Connectivity-Based Hierarchy (CBH): A Route to Highly Accurate Reaction Enthalpies of Organic Reactions with Cheap DFT Methods

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The generalized connectivity–based hierarchy (CBH) developed in our group, comprises of well-defined and reliable error cancellation schemes to derive accurate enthalpies of formation of both *open* and *closed* shell organic molecules at modest computational cost.[1-4] Herein, we demonstrate the application of the CBH schemes to calculate accurate reaction enthalpies of a broad variety of organic reactions using inexpensive computational methods such as MP2 or DFT. A benchmark set of 25 organic reactions of medium and large molecules (consisting of 17 to 81 atoms) has been composed to evaluate the performance of a range of quantum chemical methods. The isoatomic CBH-2 correction results in dramatic improvement for all the DFT methods including B3LYP, wherein an error of 45 kcal/mol is reduced to only 6 kcal/mol. The present protocol cancelling out the intrinsic errors within each method across different reaction types offers a unique platform to assess the universal proficiency of different *ab-initio* and DFT based methods. The CBH-2 corrections in BMK, B3LYP-D3, B2PLYP, and B2PLYP-D3, resulted in mean absolute errors < 1.5 kcal/mol against G4 method.

References:

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