

[Paper #8 – “*o*-Fluoranil Chemistry: Diels–Alder versus Hetero-Diels–Alder Cycloaddition” by D.M. Lemal, S. Ramanathan, and J. Shellito, *J. Org. Chem.*, **2007**, *73*\(9\), 3392-3396 \(DOI 10.1021/jo7026678\)](#)

Classroom discussion: Friday, April 17.

This paper combines several aspects of computational chemistry (atomic charges, frontier MO concepts, reaction energies and barriers) and experimental chemistry in an appealing way. I hope it will reveal some interesting chemistry. I also hope that it will provide a model for your final paper by showing how one can *write* productively about computational results.

Comments and suggestions:

1. Our discussion will probably focus on the first part of the paper, the section titled **Competing Pathways**, but you might as well read the second part, **Synthetic Considerations**, which is very short.
2. Can you figure out the shapes of the frontier orbitals of *o*-fluoranil using the information on the first page? Can you use this information to make FMO predictions about the direction of cycloadditions? You might build an AM1 model of this molecule and check your predictions against the model.
3. The authors also make an electrostatic argument. If you build an AM1 model of the title molecule, calculate and examine its electrostatic potential map. Is the map consistent with the calculated atomic charges?
4. At the bottom of the second page we read: “... the question remains as to the origin of the kinetic bias favoring Diels–Alder reaction. The following three factors probably all contribute to that bias ...”. Please read this material carefully (along with relevant background material) so that we can make sense of these factors together.