While the dimer is linear, the trimer, tetramer and the pentamer are cyclic. Three dimensional arrangement of water molecules starts with the hexamer, which can assume a nonplanar open book or a cage structure, depending on the experimental conditions. The 8-mer forms a stable cube and the 12-mer and the 16-mer form stacked cubes. The 10-mer and the 15-mer form pentagonoids. The 20-mer can form either a stacked cube or a stacked pentagon structure. Interestingly, the hollow three dimensional fullerene like cage structure for the 20-mer is less stable. However, if you can put a molecule of methane inside, the cage becomes stable. Gas hydrates seem to be made of such stuffed cages.

The arrangement of water molecules in a cluster is known to depend on the environment. Having studied fullerenes and water clusters, one wonders about the shape of water clusters inside the confines of a fullerene cage. The fullerene cage is so stable and the space within is so limited, water clusters inside the fullerene cage assume unusual geometries. The dimer no longer has a linear hydrogen bond as illustrated in Figure 1. The tetramer assumes a tetrahedral arrangement! The properties of individual atoms and molecules tend to change when confined to a cage of nano dimensions.

Many other molecules that can form hydrogen bonds also form readily molecular aggregates of various shapes and sizes. Solid boric acid is known to have a graphite like structure. That is, boric acid molecules are arranged in a network of hexagons in a plane

and several such planes are stacked on top of each other. However, if boric acid molecules could be made to come together to form a pentagon, the larger clusters tend to curl up and form bowls and eventually balls like the fullerenes as illustrated in Figure 2 and Figure 3. As a matter of fact, larger boric acid clusters can form cages inside cages.

Hydrogen peroxide is a textbook example of a molecule taking up a nonplanar open book structure. The dimer of hydrogen peroxide is a closed structure, with each molecule behaving as a hydrogen donor as well as an acceptor. The trimer also forms an open book structure and as more and more hydrogen peroxide molecules are added, a helical structure emerges!

References:

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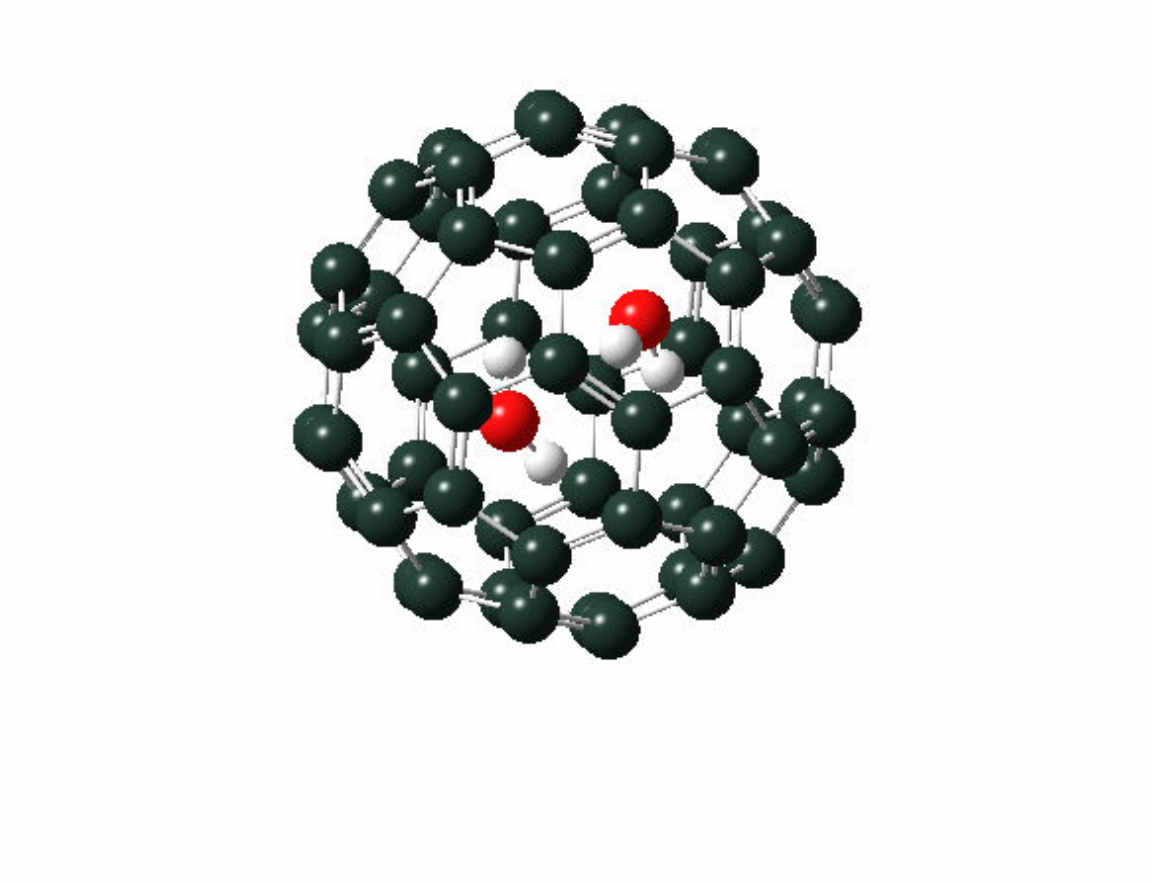

Figure 1. The optimized geometry of water dimer inside fullerene cage as obtained from Hartree-Fock calculations using 6-31G basis set.

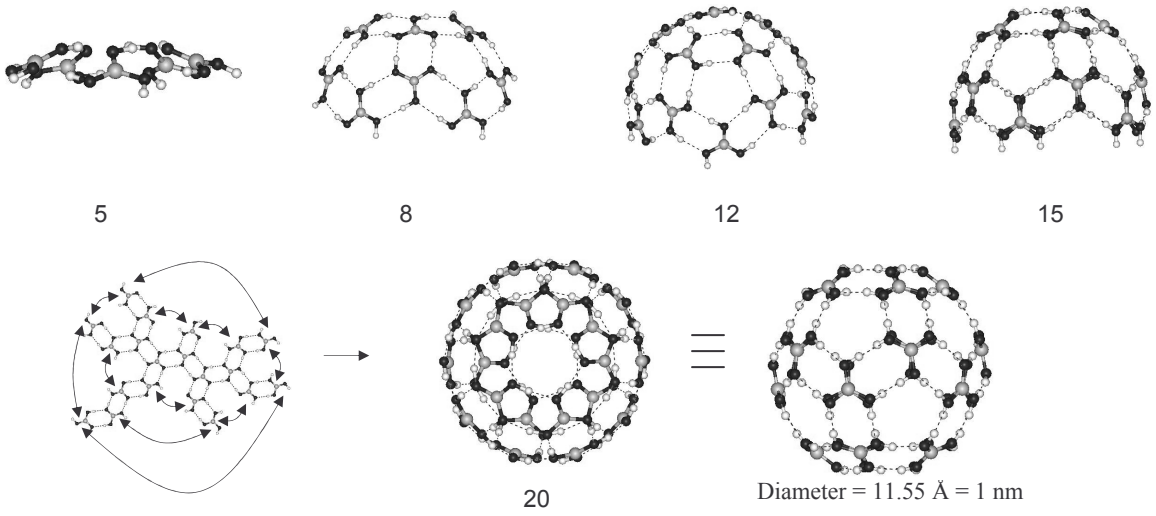

Figure 2. Optimized geometries of bowl shaped structures and boric acid ball obtained by ab initio electronic structure calculations. Initial geometry, which self-assembled to form buckyball upon optimization, is also provided. The black spheres represent oxygen atoms, large grey spheres represent boron atoms and smaller white spheres represent hydrogen atoms.

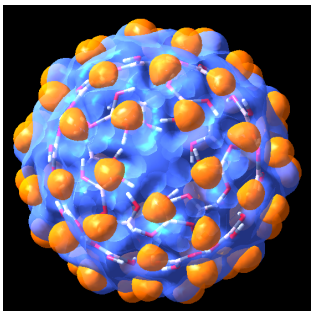

Figure 3. Molecular electrostatic potential map of $(BA)_{20}$ cluster. Blue color represents +0.01 au valued isosurface and orange color represents -0.01 au valued isosurface.