Lecture 23B • 03/15/12

[Exam #3 review: benzene, aromaticity, conjugated systems; Frost circle; ortho-para versus meta directors; activators versus deactivators]

If we had something like one of the halogens – I'll use fluorine as an example – fluorine, we know it's electronegative – but, ignore that for the moment; just think of fluorine as something that has lone pairs and is able to do resonance. Even before reaction, we technically could write a resonance structure using fluorine, where we push electrons around a bit on the ring. You might think: that's going to be a terrible resonance structure. Of course it is, but, part of the significance of it being a possible resonance structure is it does mean a bit more electron density could be at the othro-para position. If we were to further push the charge around the ring, we could get it to the para position. I previously argued that something would be a good ortho-para director because it ends up placing a positive charge on a position where it could be delocalized off the ring. This is a slightly different perspective: this is showing that, even before the reaction begins, these resonance structures are showing that there's more electron density in the ortho and para positions to begin with, which perfectly matches the idea that that's where a positive charge would want to go. Before the reaction, there's a build-up of negative charge, then after the reaction, that same build-up will occur to help the positive charge that would form there. There's nothing we can do to move charge around to put it into the meta position. Totally separate from whatever its electronegative character is, totally separate from whatever inductive capacity fluorine might have, it is an ortho-para director, purely because of resonance, no other reason.

The ability of halogens or any other functional groups that have delocalizable lone pairs, they're bond to be ortho-para directors purely because of resonance and nothing to do with the extent of electron donation or withdrawal that occurs. Another way to say it is that halides and other functional groups that have delocalizeable lone pairs cause greater electron density to exist at the other and para positions versus the meta position. This preferential, uneven distribution of electron density is caused entirely by resonance. It has no connection to whether, overall, the functional group adds or removes electron density from the benzene ring. That's what decides whether something's an ortho-para director is resonance. Remember that alkyl groups, through hyperconjugation, can also cause something to be an ortho-para director.

What about whether it's activating or deactivating? That has only to do with whether overall electron density is added to or pulled away from the ring. It has nothing to do with any of the resonance structures that occur. To say it a slightly different way: if resonance was the only thing that made something an activator, then all things that have resonance would be activators, including the halogens. But it isn't what influences whether something is an activator or deactivator; it's whether, overall, electron density is added to or removed from the ring. For the halogens, there's this conflicted behavior. Halogens delocalize; that does add electron density. It adds more density to the ortho and para positions than it would to the meta. Halogens also, then. pull electron density right back again due to induction. Overall, they remove electron density. That causes a higher activation energy of reaction, because the rate-limiting step is forming the carbocation. But, even though overall it's removing electron density from the ring, there's still more of it at the ortho and para positions than the meta position. That's the distinction between ortho-para versus meta directors and then activators versus deactivators.

[aromatic, anti-aromatic, non-aromatic – cyclobutadiene, cyclopentadienyl anion, benzene, tropylium ion, cyclooctatetraene, pyrrole, pyridine]
[mechanism – nitration, sulfonation, acylation, alkylation, and halogenation; nomenclature]

That's chloroethylbenzene, not ethylchlorobenzene because 'c' comes before 'e', so we list the chlorine first. If we went the different ways around the circle, number the compound in two equivalent ways, chlorine could be one and the ethyl group three, or the ethyl group one and chlorine three. The tie-breaker is going to be alphabetization, because chlorine is lower alphabetically and because we have a tie in how we number, we give chlorine the lowest number. This would be 1-chloro-3-ethylbenzene. The most systematic way to do it is to use numbers, but it's still very common to see this called meta-chloroethylbenzene. The reason that meta, ortho, and para are not necessarily the most systematic terms to use is what would you do in a case like this? Chlorine and methyl are both ortho and meta. But you could also look at the two alkyl groups and call those ortho. So are you going to call this molecule ortho-ortho or ortho-meta? No, you'd use numbers to name this. You'd have to name this 1-chloro-2,3-dimethylbenzene. We could look at this is and say: isn't this a form of chloronated xylene? Isn't this, in some sense, chloro-ortho-xylene? Yes, but in the IUPAC system, there are certain of these common names that are allowed to be used for the compound itself or when you're in general talking about substitution, just the way I did just then – I looked at that and said that looks like a substituted xylene. But as far as naming a compound, to reduce the zillions of variations you might start getting in naming by looking for an identifying these common names, we do everything much more systematically by making [nearly] everything a substituted form of benzene.

[hydrogenation of benzene to prove its stabilization: -120, -232, and -208] There is still a small amount of stabilization due to conjugation. Since that is essentially butadiene, just trapped in a cyclic form, there is the small stability due to conjugation. The point is, [for] benzene, there's a huge stabilization that occurs, because you have that full, cyclic conjugation.

Let's review what endo and exo are in terms of Diels-Alders reactions. Pericyclic reactions, that was our first case where used this HOMO-LUMO theory to point out and say which electrons are most energetic and where are the electrons most likely to go. In the pericyclic reaction case, that involved only one molecule, and we only looked at one molecular orbital. We looked at the molecular orbital that had the highest-energy electrons, which are the ones that are most likely to start that pericyclic process. We looked at two possibilities: whether we were at the ground state, which we have heat as the way of starting the reaction; or whether we were at the excited state, and it was light being used to initiate the reaction. We took the molecular orbitals that corresponded to those highest-energy electrons – we took the representations of those orbitals and put them on top of what the physical model looked like. We did that to show that those molecular orbitals can be used to predict why is it that the particular reaction that we did that, at room temperature, the methyl groups on the end positions of the molecule that did twist, why those methyl groups went towards each other at the ground state and why they appeared to move away from each other when they're rotating the same way in the excited state.

The Diels-Alder reaction is different in that you do have two molecules involved. The particular Diels-Alder reaction we were studying was one involving maleic anhydride. [We had reacted it with cyclobutadiene]. The mechanism for this reaction is the following: one of the double bonds starts this cascade event, one pushes one which pushes the next which reacts back with the first compound. It's because of this cyclic set of arrows that this is called a pericyclic reaction. There are two products that are generated. Notice in one product, the hydrogens are pointed down in a way that would be reminiscent of an axial position if we had a proper cyclohexane ring. The other form, the hydrogens appear to be pointed out away from the ring, as if it was like equatorial. The group that gets substituted on the first one is pointing more out from the ring, and the second one is pointing more into the ring. The first one is called the exo form, and the second one's called the endo form.

In terms of steric hinderance, which of these two forms do you think would be more favorable: the endo or the exo? Exo? Why? Because if these were like equatorial [and] axial positions, remember that when you do have something in an equatorial position, that avoids steric hinderance, where if you had it at the axial you'd have diaxial interaction. Even though this not a proper cyclohexane ring, I could still point out that we have a hydrogen over on the other side here that could potentially have some steric interaction with the groups. If you have it in the exo position, that's likely to have less steric hinderance than you would in the endo. But in this specific reaction, the endo is the major form.

There is an explanation for it. What I suggest as a model for this reaction is we look at the molecular orbital systems for the anhydride and for the cyclopentadiene. Cyclopentadiene, it's molecular orbitals look just like butadiene: there's four molecular orbitals. I just want to show which orbitals it is that might be involved in this case. When I showed you the reaction, I had told you that this occurs with heat. We need to know that because that's going to tell us we're in the ground state. The only reason I'm writing all four of these is so we can look and remind ourselves: this is a system in which in the ground state we have electrons just in two molecular orbitals. The second one up: that's the highest occupied molecular orbital, so for butadiene, that is the HOMO, and the one right above with no electrons in it would be the LUMO. We could do the exact same thing with the anhydride. I'll only write two [of the orbitals], because what I've just written here shows you: we don't care about the bottom orbital. Those electrons are not going to interact. We don't care about the top one, because that's not where the electrons are likely to go. I only drew the one that's the HOMO and the LUMO.

In this case, since it's an even number of orbitals, we have half the orbitals bonding, half the orbitals antibonding. We have six orbitals total; that means there's three bonding and three antibonding. We want the third bonding orbital for the HOMO and the first antibonding orbital for the LUMO. Since we want the third bonding orbital, that would correspond to n = 3, which means you have two nodes. What happens is that either an electron goes from the HOMO of the six-orbital system to the LUMO of the four, or, the other way around: one goes from the HOMO of the four system to the LUMO of the six. It doesn't matter which way we allow this reaction to occur – not for our purposes – because the orbital argument we would make turns out to be exactly the same.

What I did was take the pictures of the molecular orbitals and put them on top of the molecules themselves to see what kind of interaction we have. We could have the five-membered ring – relative to the anhydride – oriented in two different ways. Another way to say it is that the anhydride itself is oriented two way, potentially, relative to the cyclopentadiene. I'm going to declare that we'll use the HOMO of the anhydride and the LUMO of the cyclopentadiene. For cyclopentadiene, if we're using that LUMO, we'll shade the orbitals in this way. Let's draw the anhydride. This first way that I've done this would effectively correspond to the exo reaction, cause as the bond connection gets made, that would just sort of push down on that ring, the oxygen pops up and ends up like the exo form. Let's turn that compound upside down, though; this system then would effectively end up endo. Now I'm going to put the orbital on top of it. Remember that it's arbitrary whether I had this up, down, down, up shaded or down, up, up, down.

You can see that we do have the appropriate matching of phase between the two molecules. That overlap occurs. Notice that means you're going to start making sigma bonds, because you're going to have head-to-head overlap here. That means that the pi bond that used to be there has to go away; that happens for both ends here, so you end up with two lone p orbitals, which end up forming the new double bond that you find in the product. We'll do the same thing on the other side here. Now I'm going to pretend that I just turned the molecule 180° around so I can keep my phases the same. Notice what happens. We have

the same primary orbital overlap. But, we have the neighboring orbitals. Now can see this secondary overlap. Since there's that much more interaction between the orbitals, that now make that a more favorable interaction, which is why it'd prefer to be endo, even though that's not sterically the best result to occur. Of course, if you don't have this secondary overlap, it could be sterics that control the reaction. This is just a classic example that's often shown that helps show why fronteer orbital theory might be a reasonable explanation, because it is able to predict these otherwise strange results. All that's gone on is I've done two different geometries, the molecule's facing two different ways, to show why one way versus the other gives us a better electronic interaction.

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Halides and other functional groups that have delocalizable lone pairs cause greater electron density to exist @ the ortho & para positions versus the meta position. This preferential/unequal distribution of electron density is due to resonance, and has no connection to whether the functional group overall adds or removes electron density.

Whether a functional group is activating or deactivating is solely due to whether (overall) electron density is added to or removed from the ring, not on what occurs during delocalization.

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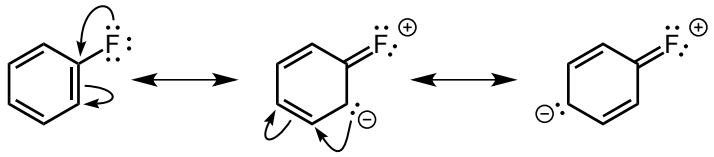
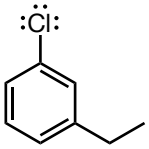
Structures

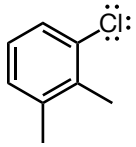
03/15/12 lec • 1



03/15/12 lec • 2



1-chloro-3-ehtylbenzene (*systematic*)
m-chloroethylbenzene (*quasi-systematic*)



1-chloro-2,3-dimethylbenzene