ELECTRONIC STRUCTURE OF ETHYNYL SUBSTITUTED CYCLOBUTADIENES

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We investigated the effects of ethynyl substitution on the electronic structure of cyclobutadiene. These species are involved in Bergman Cyclization reactions\textsuperscript{a} and are possible intermediates in the formation of fullerenes and graphite sheets.\textsuperscript{b} Prediction of the electronic energy of cyclobutadiene is challenging for single-reference \textit{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.\textsuperscript{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.