

Spin-Flip Characterization of Thiophene Diradical Isomers

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This project focuses on characterizing the various diradical isomers of thiophene, a product of tobacco and petroleum-based fuel combustions. These highly reactive species are difficult to describe both experimentally and computationally, due to their short lifetimes and the multi-configurational nature of their wavefunctions. To rigorously characterize their structures and energetics, as well as their singlet-triplet splittings, we used Q-Chem to perform geometry optimizations and energetics & wavefunction analysis via the spin-flip formulation of equation-of-motion coupled cluster theory with single and double substitutions (SF-EOM-CCSD). To further assess the role of aromaticity for stabilizing these diradical species, we also performed nucleus-independent chemical shift (NICS) analysis with Gaussian16. We observe planar structures for all isomers, with the 2,5-didehydrothiophene and 3,4-didehydrothiophene diradicals exhibiting C_{2v} symmetry. Each diradical exhibits a large S/T gap. NO analysis, however, suggests that for systems with adjacent diradical centers, through-space coupling is present.