1. (5 pts) In Chapter 11 we learned that linking pi bonds together in conjugated polyenes has consequences for bonding, light absorption, and reactivity. We noted that there’s a higher barrier to rotation about the C2-C3 bond in 1,3-butadiene than might be expected if it were just a simple single bond, and the molecule is slightly more stable than a hypothetical reference structure with two isolated double bonds. Despite this stabilization, the pi electrons in the diene’s HOMO are not lowered in energy; they are actually higher in energy than they are in ethylene. Make a good diagram of 1,3-butadiene’s pi orbitals (and their energies) and use it to explain this apparent inconsistency. (Hint: the HOMO is only one orbital).

Here is a picture where the \( \pi \) MO’s of 1,3-butadiene are formed by combining two ethylene \( \pi \) systems end-to-end. The "b" and "a" labels respectively signify bonding and antibonding combinations of the ethylene orbitals to construct the butadiene MO’s. Though the HOMO of butadiene is higher than that of ethylene, the otherfilled orbital below, which is all bonding, is lower in energy by a slightly larger amount, so that the total \( \pi \)-bonding is slightly greater than in two isolated ethylene \( \pi \) bonds.

2. (10 pts) One of Maitland Jones’s early contributions was to develop the chemistry of bridgehead double bonds via carbene rearrangements. Since they can be thought of as “1,1-diradicals,” carbenes are generally high energy intermediates, and their reactions can give access to other high energy species such as strained rings (we’ve seen them used to make cyclopropanes) and “Bredt olefins.” In this case, the starting carbene undergoes a 1,2-shift, much like those of carbocations, except that it leads to a “1,2-diradical” or alkene product.

The general case is shown in Scheme 1, and Jones’s reaction to form the bridgehead alkenes A is shown in Scheme 2. Migration of one of the other bonds would give B. Importantly, he and his coworkers never explicitly saw either bridgehead alkene; instead, they isolated triene C. Draw the mechanisms (6 pts) to show how the triene could be formed from both A and B and explain (4 pts) why it’s the energetically preferred product. What kind of reaction is this?

Scheme 1

Scheme 2

Retro Diels-Alder

C (actual product seen)

So twisted it's hardly bonding, Bredt alkene A's "\( \pi \) bond" is so strained that A is above the triene, unlike the normal D-A case which releases ca. 40 kcal/mol making cyclohexene.

3. (5 pts) Jones and his team then put an isotopic label (the black dot) into the starting carbene, as shown below. The label ended up in the triene as shown; explain which of A or B must have been formed, and how this observation allows you to know.