

THE RESPONSE OF THE ELECTRONIC STRUCTURE TO ELECTRONIC EXCITATION AND DOUBLE BOND TORSION: A COMBINED QTAIM, STRESS TENSOR AND MO PERSPECTIVE

Samantha Jenkins^{a*}, Lluís Blancafort^{b*}, Steven R. Kirk^a, Michael J. Bearpark^c

^a*Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China) and Key Laboratory of Resource Fine-Processing and Advanced Materials of Hunan Province, College of Chemistry and Chemical Engineering,*

^a*Hunan Normal University, Changsha Hunan 410081, China.*

^b*Institut de Química Computational and Departament de Química, Universitat de Girona, Spain.*

^c*Department of Chemistry, Imperial College, London, SW7 2AZ, UK*

New insights into the double bond isomerization of fulvene in the ground and excited electronic states are provided by newly developed QTAIM and stress tensor tools. The S_0 and S_1 states follow the ‘biradical’ torsion model, but the double bond is stiffer in the S_0 state; by contrast, the S_2 state follows the ‘zwitterionic’ torsion. Differences are explained in terms of the ellipticity and bond critical point (BCP) stiffness for both QTAIM and the stress tensor. Overall, the wave-function based analysis is found to be in agreement with the work of Bonacic-Koutecky and Michl that the bond-twisted species can have biradical or zwitterionic character, depending on the state. Using QTAIM and the stress tensor a new understanding of bond torsion is revealed; the twisted bond is found not to rotate in concert with the nuclei of the rotated $-CH_2$ methylene group. The ability to visualize how the bond stiffness varies between individual electronic states and how this correlates with the QTAIM and stress tensor bond stiffness is highlighted. In addition, the most and least preferred morphologies of bond-path torsion are visualized. Briefly we discuss the prospects for using this new QTAIM and stress tensor analysis for excited state chemistry.