

## Using high-level quantum chemical approaches to elucidate the electronic states of 2,5-didehydrothiophene

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Multi-configurational self-consistent field (MCSCF) and configuration interaction (MRCI) methods were used to calculate the optimal geometries, energies, and vertical excitations of three electronic states of 2,5-didehydrothiophene. The three states under consideration –  $^1A_1$ ,  $^1B_1$ , and  $^3B_1$  – arise from different possible occupations of the in-phase and out-of-phase open shell orbitals under  $C_{2v}$  symmetry, i.e.  $a_1^2$ ,  $a_1^1b_1^1$ , and  $a_1^1b_1^2$ . The 2,5-didehydrothiophene diradical is a known reactive intermediate of reactions involving thiophene constituents, which are found in systems whose applications extend from biomedical to astrophysical.<sup>1,2</sup> While work has been done in the analysis of the molecular orbitals and excitation states of thiophene, significantly less has been done in exploring its diradical analogues, particularly the 2,5- diradical. High-level theoretical methods such as those previously mentioned are essential to correctly describing this system due to its multireference nature. The COLUMBUS program was used to characterize its structure and excitation energies with a complete active space (8,8) MR-CISD (including single and double excitations) and MCSCF approach.

Results from state-averaged geometry optimizations at the MCSCF and MRCISD levels of theory indicate an ordering of the selected states in increasing energy, with  $^1A_1$  being the ground state:  $^1A_1$ ,  $^3B_1$ , and  $^1B_1$ . Geometries of the  $A_1$  and  $B_1$  states differed significantly in the distances between the C2 and C5 carbons. This distance was longer by 0.56-0.75 Å for both the triplet  $B_1$  and singlet  $B_1$  states than for the singlet  $A_1$  state. State-averaged as well as single-state optimizations were then performed to calculate the singlet-triplet splitting of 2,5-didehydrothiophene. Lastly, these geometries were used to further explore vertical excitations in the diradical.

[1] Seol Kim, Y. and R. J. McMahon. *Journal of Organic Chemistry*. **2005**, 70, 8171.

[2] Pastore, M.; Angeli, C. and R. Cimiraglia. *Theoretical Chemistry Accounts*. **2007**, 118, 35.