

Spin Flip Characterization of the Bergman Cyclization

Adam Luxon, Carol Parish, René Kanters, Anna Krylov

Department of Chemistry, University of Richmond, Richmond, VA 23173

Department of Chemistry, University of Southern California, Los Angeles, California 90089

The enediyne (Z)-hex-3-ene-1,5-diyne (**R**) undergoes Bergman cyclization via **TS** to form *p*-benzyne (**P**), a highly reactive diradical species that will readily abstract hydrogens. Stationary points along the singlet and triplet potential energy surfaces for the thermodynamically induced Bergman cyclization of **R** have been optimized using spin flipping couple clustered methods with single and double excitations (EOM-SF-CCSD). Excited state energies were obtained using EOM-CCSD(T) and EOM-SF-CCSD(T) methods. The triplet enediyne was found to distort out of C_{2v} symmetry into C_2 symmetry. The adiabatic singlet triplet gap for the product was found to be 4.06 kcal/mol, in agreement with the experimental value of 3.8 kcal/mol. The singlet reaction was found to be endothermic ($\Delta E_{\text{rxn}} = 13.5$ kcal/mol) and the triplet reaction was found to be exothermic ($\Delta E_{\text{rxn}} = -29.3$ kcal/mol).

