

Visualizing the Evolution of Charge Density in Fulvene Bond Torsion

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Research Motivation

Understanding the evolution of the charge density through molecular motions is a challenging and important problem. Knowledge of this process can be utilized for applications such as molecular rotary motors that use light induced cis-trans isomerization to convert light energy into mechanical motion at the nanoscale. As a bond twists, the charge density around the bond changes. By looking at this evolution we can understand the properties associated with molecular motion. Bond torsion was recently studied by Jenkins *et al.* on the dihedral C-C bond in fulvene. The paper focused on the transition from double bond to a biradical as the C-C dihedral bond rotates in the ground and excited states. A variety of methods were used to study the rotation including a visualization method called atomic basin set paths. While this technique is rich with information, it is also difficult to visualize and interpret. To complement Jenkins' *et al.* work, we use bond bundles, an extension of the Quantum Theory of Atoms in Molecules (QTAIM) to visualize the evolution of the charge density around the C1-C6 bond in a more intuitive way.

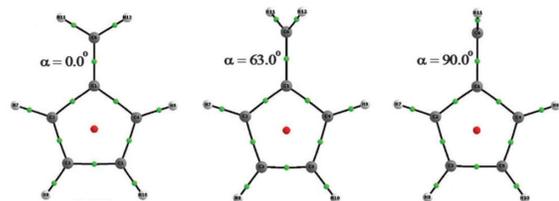


Figure 1: Fulvene bond torsion for 0, 63 and 90 degrees

QTAIM uses the topology of the charge density to describe the molecular structure of atoms and bonds. Bond bundle analysis builds on QTAIM. The shapes and sizes of bond bundles have been used to explain chemical properties because of their well defined volumes and energies. Bond bundles can be decomposed into smaller gradient bundles, which contain additional chemical property information.

Research Approach

We use bond bundles and gradient bundles to study the bond torsion in fulvene to see if we observe the changes in bond order from double to single bond as Jenkins observed. We begin with the ground state planar, 63 degree, and perpendicular geometries of fulvene specified in the Jenkins paper that were chosen to represent angles where transitions between ground and excited states are allowed. We added additional calculations between 10 and 90 degrees to determine more specific changes in the charge density. We first qualitatively compare the bond bundles observed in ethane (single bond) and ethene (double bond) to the bond bundles found in fulvene to determine bond order in the ground state. Then we use gradient bundle analysis to quantitatively determine bond order of the C-C bond in fulvene.

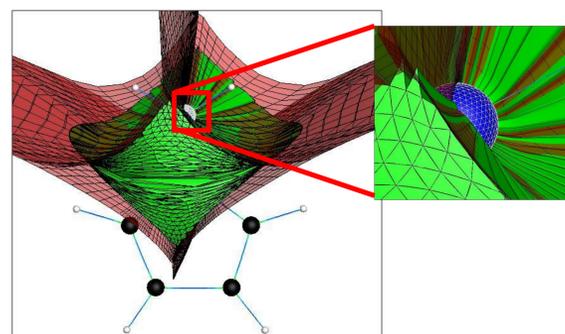
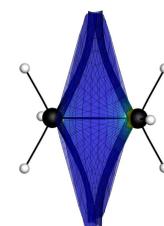
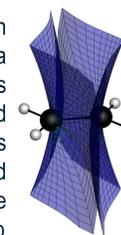


Figure 2: Activated gradient bundles within a bond bundle for 0 degree twist. Close-up shows how gradient bundles are positioned around the isosurface.

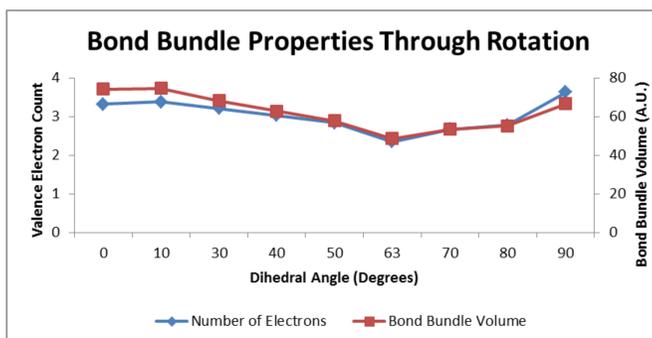
Charge densities were obtained using Amsterdam Density Functional Package, ADF, version 2016. Jenkins shared the nuclear critical points used for their study and the same points were used in the ADF calculations. All molecules were optimized using spin-unpolarized calculations with non-relativistic tripled ζ singly polarized basis set, no frozen core, and the CAMY-B3LYP functional. Values of charge density were imported into Tecplot on a 0.049 grid size.

Results

Starting with planar fulvene in its ground state, the open bond bundle pictured below most resembles ethene with a C-C double bond. Our calculations of the gradient bundles confirm there are 33.3 valence electrons within the bond bundle, which is similar to that of ethene (right) at 3.44. As the bond twists, the bond bundle begins to zipper closed starting at one side and begins to resemble more single bond character. The electron count in the bond bundle also decreases as the bond becomes more single bond like. At 63 degrees, the bond bundle is halfway closed off, and the electron count is 2.36 electrons. As the bond continues to twist, the bond bundle continues to



close, however, the electron count within the bond bundle increases. Once the bond is perpendicular, the bond bundle is completely closed, resembling a single bond like that of ethane (left), but there are 3.64 electrons in the bond bundle which would be consistent with a double bond. Upon further investigation, the volume of the bond bundle resembles that of a double bond. We conjecture that



this mix of single and double bond character is indicative of biradical bonding interaction

Results Cont.

Planar fulvene has C_{2v} symmetry and the orbital coupling is not allowed. However, once the bond begins to twist, the symmetry changes to C_2 and now the coupling is symmetry allowed. We see this progression in the molecular orbital diagrams (shown below) that show the coupling of the HOMO-1 (blue and red) and the LUMO (cyan and orange) through bond torsion. As the twist progresses, the energy gap between the two molecular orbitals begins to shrink as seen in the levels diagram. The molecular orbitals seen in the 63 degree twisted molecule, the LUMO and HOMO-1 are twisted together and interact. The HOMO molecular orbitals never change through the process.

From the bond torsion in fulvene, this is the first time a biradical bond has been characterized using bond bundle analysis. In addition to bond length and bond angles, bond torsion is an important parameter of many organic and bioorganic molecules. Properties of the isomer directly relates to changes in the electron density of the molecule. Because fulvene has been extensively studied, this molecule makes an excellent benchmark for studying the movement of the charge density and the resulting properties.

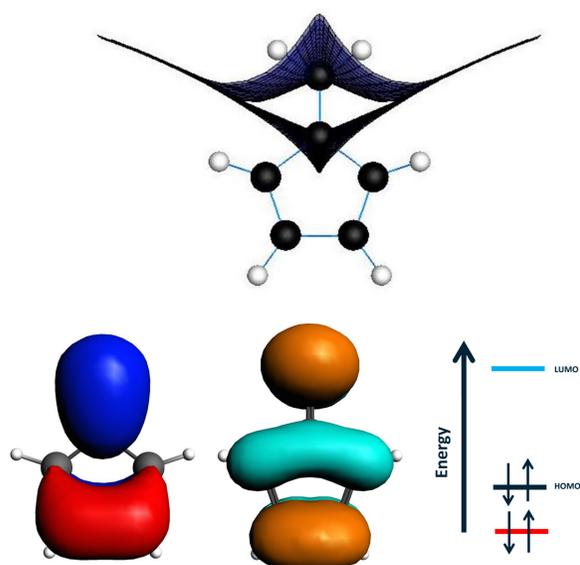
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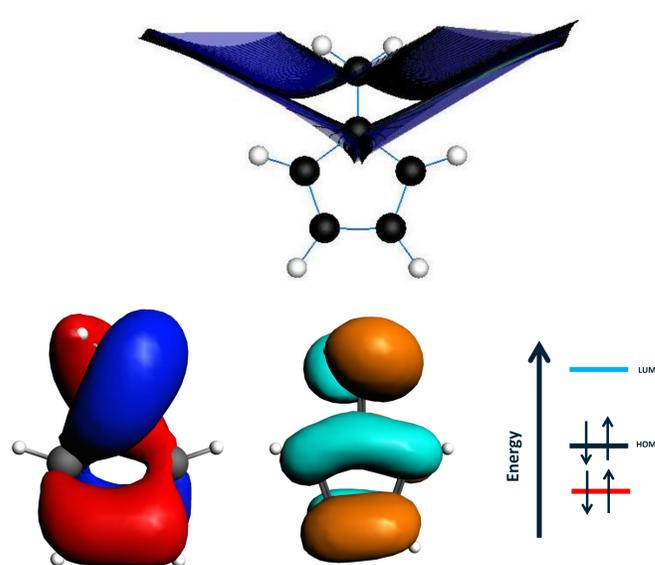
Acknowledgements

I would like to thank Tim Wilson and Dr. Jonathan Miorelli for useful discussions and technical assistance.

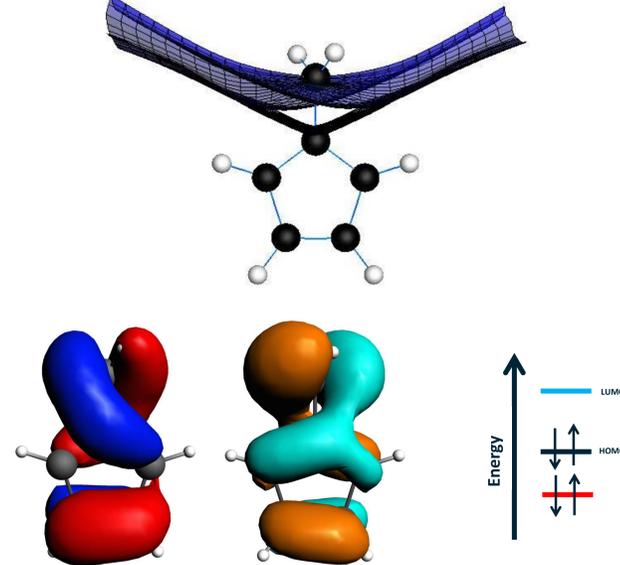
0 Degree



30 Degree



63 Degree



90 Degree

