Chemistry 324, Spring 2008
Paper #5

Paper #5 – "A New Look at the Diels-Alder Transition State" by C. Spino et al., *Angew. Chem. Int. Ed.*, **1998**, *37(23)*, 3262-3265
(**DOI 10.1002/(SICI)1521-3773(19981217)37:23<3262::AID-ANIE3262>3.0.CO;2-T**)

This paper comes from a different journal than our customary one. Angewandte Chemie is one of the oldest journals in chemistry and is published in German, but many years ago they began publishing an International Edition in English. If you burrow around in the Reed library stacks, you can find German versions (older) and English versions (newer) of the journal.

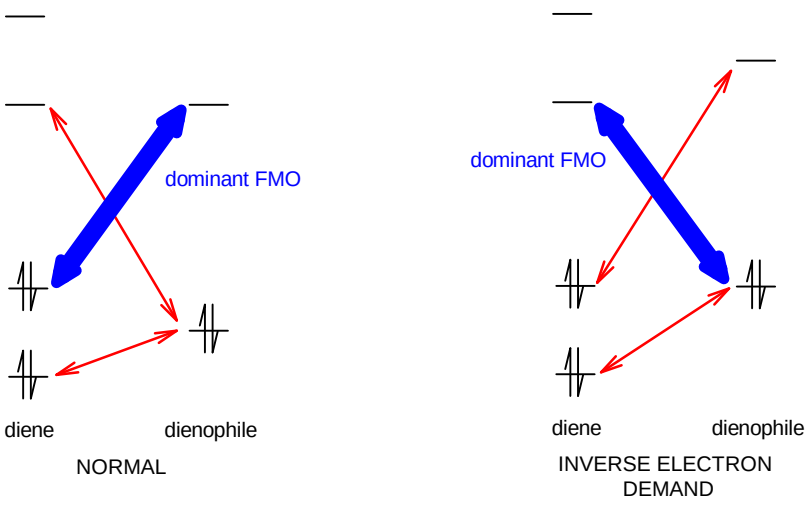
The paper critiques a particular aspect of Frontier MO theory. Therefore, in order to read it you must already possess a basic familiarity with FMO theory.

I strongly recommend that you do some additional reading as part of your preparation for our discussion:

1. Figure 1 contains colored images. Look at it on-line.

2. Read at least some of a follow-up paper by the same authors: "Characteristics of the Two Frontier Orbital Interactions in the Diels-Alder Cycloaddition" by C. Spino et al., *J. Org. Chem.*, **2004**, *69(3)*, 757-764 (**DOI 10.1021/jo0353740**). The follow-up paper is only slightly longer and contains a clearer explanation (I think) of some of their ideas. The main points:

    a. Diels-Alder rxns actually involve several pi MO-pi MO interactions



    b. The dominant FMO interaction in a normal reaction (heavy arrow) mixes $HOMO_{diene}$ with $LUMO_{dienophile}$ only

    c. The dominant FMO interaction in an inverse electron demand reaction mixes $HOMO_{dienophile}$ with $LUMO_{diene}$ (this is captured by FMO theory) *and with* *HOMO-1*$_{diene}$ (this is ignored by FMO theory)