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Thermochemistry and Charge Delocalization in Cyclization Reactions Using Accurate Quantum Monte Carlo Calculations KAYAHAN SARITAS, JEFFREY C. GROSSMAN, MIT — Molecules that undergo pericyclic isomerization reactions find interesting optical and energy storage applications, because of their usually high quantum yields, large spectral shifts and small structural changes upon light absorption. These reactions induce a drastic change in the conjugated structure such that substituents that become a part of the conjugated system upon isomerization can play an important role in determining properties such as enthalpy of isomerization and HOMO-LUMO gap. Therefore, theoretical investigations dealing with such systems should be capable of accurately capturing the interplay between electron correlation and exchange effects. In this work, we examine the dihydroazulene isomerization as an example conjugated system. We employ the highly accurate quantum Monte Carlo (QMC) method to predict thermochemical properties and to benchmark results from density functional theory (DFT) methods. Although DFT provides sufficient accuracy for similar systems, in this particular system, DFT predictions of ground state and reaction paths are inconsistent and non-systematic errors arise. We present a comparison between QMC and DFT results for enthalpy of isomerization, HOMO-LUMO gap and charge densities with a range of DFT functionals.

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