

## Lecture 21B • 03/09/12

[exam review: ortho/para versus meta; activators versus deactivators; and the fact that those are two different questions; molecules: cyclooctatetraene; using hydrogenation to demonstrate the relative stability of benzene]

### Pericyclic reactions

Let's start out with an example. Is the starting molecule aromatic? No; why not? Not cyclic. It turns out this will react with itself, either under heat or under light. Notice that I have the same reaction going on but two different starting reaction conditions. It turns out, with either set of conditions, you're going to form cyclo[hexa]diene. We can propose a pretty straightforward mechanism for this: if we imagine the double bonds – even though it's not aromatic, because it's not cyclic, but they are close enough to each other that maybe somehow – one side of the molecule starts with the other, starts to form a sigma bond. That's going to have a cascade effect, because if we said something like that happens – one double bond interacting with another – it's going to cause that double bond that's attacked to shift, which you could move over, attack the other double bond, which can then move over and attack the original position that reacted. That's why these are called pericyclic reactions, because even though you may not have a formal ring, you still have a cyclic form of mechanism. One of these molecules ends up optically inactive, and one of them ends up optically active. How would it be that, if I had two methyl groups – one methyl group is going to end up at the top, one's going to end up at the bottom – what is the only way that you could end up with one molecule being optically inactive? If we have two enantiomers in equal proportion – or, if the molecule itself had an internal plane of symmetry. If we had both of those methyl groups pointed the same direction, we would have that symmetry, which means we'd have a meso molecule. One of these ends up with the two methyl groups cis; one of them ends up with the two methyl groups trans. Our job this lecture is to figure out which one's going to be which.

Let's discuss. Back when you learned general chemistry, we had this idea of what valence electrons are. Why is it that valence electrons are the electrons that – 99% of the time – we're going only concerned about those when we're talking about reactivity of atoms? They're the electrons that participate in bonding; why are they the ones that participate in bonding? They're the farthest from the nucleus; they're the highest in energy. If anything's got enough energy to react, it's going to be the ones that already have that highest energy. There's a molecular equivalent. That highest occupied molecular orbital (HOMO) – it was the electrons that, in all of these different pi system orbitals, they're the electrons that had the most energy; they're the ones most likely to react. There's this general branch of molecular orbital theory called frontier orbital theory. Frontier means at the edge, and frontier is referring to exactly these two types of situations – the orbital that has the highest energy electrons, which are therefore the electrons that are most likely to react; and, the place where those electrons can end up. If you're going to receive electrons, it doesn't make sense that the electrons are going to somehow levitate and float in some highest energy level; if you're following the Aufbau principle, they're going to fill from the lowest energy level first, the lowest available, the lowest unoccupied molecular orbital (LUMO). Frontier orbital theory characterizes reaction as occurring between one molecule's highest occupied molecular orbital (HOMO) and another molecule's lowest unoccupied molecular orbital (LUMO). The Diels-Alder reaction is a variation of this type of reaction. We still have a cyclic mechanism that's going to occur, but it really does involve two different molecules, or two very different parts of a molecule. This is a slightly simpler example where we're only dealing with one molecule to begin with.

Frontier orbital theory describes reactions between pi systems in a similar way that we would describe valence electrons in atomic systems. In this system, it's a reaction of the electrons that are in the highest occupied molecular orbital. We're dealing with pi systems – molecular orbitals, not atomic; that's why the terminology's a little different. You have the electrons in the highest occupied orbital going to the orbital that has the lowest energy available for the electrons to go into – the lowest unoccupied molecular orbital. Even though we only have one molecule involved, turns out that we can use frontier orbital theory to predict which one of these two molecules, these products, is going to be the one that is optically inactive and which one's going to be optically active. To do this, we're going to need to figure out what the orbitals for this conjugated system are going to look like. We have previously done the molecular orbital pictures for benzene, but we never did do the six-orbital linear example. Let's do that now.

If we stretch both of these molecules out in their linear form, we can see that we've got a six p-orbital system. Actually, we don't – we have a six molecular orbital system that we're going to use p orbitals to model. Since six atoms are involved that product those six orbitals, we're going to use six p orbitals to do this. Referring back to that example of the wiggling phone cord, or using the example of the particle in a box, in a linear system, the lowest-energy wave is going to be one that has zero nodes; next-highest energy, one node; then two nodes, three, four, five. Five is the maximum number of nodes we have cause we're only using six p orbitals to begin with; put a node in between each one, the maximum number of nodes is five. We'll have six molecular orbitals, ranging from nodes zero through five; that's six different orbitals, which are going to have six unique energies. In linear systems, we do not have degenerate orbitals, which means we don't have orbitals of equal energy.

Zero nodes, let's start there. That is always our lowest-energy case. Because there's only constructive interaction – notice I didn't say there the maximum bonding going on, because bonding is what happens when you put electrons in favorable molecular orbitals. Bonding is not what happens within this orbital here. What we have, in our representation, are favorable and unfavorable interactions – except in this case we only have favorable interactions, so automatically this makes it a bonding orbital. The way that we did this oh so technical a fashion before was to show you only have those favorable overlaps [smiley faces]. One energy level up, we add a node. Geometric or symmetric restriction is that the node must be symmetric across the whole system which means it goes straight down the middle, which means one half has one phase, the other half has the other phase. You can see that we have a total of four favorable and one unfavorable interaction. The favorable outnumber the [un]favorable, and that's why it is a bonding orbital still.

We move up one step, we get one more node; it divides the system equally, so we'll get two, two, two, which means we'll now have three favorable, two unfavorable interactions. Since that would appear, then, that we're about to flop between favorable and unfavorable, I'm going to go ahead and draw the line in to show that all three of these are bonding. The other three orbitals, because we're going to show that there is overall more unfavorable interactions than favorable, they're going to be antibonding. The general rule for a linear system is: if you have an odd number of orbitals, one molecular orbital that results will be non-bonding; that will be because we end up with an equal number of favorable and unfavorable, it always works out that way for odd systems. Take that one orbitals out, half the remaining ones are bonding, the other half are antibonding. If you have an even number of p orbitals, it will always be this situation: exactly half the orbitals are bonding, half the orbitals are antibonding. Because you can see, in this case, if we have six orbitals, there's a total of five interactions. You can't half good, half bad if the number's five, cause there's no such thing as a half interaction. That's why for even numbers of orbitals, you never have non-bond; for odd numbers, you always end up in a situation where have half favorable and unfavorable. That's why for odd numbers of orbitals you always have a non-bonding orbital.

We need to move up one more step. Let's go up to highest one of these, cause that's easier than either of these last two.

When we have non-bonding, that means inside the orbital we have equal favorable and unfavorable interactions. In benzene, there's no non-bonding because symmetry doesn't allow it; you never end up in a situation where you have equal numbers of favorable and unfavorable interactions. In cyclobutadiene, you do, because you end up with two orbitals, in fact, that exactly cut the molecule in half, which means you have exactly the same amount of favorable and unfavorable, which is why they end up being non-bonding orbitals. It turns out, for a general case, that if you have  $4n$  cyclicly-arranged orbitals, you'll always have two orbitals that are non-bonding, and then half the remaining bonding and antibonding; if you have  $4n+2$  orbitals, you'll always have exactly half bonding and half antibonding; if you have  $4n+1$ , like cyclopentadiene, you'll have one more bonding than antibonding orbitals; and if you have something like  $4n+3$ , you'll have one more antibonding than bonding orbitals. It'll always work out that way.

Back to this. The worst-case scenario is where we have nodes between everything, which means we have five nodes, so every other one shaded. Let's come back down to the three node case. One of the previous times we did this molecular orbital development, I wrote some sine waves in. The only reason I did that is because for a few people, the connection between the particle-in-the-box or the phone cord and then this extended pi system, some people see that similarity, so it helps some people see that: oh, when you have zero nodes, it's like a wave that goes all the way across here, which is why all of these have the same phase. In a more advanced treatment of the same topic, this molecular orbital would not be made up of p orbitals all of the same size, because technically the wave has a smaller amplitude on the left than it does in the center, then does it make sense that we're using six p orbitals that all have exactly the same weight to them? The answer is no, and so in a more formal treatment, each p orbital has a coefficient that goes along with it, and the coefficients are not equal to each other. But, that is a more advanced treatment, and so most first-year organic textbooks don't show you any of that, but in case you're going to other resources to study and you see big and small orbitals, that's what's going on.

Back to this case. The three-node one, part of the way we could rationalize this is to write that waveform in. [picture in text] Filling in the orbitals, we're going to find that we only have two favorable but three unfavorable interactions, which is why it makes it an antibond. And then the last one, where we have four nodes, we only have one favorable and four unfavorable interactions. There's our set of six molecular orbitals.

Which of these orbitals is the highest occupied and which of these is the lowest unoccupied? Have I filled the electrons in here yet? How many electrons are going to go into this? Why six? [Because there's three pi bonds.] Does it matter that I've shown heat versus light? Yes. It depends on where you are in what is known as the ground state or the excited state. The whole point of why there's two different outcomes of the reaction is because there's two different electronic structures. You learned about [ground versus excited states] in Chem 1A. I [had also mentioned] that UV spectroscopy is often performed on molecules like this, because the energy gaps are in the right range of UV light. Back in Chem 1A, what did it mean to be a ground state? What did it mean to be an excited state? [In the ground state, the electrons are in lowest possible state.] In other words, you follow the three filling rules correctly, the main one of which being the Aufbau principle. If there's a higher-energy orbital available, you ignore it.

The lowest energy, the ground state, is when you have electrons in their minimum possible energy configuration. Leaving the pictures of these six molecular orbitals out, if I just draw the energy levels themselves, then this is going to be the ground state.

But there are a range of excited states – not just one excited state, but a range of excited states. What occurs is a photon gets absorbed, and an electron can bounce up to a higher energy level. In the first excited state, which is the next energetic level up, the least you could do energetically is just to move one electron up just one level. So between the two, light is absorbed, and that's why the electron moves up. Earlier, when I asked you which is the highest-occupied and lowest-unoccupied, it wasn't a trick question, but we have to ask the question: do you mean the ground state, or do you mean in that first excited state? Because, in the ground state, it is a bonding orbital that is the highest-occupied orbital, and it is an antibonding orbital that is the lowest-unoccupied. That doesn't really necessarily mean anything; it's just fact. But in the excited state, look what we've got: we now have just one electron in a higher-energy orbital, but that higher-energy orbital now has an electron, so it becomes the highest-occupied molecular orbital, and then the orbital above that now becomes the lowest-unoccupied orbital.

Why do I have one electron there, one electron up there? Imagine that we started with the ground state. If I only added one photon of energy, only one electron's going to move. I don't move the pair unless I have two photons. Two photons is more energy than one, and if we're talking about the first excited state, we're talking about the closest one to the ground state, where only one photon gets absorbed. One electron moves up if it absorbs light. There are actually selection rules for what happens to electron spin. This is related to fluorescence and phosphorescence. [singlet and triplet states] There is some restriction as far as what the change in the overall orbital angular momentum is and spin angular momentum, and then you can have spin-orbit coupling, which causes all kinds of crazy exceptions to occur.

How does this relate to the way I started the lecture off? I said: here's this thing that can make a ring, here's this other thing that also makes a ring, but one's optically active and one isn't. What if it is the electrons in the highest-occupied orbital that are responsible for getting that cyclization reaction to start? Wouldn't it make sense that the shape of that orbital would influence the way the reaction occurs? In other words, what if we did: take the molecule ... take the pi system and placed it on top of the drawing of the molecule itself. Let's shade it in according to the ground-state highest orbital. A pericyclic reaction is one that, even though you might not have true bonding between all the atoms, you're going to have an interaction, so what's going to happen is one side of this gap is going to interact with the other. In fact, if we think of the two p orbitals swinging together in one way or another, as those p orbitals start to overlap head-to-head ... we're not making a pi bond, they're not going to overlap them side-to-side, but the sigma bonds rotate, and those two p orbitals start to overlap with each other. Are the two p orbitals going to rotate like this, which means they're going to come together and rotate in an opposite way? Or, are they going to fall the same direction? Opposite; why? How do we know it's going to rotate that way? Look at the phase of the molecular orbital itself. We have the same phase on both the tops of those p orbitals, which even if they don't exist, that means that it's the same phase on the end[s] of the molecular orbital, so if the molecular orbital's going to interact with itself, it's going to interact this way so that the phase lines up. [showing nodes] Because of the shading, because of the sign of the function, they're going to rotate in opposite in opposite directions, which is called disrotatory.

If we look at that reaction that I started with .... Name that molecule. You don't put methyl groups on something that's part of the main chain; the methyl group is part of the main chain. This is not dimethyl something, this is an octatriene. The double bond right here: should we use the term cis, trans, E, Z, or none of the above to describe it, when naming it? We can't use trans because we have three double bonds that need specification. Remember that you can only use cis and trans if we're talking about a single double bond, so when naming it, I have to use E or Z. Is that one E or Z? It's not the same; it's opposite, so it's E. The next double bond over, is that E or Z? That is Z. The last one is also E. Thankfully, because they're both E, we don't have to worry about the rule that says E is more important than Z, but if you ever end up in a tie like that, if you have to name another compound, E wins in terms of number over Z, if you would number the same way both directions. But since from either end I get the same carbon number, and from either end I get the same stereodescriptor, this one is (2E,4Z,6E)-octa-2,4,6-triene. When it reacts with heat, it is going to make only one product. Remember that in a meso compound, enantiomers don't exist, cause it is its own mirror image, so you only form one product, and because it's meso, it is optically inactive.

Now let's go back and look at the light case, the photochemical reaction. Photochemistry can be described as chemistry involving light as a critical component of the reaction mechanism. In this case, a photon being absorbed causes an electron to go from what used to be the highest-occupied orbital to the new highest-occupied orbital. Notice that that causes a change in the molecular orbital's symmetry. Before, when we took the molecular orbital and put that on top of this structure, the two ends that ended up rotating had the same phase on the same face of the molecule. Ground state, we had to the two orbitals pointed the same way, the same phase. In the first excited state, what is now the highest-occupied orbital is going to have the two end p orbitals opposite in phase. Here are our three nodes that are present. Now notice that, in order for the phases to line up, the orbitals are going to have to move the same direction. Realize that, in terms of rotation, this is the same direction, even though from our physical perspective, you might say one arm is going to my interior, one's going to my exterior, but they're rotating the same way. This is known as conrotatory bond formation. The way that I just wrote it, here's what we would get.

Just to prove to ourselves that this is an optically active compound, is this top stereocenter R or S? We'd have to use phantom atoms in order to figure it out, because we have carbons attached to both points, so that doesn't help, so we have to expand out. Remember that when we use phantom atoms, you double whatever atom that is being attached there, so add one phantom carbon to each of the carbon positions. It still has its hydrogen that was there as well, but that's not a phantom atom, it's just me writing that part of the structure in. So now I compare. At one position, I have [C, C, H] attached, but that happens to be exactly what I have attached here as well. Whenever you end up with another tie, then you go to the next most-important chain. Even though there's two carbons that I could examine, I choose the carbon that's more substituted, the more important one. So, the decision's not going to be made here where the methyl and this phantom carbon are; the decision's going to be made as we go further along the ring. As we go further along the ring, I now have to write phantom atoms again, which means this position is going to appear to have .... Point it, it's optically active, and it's because the rotation happened a different way because we had a different electronic structure than we had when we used heat.

You're going to find that there are patterns, there are sets of rules, much like there's this  $4n+2$  rule for the Hückel rule; they are what are known as the Woodward-Hoffman rules for pericyclic reactions that get into how many carbons are involved and whether heat or light's involved. Depending on how many carbons and heat or light, you can figure out whether it's conrotatory or disrotatory. Don't memorize any of those rules, because they're going to be useless for what we're going to do.

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Frontier orbital theory – Frontier orbital theory describes reactions between pi systems in much the same way as valence electrons in atomic systems; specifically, that reactions occur between the electrons in the highest occupied molecular orbital of one system (HOMO) and the lower unoccupied molecular orbital (LUMO) of another system.

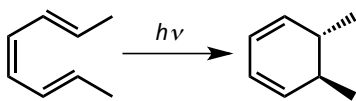
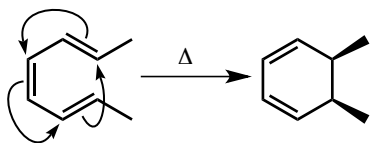
Ground vs excited states

Ground state – When electrons are in their lowest-energy electron configuration

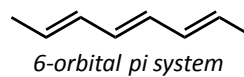
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Structures

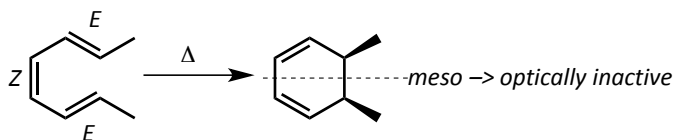
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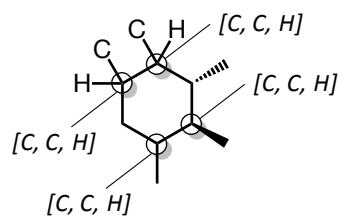


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(2E, 4Z, 6E)-octa-2,4,6-triene

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