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.

[a] O. L. Chapman, C. L. McIntosh, J. Pacansky, Cyclobutadiene. *J. Am. Chem. Soc.* 1973, 95, (2), 614-617.

[b] N. S. Goroff, Mechanism of Fullerene Formation. *Acc. Chem. Res.* 1996, 29, (2), 77-83.

[c] L.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.