Accurate Three-body Noncovalent Interactions: the Insights from Energy Decomposition

Sharon Ochieng and Konrad Patkowski

Department of Chemistry and Biochemistry, Auburn University, Auburn, AL 36849

E-mail:

Abstract

Noncovalent interactions exhibit a wide range of binding characteristics governing the complex structure, energetics, and material self-assembly; as such, accurate models are required to predict these interactions. While there exist ample datasets of accurate interaction energies for bimolecular two-body complexes, the benchmark data for nonadditive three-body interactions are quite scarce. In this work, we present a benchmark dataset of noncovalent interaction energies for a diverse selection of 10 heteromolecular trimers in 20 structures. The new 3BHET dataset presents complexes that model different interactions ranging from $\pi - \pi$, anion$-\pi$, cation$-\pi$, and various motifs of hydrogen and halogen bonding and their combinations within each trimer. A detailed symmetry-adapted perturbation theory (SAPT)-based energy decomposition analysis shows that, at the two-body level, 3BHET spans the electrostatic and dispersion-dominated regions of the ternary diagram. Among the nonadditive three-body contributions, the induction energy plays a particularly important role.