BENCHMARKING DFT FOR ALKANE CONFORMERS

Another benchmark study of the performance of different functionals – this time looking at the conformations of small alkanes.[1] Martin first establishes high level benchmarks: the difference between the *trans* and *gauche* conformers of butane: CCSD(T)/cc-pVQZ, 0.606 kcal mol^{-1} and W1h-val, 0.611 kcal mol^{-1}; and the energy differences of the conformers of pentane, especially the TT and TG gap: 0.586 kcal mol^{-1} at CCSD(T)/cc-pVTZ and 0.614 kcal mol^{-1} at W1h-val.

They then examine the relative conformational energies of butane, pentane, hexane and a number of branched alkanes with a slew of functionals, covering the second through fifth rung of Perdew's Jacob's ladder. The paper has a whole lot of data – and the supporting materials include Jmol-enhanced visualization of the structures! – but the bottom line is the following.

The traditionally used functionals (B3LYP, PBE, etc) overestimate conformer energies while the MO6 family underestimates the interaction energies that occur in GG-type conformers. A dispersion correction tends to overcorrect and leads to wrong energy ordering of conformers. But the new double-hybrid functionals (B2GP-PLYP and B2K-PLYP) with the dispersion correction provide quite nice agreement with the CCSD(T) benchmarks.

Also worrisome is that all the functionals have issues in geometry prediction, particularly in the backbone dihedral angles. So, for example, B3LYP misses the τ_1 dihedral angle in the GG conformer by 5° and even MO6-2x misses the τ_2 angle in the TG conformer by 2.4&deg.

Source: http://comporgchem.com/blog/?p=480