Low-Lying ππ* Excited States in Five-Membered Ring Heterocycles: a Continuing Challenge

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Five-membered ring heterocycles are simple model systems that have been extensively studied in both experimental and theoretical works, as they are essential building blocks of biomolecules and systems relevant for optoelectronic applications [1]. Despite their small size, quantum chemical methods often fail to accurately describe their excited states, leading to inconsistent predictions of excited-state ordering [2]. Therefore, understanding how the choice of theoretical approach influences excited-state characters is essential for further progress in the field.

In this work, we investigate the hidden character of low-lying ππ* excited states in five-membered ring heterocycles. Heterocycles are compared to the simplest polyenes (cis-butadiene) and acenes (benzene) using various computational methods combined with wavefunction analysis. We focus on analyzing the configuration weights of the first bright and dark excited states, commonly referred to as L_a and L_b, respectively. The performance of different excited-state methods is evaluated by comparing their predictions with the coupled-cluster singles, doubles, and triples (CC3) reference method [3]. Correlation effects are further examined through the series of algebraic diagrammatic construction (ADC) methods, as well as linear-response time-dependent density functional theory (TDDFT).

ADC(1) fails to correctly predict the L_b state since it cannot capture any double-excitation character. In contrast, ADC(2) provides a good balance for both states, with relatively small errors in case of heterocycles. ADC(3) yields only a slight improvement over ADC(2), despite its high computational cost. For the TDDFT, we found that different functional families exhibit varying accuracy for the L_a and L_b states, often leading to incorrect state ordering.

References:

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