Intramolecular Dispersion

Brandon D. Magers and Wesley D. Allen

Center for Computational Quantum Chemistry & Department of Chemistry,
University of Georgia, Athens, Georgia 30602

Recently synthesized diamondoid dimers such as 1-(1-diamantyl) diamantane and 2-(1-diamantyl)[121]tetramantane exhibit the longest C–C covalent bonds ever observed, up to 1.71 Å in length [1]. Despite severe steric crowding and highly stretched central bonds, these compounds are stable even at temperatures above 200 °C. This stability has been attributed to "attractive dispersion interactions" between the coupled diamonoid units of these molecules. Such phenomena, as well as ongoing debates over the protobranching concept, highlight the need for defining and quantifying dispersion interactions *within* rather than between molecules. In the 1-(1-diamantyl) diamantane case, our formal thermochemical analysis based on massive MP2, CCSD, and CCSD(T) wave function computations with aug(H)-cc-pVDZ and aug(H)-cc-pVTZ basis sets reveals that intramolecular dispersion greatly stabilizes the central C–C bond by nearly 36 kcal mol^{-1}. In comparison, DFT methods that seek to incorporate dispersion yield a disturbing scatter of results.

In order to place the concept of intramolecular dispersion on a firm theoretical footing that does not involved artificial partitioning into molecular fragments, we have developed a new approach for dividing electron correlation energies given by general wave function methods into long- and short-range components.   By means of new analytic integrations and inverse error-function transforms, we show how the Coulomb operator within two-electron integrals can be split using switching functions previously inaccessible to electronic structure theory. An optimal form of the switching function allows MP2, CCSD, and CCSD(T) correlation energies to be computed as a function of a sharp cutoff distance over which electrons are allowed to interact. Preliminary results from this methodology are presented for the benzene dimer and other benchmarks that challenge common understandings but are supported by simple physical models.

[1] P. R. Schreiner, L. V. Chernish, P. A. Gunchenko, E. Yu. Tikhonchuk, H. Hausmann, M. Serafin, S. Schlecht, J. E. P. Dahl, R. M. K. Carlson, and A. A. Fokin, *Nature* **477**, 308–311 (2011).