

ELECTRONIC STRUCTURE OF ETHYNYL SUBSTITUTED CYCLOBUTADIENES

FRANK LEE EMMERT III, STEPHANIE J. THOMPSON, and LYUDMILA V. SLIPCHENKO,
Department of Chemistry, Purdue University, West Lafayette, IN 47907.

We investigated the effects of ethynyl substitution on the electronic structure of cyclobutadiene. These species are involved in Bergman Cyclization reactions^a and are possible intermediates in the formation of fullerenes and graphite sheets.^b Prediction of the electronic energy of cyclobutadiene is challenging for single-reference *ab initio* methods such as HF, MP2 or DFT because of Jahn-Teller distortions and the diradical character of the singlet state. We determined the vertical and adiabatic singlet-triplet energy splittings, the natural charges and spin densities in substituted cyclobutadienes, using the equations of motion spin flip coupled cluster with single and double excitations (EOM-SF-CCSD) method that accurately describes diradical states.^c The adiabatic singlet-triplet gaps decrease upon substituent addition, but the singlet state is always lower in energy. However, we found that the results are affected by spin-contamination of the reference state and deteriorate when an unrestricted HF reference is employed.

^aO. L. Chapman, C. L. McIntosh, J. Pacansky, Cyclobutadiene. *J. Am. Chem. Soc.* 1973, 95, (2), 614-617.

^bN. S. Goroff, Mechanism of Fullerene Formation. *Acc. Chem. Res.* 1996, 29, (2), 77-83.

^cL.V. Slipchenko and A.I. Krylov, Singlet-triplet gaps in diradicals by the Spin-Flip approach: A benchmark study, *J. Chem. Phys.* 2002, 117, 4694-4708.