ELECTRONIC STRUCTURE AND SINGLET-TRIPLET ENERGY SPLITTINGS IN ETHYNYL CYCLOBUTADIENES

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We investigated the effects of ethynyl substituents on singlet-triplet gaps in 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 singlet-triplet splitting in 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. Ethynyl substituents in cyclobutadienes are thought to stabilize the triplet states and invert the order of the singlet and triplet in some of them. We determined the singlet-triplet energy splittings 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 and singlet-triplet gaps in diradicals.[c]

[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.