

Lecture 15B • 02/24/12

Benzene

[I first want to go over] a molecular orbital description of benzene. The other day when I was talking about single bonds and double bonds, the type of special single bond that's in a compound like 1,3-butadiene; the shortness of that single bond is due to conjugation that gives 1,3-butadiene is unusual reactivity. That's even more pronounced in benzene. There's also other experimental evidence in the fact that we can do experiments, do a chemical reaction, look at the energies of a series of chemical reactions to demonstrate that there's something special going on in benzene. I want to jump to the molecular orbital description in the context of conjugation.

Just as the backdrop: benzene can be written two different ways. Resonance doesn't really exist; resonance is directly due to the fact that we have a writing system that's inadequate to represent delocalization of electrons. Benzene's the ultimate example of this, because there is no difference between any of the six carbon-carbon bonds in benzene; it's because, if you look at the hybridization of each of the carbons on benzene, they're all sp^2 -hybridized, which means in our representation of the system, each of those positions is going to have a p orbital. We're stuck in exactly the same position we would be with an allyl system. If you had three p orbitals right next to each other, how could just two interact without the third? In this case, all six orbitals are going to interact, which is exactly why we don't have any difference in the bonds from one position to another. Even though we write benzene as a series of double and single bonds, none of the bonds are really either double bonds or single bonds. Although the structure of benzene is represented as a series of alternating single and double bonds, all the carbon-carbon bonds are equal in length and are in between the average length of a carbon-carbon single bond and a carbon-carbon double bond. This is due to the fact that there's complete delocalization of the pi electrons across all six carbons.

When we talk about experimental evidence showing the stability of benzene, we'll get more of an explanation of the fact that benzene does not participate in the standard types of reactions that alkenes would – more evidence that this is not really a system of alkenes. For today, I'll just say that this delocalization is not just a little bit of a stabilizing influence. What can happen in conjugated systems is, since you have all of this overlap of electrons going on, that can effectively lower the energy of the entire molecule – compared to some other molecule that just has individual double bonds. What we're going to build up to is we'll investigate a cyclohexene, with just one double bond, and look at how it reacts. Then we'll look at cyclohexadiene, a conjugated system, and then we'll compare it to benzene. We're going to find out there's this enormous amount of stability that comes. That enormous stability isn't just called delocalization; it's called aromaticity. That's the part I want to talk about today.

Aromaticity is an unusually large degree of stabilization due to complete delocalization of pi electrons, specifically in a cyclic system. We're going to start with a different puzzle: something that has what is known as anti-aromaticity, which is a significant destabilization of molecular structure due to cyclic conjugation. Something happens, in other words, when we take a pi system and wrap it around in a circle. Part of the reason for that is because of the symmetry of the nodes that are formed once you bring a system into a circle. You might recall that in a linear system[, like the particle-in-a-box,] that's another system where we have standing waves. The different types of standing waves, we had one that was completely symmetric spanning just across the system, or you'd have one that would cut the system exactly in half, or another one that would cut the system exactly in thirds, so all those waves have a certain symmetry to them. It turns out, for similar reasons, when you pull this around in a circle, you have additional restrictions on what types of waves would actually be able to manifest inside that circle. It turns out that the nodes that are present in a cyclic system must all pass through the middle of the molecule. How's that going to affect the energy levels? Let's see. What we're going to start with is the example of the molecule cyclobutadiene.

The nodes have to pass through the center, even though there's no atom there.

Cyclobutadiene has this structure. Cyclobutadiene is not easily isolatable at all. You can only isolate it at temperatures far below zero degrees Celsius; as you start to heat it up at all, the molecule just falls apart. In fact, the true structure looks more like this: the single bonds are unusually long, and because they're long, they're weak – due to the two pi bonds attempting to separate from each other. Why would two bonds want to move away from each other? Because there's an unusual instability that happens in this kind of molecule. Why would this be anti-aromatic if just by making a slightly bigger ring and having one more pi bond in there, how does that suddenly make a really favorable molecule that easily forms and is tough to react? Let's draw a SMOG for cyclobutadiene. It turns out it's not the size of cyclobutadiene, it's not ring strain that's the issue; it is the pi system itself.

The SMOG would look like this: each carbon is sp^2 -hybridized, and we have the four p orbitals, which, in theory, are all overlapping with each other. If this was the same as benzene, you might think that all four carbon-carbon bonds should therefore be the same length, but I told you that you do have what act like single bonds, and they're, in fact, longer than a normal single bond. Remember that when we saw conjugation in the butadiene system, we saw a single bond that shrank, so there's some kind of opposite effect going on here.

There are four atomic orbitals, four p orbitals that we use to represent that pi system; that's going to translate into there being four molecular orbitals; that's what we say in linear butadiene – the number of nuclei end up being the same as the number of bond or antibonding orbitals that we end up with. So, there's going to be four molecular orbitals for this cyclic system.

What do you think the lowest-energy molecular orbital's going to look like? If we were to simplify and just write the p orbitals in, if you think about the molecular orbitals that we've drawn before, shading one versus the other, talking about favorable versus unfavorable overlap, what is the most favorable overlap that could occur in any kind of pi system? Where are of the p orbitals that you use to represent that orbital, all are shaded the same way. That would put electron density between all of the nuclei, which would make that favorable; that's the lowest energy molecular orbital, cause you only have favorable overlap occurring. For the linear systems, what was the ultimately unfavorable orbital, the most energetically-unfavorable orbital? Where every other one was shaded the opposite way. Turns out, that works for this kind of system as well, because we could draw those four p orbitals, shade each one oppositely, which means we could draw nodes like this. If you look at the two p orbitals that are on the southwest side of the drawing, they are both opposite from the other two p orbitals, and so that means a node effectively passes between those two pairs. Of course, if we look at the southeast versus the northwest side, we still also have two pairs that flip relative to each other. So the nodes pass through the middle of the molecule, which is one of the restrictions of symmetry that must hold true.

But there are four molecular orbitals, because we have four nuclei that we start with. If the minimum number of nodes that we have is zero, if the maximum number of nodes that we have is two, what do you think the other molecular orbitals have to look like? How many nodes would be in those molecular orbitals? Just one. Notice I said molecular orbitals. If they each only have one node, that means that, in principle, they are both equal in energy. We have to have it that way because there is no other more unfavorable way to do the p orbitals than we've already done, so we can't have more than two nodes. There's no more favorable to make the orbital than we've already done; you can't have fewer than zero nodes. So we'll have two different systems that have one node. It's arbitrary how we draw the nodes, but by convention, we try to draw the two most different-looking structure that we can, the two most different-looking representations that we can. They would look like the following: in one case, we just draw one node straight down the middle of the molecule, so two on one side would be shaded the same, and the two on the other side would be shaded the same. Notice that that means that, as you go around the molecule, you alternate between favorable and unfavorable interactions. If you have as many favorable as unfavorable interactions, that means, overall, you're going to have a non-bonding orbital. This orbital we're going to call zero energy.

How does the other orbital look, the other one that also has just one node in it? To make one that's orthogonal to the first one – this is another symmetry argument that has to be made, buried in quantum mechanics is the fact that each orbital that you have has to entirely fail to overlap mathematically with any other orbital. So, we twist the node the around; we have it pass between two of the atoms. When that occurs, those atoms don't get used in representing the molecular orbital. We already saw a situation like this when we did the allyl system: we had a bonding, an antibondin, and a non-bonding orbital. In that non-orbital orbital, the nodes similarly passed right through the middle of the molecule, through an atom, which means we didn't include the p orbital in representing that structure. Similar to that allyl system, then, we're going to end up with two p orbitals that are so separated from each other that there really isn't any favorable or unfavorable interaction.

What do the energies look like if we got rid of the orbital representations, what would the energies of these systems look like? The following: remember that, in all bonding diagrams, we define zero energy as the energy as if atoms had never interacted in the first place – which is not non-bonding, it's not doing anything. Non-bonding is still a situation where orbitals are interacting, but just in a way that doesn't lose you or gain you any energy. So we have two non-bonding orbitals; we have antibonding; and we have one bonding orbital. How many pi electrons are in this system? Even if we can argue about whether they're there or not, how many pi bonds are we writing this structure with? Two. How many electrons in each pi bond? Two. Two times two gives us four, so we have to put four electrons into our energy diagram. Notice that two of them go into a bonding orbital, but two of them go into a non-bonding orbital. If we were to calculate bond order, we have two bonding electrons, we have no antibonding electrons; non-bonding electrons don't count either way, so we ignore them. Two divided by two gives us one – only one bond, yet we're writing two bonds in the structure. What that means is that the structure we're writing is wrong, if it really existed that way. But it doesn't want to exist that way. Imagine that the single bond was flexible enough that you could stretch it infinitely, stretch the two pi bonds infinitely away from each other. Then you'd have two individual pi bonds.

Let me compare. If we had two individual pi bonds, we would have two systems in which we have a bonding and an antibonding orbital. For each individual pi bond pi, there would only be two electrons in that system, so in each pi bond the electrons would go into a bond. That means the total bond order is two. So what? By those two double bonds getting as far away from each other, you end up with four bonding electrons. When they come together to become fully conjugated, two of the electrons are forced from bonding into non-bonding orbitals; that means it's an increase in energy, which is super unfavorable, which is why the molecule tries to stretch apart, and why with any amount of heat it just falls apart. When you make it cyclic, you change the way the nodes work. By bringing those two things completely far apart, you change the molecular orbitals, you change the node system. When you bring the orbitals together and force them all to interact, symmetry causes the orbitals to change, which causes the energies to change. If you have four nuclei and you only have one bond to share between them, that's a lot of positive charge.

That's another way of saying you're going to have a higher-energy system. The more precise way to say it is that electrons are forced into non-bonding orbitals. Both of those explanations say, therefore, it's unfavorable. You don't have enough negative charge to help pull together the positive charges. That's also what this bonding picture tells us: only two bonding electrons, and two electrons that are useless.

When the two double bonds are separated, there are four bonding electrons; when they are cyclicly conjugated, there are only two bonding electrons, which makes cyclobutadiene an unfavorable molecule. When two pi bonds are cyclicly conjugated, a set of molecular orbitals forms in which two electrons are forced into higher-energy non-bonding orbitals. This is why the structure of cyclobutadiene is distorted. Since, by the two pi bonds separating from each other, the energy of the electrons in the pi system is lowered. What we're going to find out is that the exact opposite is true with benzene. When we draw the molecular orbitals of benzene, we're going to find there's more stabilization.

Let's just get through drawing the molecular orbitals of benzene. [Neutron] Six molecular orbitals are going to result from the six p orbitals that we use to represent benzene. A similar story's going to happen as happened with cyclobutadiene, where the lowest-energy orbital will be the one where you have all six of the p orbitals with the same phase. The highest-energy orbital is still going to be the one where every other orbital is opposite of phase, so it'd look like this. Notice that's one and only one highest energy and one and only one lowest-energy orbital. This only holds true for even numbers of p orbitals. We're going to learn how to generalize this kind of diagram and simplify predicting what's going to happen; we're going to learn a way where we don't have to write all these orbital pictures. There's this very amazing coincidence of symmetry that occurs where we're going to use polygons, we're going to do inscription of polygons as a way of predicting the energy levels of these molecules. For now, let's do it the rough way. Lowest energy, all orbitals the same, which means we have zero nodes. The highest energy is where every other orbital is opposite in phase, which means we're going to have three nodes. It means we're going to end up with systems that have, respectively, two nodes and one node. As we're going to find out, that means we have just bonding and antibonding orbitals, no non-bonding.

How do we draw the remaining four orbitals? We're going to have a similar approach again as we did with cyclobutadiene. We'll have one system that has one node that passes through the molecule between atoms. That's equivalent to having two allyl systems. There ends up being more favorable than unfavorable overlap, and so this is a bonding orbital. Another way to draw the same system is to put the node through the atoms, which means it's going to be like we have two pi bonds that are totally separated from each other. That means it's still bonding; there's still more favorable than unfavorable going on. We could stop right here, in fact, to explain the stability of benzene, because there's only six pi electrons in benzene; they go into the three bonding orbitals. The lowest orbital has conjugation, which individual double bonds would not. Conjugation causes stability, so these orbitals are automatically more stable, in total, what you could possibly ever get from individual double bonds.

What do the last two orbitals look like? The nodes themselves must be orthogonal mathematically. You're going to have one system in which you have the nodes like this – one passes through the atoms, one's at a right angle to that and passes between atoms. Notice how, in this representation, we end up with two antibonds that are separated from each other; that's going to create an antibonding orbital. The last case is the toughest to remember. The nodes appear to pass unevenly through the atoms, and you end up with an alternating series of constructive and destructive interactions. There's four unfavorable interactions, two favorable ones, so overall, it's still an antibonding orbital.

- Although the structure of benzene is represented as a series of alternating single and double bonds, all of the C-C bonds are equal in length (in between the average length of C-C and C=C). This is due to the fact that there is delocalization of the pi electrons across all six carbons.

Aromaticity – An unusually large degree of stabilization due to complete delocalization of pi electrons in a cyclic system.

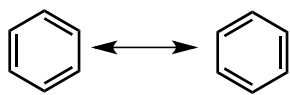
Antiaromaticity – A significant destabilization of molecular structure due to cyclic conjugation.

The single bonds in cyclobutadiene are unusually long and weak, due to the two pi bonds attempting to separate from each other.

- When two pi bonds are cyclicly conjugated, a set of molecular orbitals forms in which two electrons are forced into higher-energy, non-bonding orbitals. This is why the structure of cyclobutadiene is distorted, since by separating the two pi bonds, the energy of the electrons in the pi system is lowered.

Structures

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