Comment on "Thermodynamic stability of neutral and anionic PFOS: A gas-phase, n-octanol, and water theoretical study"

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In their article, Montero-Campillo et al. [1] use the B3LYP density functional with the 6-311+G(d,p) basis set to calculate the relative thermodynamic stabilities of the 89 linear and branched perfluorooctane sulfonic acid (PFOS) isomers in their molecular acid and dissociated anionic forms for the gas phase and aqueous and n-octanol solvent phases. A substantial body of work over the past decade has clearly demonstrated the inability of the B3LYP functional (and the majority of other widely employed density functionals) to accurately represent the relative thermodynamic stabilities of linear and branched alkanes (including perhydro, poly- and perhalogenated, and other functionalized derivatives) [2–13].

In prior [14, 15] and more recent [16, 17] work, we have specifically demonstrated using a range of theoretical methods (semiempirical, Hartree-Fock [HF], various density functionals, and second order Moller-Plesset perturbation theory [MP2]) that the B3LYP branching error for perhydroalkane isomerizations also applies to perfluoroalkanes, and particularly to classes of compounds such as the 89 PFOS isomers, as well as the perfluoroalkanoic acids and perfluoralkyl sulfonyl/acyl fluorides in their acid and (where applicable) anionic forms. Consequently, the relative thermodynamic stabilities of the molecular acid and anionic PFOS isomers at the B3LYP/6-311+G(d,p) level of theory in ref. [1] are in substantial error, and the authors and readers are referred elsewhere to more accurate calculations.

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