

# Effect of the exchange-correlation functional on the synchronicity/nonsynchronicity in bond formation in Diels-Alder reactions: A reaction force constant analysis

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In this paper, we assess the performance of 24 density functional theory (DFT) based methods classified into 5 categories (GGA, MGGA, HGGA, HMGGA and DHGGA) in predicting reaction energetics, transition state geometries, and the degree of synchronicity/nonsynchronicity in the formation of two new C-C single-bonds in three Diels-Alder reactions between symmetrically and unsymmetrically substituted cyanoethylenes and cyclopentadiene, which gradually proceed from fully synchronous to highly asynchronous concerted mechanisms. This important concept in reaction mechanisms is revealed by the fine structure of the reaction force constant  $\tau$  along the transition region. Some wave function theory (WFT) based methods are also assessed against the CCSD(T) and CCSD benchmarks for the energy and geometry, respectively. The results and the statistical analysis of the errors confirm the robustness of SCS-MP2 (a WFT-based method) as one of the most reliable computational approaches. Regarding DFT-based methods, hybrid exchange-correlation functionals combined with medium-range electron correlation effects or long-range corrected exchange appear as the best performing methods, highlighting both M11 and M06-2X, since a certain percentage of exact Hartree-Fock exchange could counterbalance the delocalization errors that affect pure functionals. Thus, they reliably describe energetics, geometries and the degree of synchronicity in the formation of new C-C single bonds in Diels-Alder reactions. Noticeably, moderate performance for double hybrid functionals and poor performance for the most popular B3LYP method were found as well.