

A LC-DFT+vdW Study of the Diels-Alder Reactions and the Global Hardness Response Analysis

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[Introduction] There have been considerable attentions drawn to the Diels-Alder reactions especially in chemical reactivity calculations. The development of computational methods for the exploration of reaction energetics, barrier heights, and frontier orbital energies are facilitated by the benchmark results. Over the past two decades, density functional theory (DFT) has been frequently used to investigate Diels-Alder reactions and previous reports indicate that many conventional DFTs show serious errors to give quantitative thermodynamic properties without clarifying the underlying reasons. Besides this, these reactions have often been discussed on the frontier orbital theory and the corresponding frontier orbital energies were used for explaining their chemical reactivities and kinetics but it is difficult for most quantum chemistry methods to obtain correct orbital energies. In this study, we apply various types of long-range corrected (LC) and other major functionals to the Diels-Alder reactions (Figure 1) to ascertain the reasons for poor enthalpies and then investigate the accuracy in the barrier height results. Furthermore, the maximum hardness rule on the reaction pathways was explored based on the orbital energies.¹

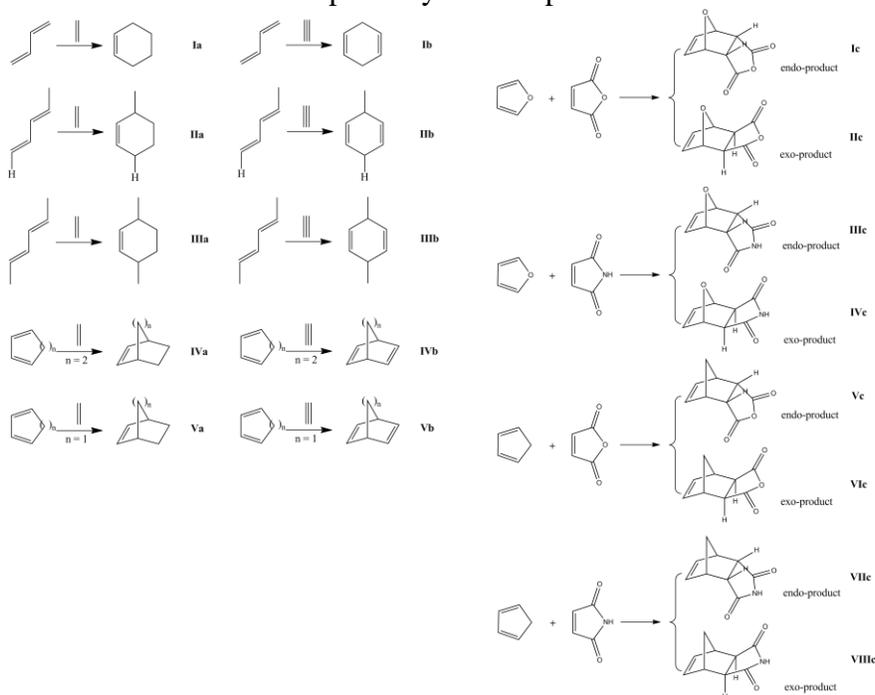


Figure 1: Diels-Alder reactions involving ethylene, acetylene, maleic anhydride and maleimide as dienophiles.

[Computational Details] We carried out calculations employing various types of DFT functionals: LC, pure, hybrid and semiempirical functionals. The LC functionals include LC-BOP, LCgau-BOP, LC-BLYP, CAM-B3LYP, LC- ω PBE and ω B97X. The LC-BOP and LC-BLYP functionals were combined with local response dispersion (LRD) to evaluate the dispersion correlation effects on the Diels-Alder reactions. For comparison, pure BOP, hybrid

B3LYP, semiempirical dispersion-corrected B97-D, semiempirical hybrid meta BMK and M06-2x functionals were considered. The geometries have been optimized by each functional using the cc-pVTZ basis set. All the optimized structures have positive and real frequency. The Gaussian 09 suite of the program has been used to perform all the computations.

[Results and Discussion] Figure 2 clearly shows that the long-range correction significantly improves the reaction enthalpies and the LRD correction has no effect on it. However, dispersion correlation correction is crucial to give accurate barrier heights as can be seen in Fig. 3. Finally we calculated the global hardness responses (GHRs), which are half of the HOMO-LUMO gaps, along the intrinsic reaction coordinates (IRCs). Figure 4 depicts the calculated GHRs and the corresponding total energies along the IRCs, where the GHRs and total energies are set to be zero at the reactants. These figures show that LC-BOP GHR results first decrease slightly when the reaction proceeds from the reactants to the transition state and after that increase drastically toward the product, while B3LYP GHR curves increases monotonically right from the reactants to the product via transition state. The former results suggest that the minimum GHR in the reaction pathway of such reactions is obtained either at the transition state or when the reacting species are about to reach the transition state. We also get GHR curves similar to the B3LYP one by the functionals examined here except for LC-BOP, LCgau-BOP and LC-BLYP. These outcomes demonstrate that LC-DFT results satisfy the maximum hardness rule for overall reaction paths while conventional functionals violate this rule on the reaction pathways.

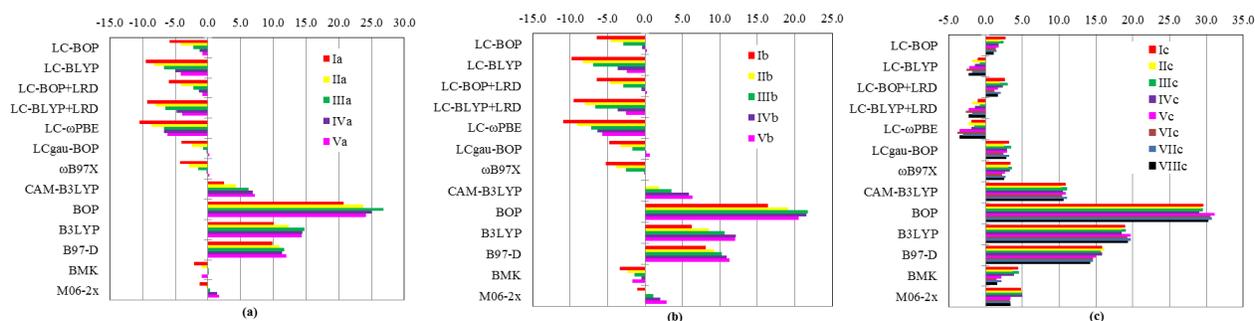


Figure 2: Errors in the computed enthalpies (in kcal mol⁻¹) with respect to CBS-QB3 results.

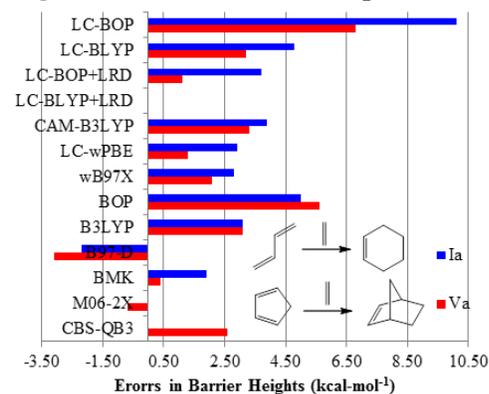


Figure 3: Errors in calculated reaction barrier heights with the experimental results.

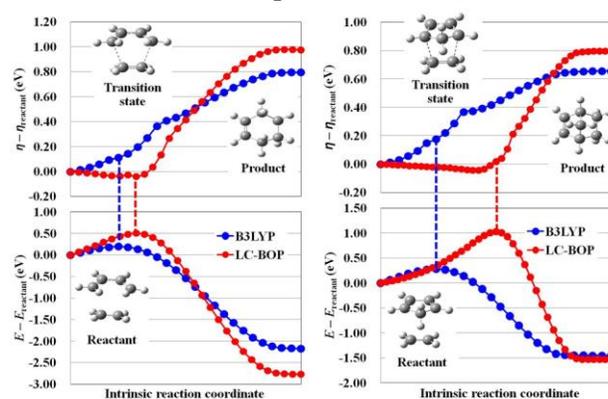


Figure 4: GHRs, η and total energies E along the IRC.

[1] Singh, R.K., Tsuneda, T. J. Comput. Chem. **2013**, *34*, 379–386.