LARGE WATER CLUSTERS AND DFT PERFORMANCE

Truhlar has made a comparison of binding energies and relative energies of five $(H_2O)_{16}$ clusters.[1] While technically not organic chemistry, this paper is of interest to the readership of this blog as it compares a very large collection of density functionals on a problem that involves extensive hydrogen bonding, a problem of interest to computational organic chemists.
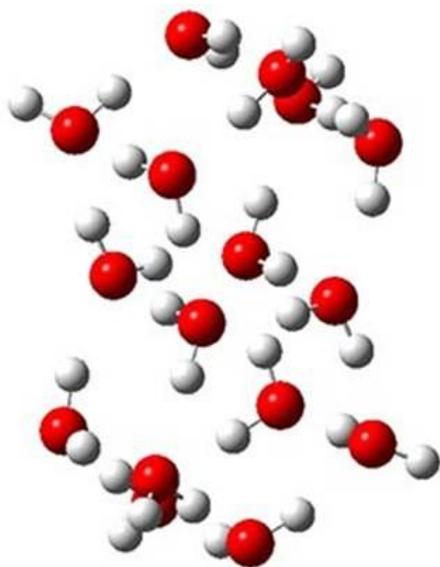
The CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ energies of clusters **1-5** (shown in Figure 1) were obtained by Yoo.[2] These clusters are notable not just for their size but also that they involve multiple water molecules involved in four hydrogen bonds. Truhlar has used these geometries to compute the energies using 73 different density functionals with the jun-cc-pVTZ basis set. Binding energies (relative to 16 isolated water molecules) were computed along with the 10 relative energies amongst the 5 different clusters. Combining the results of both types of energies, Truhlar finds that the best overall performance relative to CCSD(T) is obtained with ωB97X-D, a hybrid GGA method with a dispersion correction. The next two best performing functionals are LC-ωPBE-D3 and M05-2x. The best non-hybrid performance is with revPBE-D3 and B97-D.
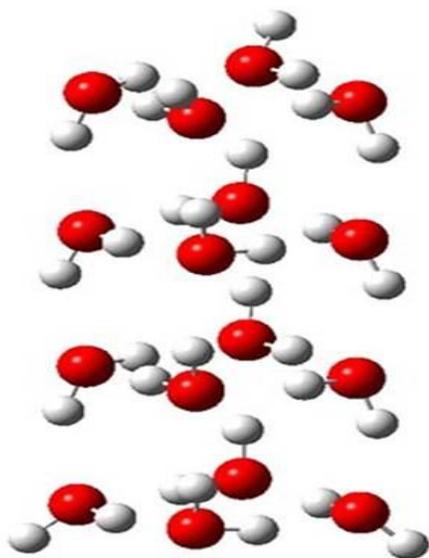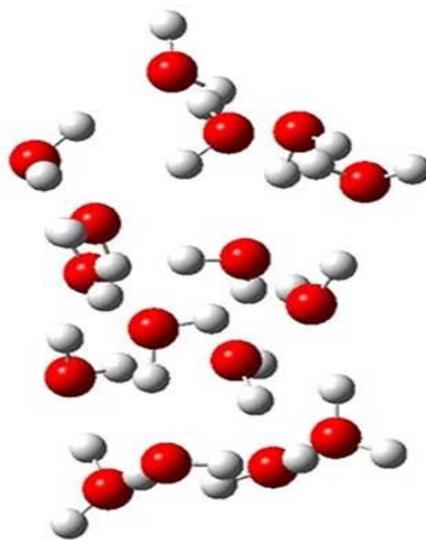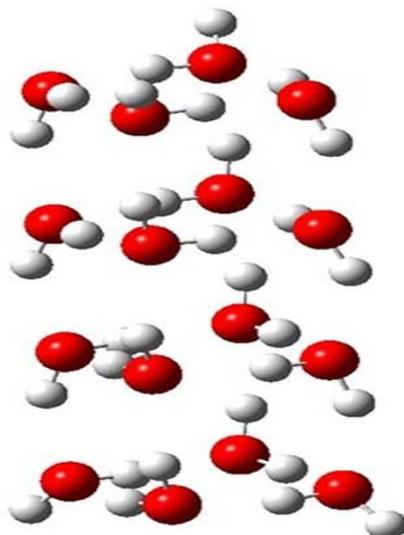
1 (0.0)
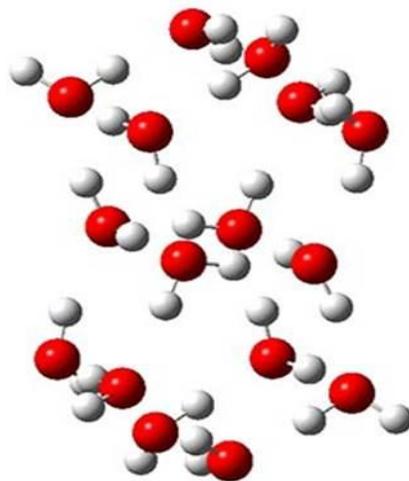
2 (0.25)

3 (0.42)

4 (0.51)

5 (0.54)

Figure 1. MP2/aug-cc-pVTZ optimized geometries and relative CCSD(T) energies (kcal mol^{-1}) of (water)$_{16}$ clusters **1-5**. (**Don't forget to click on any of these molecules above to launch *Jmol* to interactively view the 3-D structure.** This feature is true for all molecular structures displayed in all of my blog posts.)

While this study can help guide selection of a functional, two words of caution. First, Truhlar notes that the best performing methods for the five (H$_2$O)$_{16}$ clusters do not do a particularly great job in getting the binding and relative energies of water hexamers, suggesting that no single functional really stands out as best.

Second, a better study would also involve geometry optimization using that particular functional. Since this was not done, one can garner little here about what method might be best for use in a typical study where a geometry optimization must also be carried out.