

Lecture 14A • 02/27/12

There are two molecules I'd like to discuss today. One of them, benzene; the other of them, what would look like to be a smaller cousin, cyclobutadiene. They are both cyclic systems; they're both systems in which each carbon is sp^2 -hybridized; but, they're very different in their behavior. Cyclobutadiene can only be isolated at sub-zero temperatures, and is extremely reactive if you can isolate it. In the linear butadiene case, we talked about how the single bond that's between the two double bonds ends up shorter than your average single bond would; that was part of the evidence that there is conjugation. The exact opposite happens in cyclobutadiene – either of those two single bonds is stretched compared to a normal single bond, so much so that that's why the compound can only be isolated at extremely cold temperatures. You have to remove enough energy from the system that heat itself doesn't pull the molecule apart. The single bonds – they are single bonds, that's part of the difference between this system and the linear system, where there we can say there's really a single bond there but there's a lot of interaction between the pi bond – here the pi bonds are trying not to interact, so the single bonds are unusually long and weak.

Everything is opposite with benzene. Benzene can very easily be isolated at any temperature (except maybe extraordinarily high temperatures). Benzene does not react the way that a normal alkene would. Benzene does not react with a normal like HBr, it won't react with borane the same way that alkenes would, it won't react with the mercury acetate in oxymercuration-demercuration. It will react with bromine, but not in the type of mechanism that you've seen before. Even though we write the structure of benzene with double bonds, it doesn't act like it's a compound that has double bonds. In fact, the single bonds here are much like what you'd seen in the linear butadiene case – even more so. Instead of there being just shortened single bonds, really between any of the carbon-carbon bonds there's no difference. There really isn't a single versus a double bond in that compound; they're all equal in length and, therefore, in reactivity. Benzene is easily isolated across a range of temperatures. It can only react with strong electrophiles or nucleophiles; this is opposite the behavior of cyclobutadiene. There's no difference between any of the carbon-carbon bonds in benzene. All of the bonds are between a single and a double bond in length.

There's something going on by making these systems cyclic that's unusual. Aromaticity. Aroma means smell, and aromatic is related to the fact that a lot of benzene derivatives do have a very noticeable fragrance to them. But, aromatic, the term, does not just have something to do with the smell. By it being associated with benzene, it refers to this really extraordinary stabilization that can occur when you take a pi system, like what benzene has, and wrap it around in a circle. You notice that every position on that benzene ring is sp^2 -hybridized, which means every carbon on that ring interacts with each other. In the case of benzene, that ends up being favorable; that high favorability is what we call aromaticity. To do that for cyclobutadiene, though, makes it incredibly unstable. It's not the fact that it's a four-membered ring. If I only had one double bond in that compound, cyclobutene, that is isolatable – still reactive, but very isolatable. But for some reason making a system where you have four carbons only that are all overlapping in the same way as benzene, it makes it a worse compound than if it had just been uncyclized to begin with. There's some kind of destabilization that occurs; we're going to call that antiaromaticity.

Cyclobutadiene

The point of the particle-in-the-box example was that it was a thought problem that gives very similar solutions to what we say in that phone cord demonstration. Both of those were ways of trying to model what happens in one of these pi systems, where you've got carbon after carbon after carbon that are all connected to each other like they're in a line. These molecular orbitals that those pi electrons go into, they cover across that line and have the ends of the lines as the end points, which matches what happens in that wiggling phone cord, which matches what happens in the particle-in-a-box problem. The point is to look at what the shapes of the waves generated are and notice something about the symmetry of those waves. As a reminder, we get something like this: that the lowest-energy wave evenly spans across the whole system. The next-highest energy wave has one and exactly one node, and it causes the wave to cross the axis in the middle. One half is symmetric with the other half, except for them being reflected across the axis compared to each other. There's a third level where it easily splits the system into three parts – in other words, for zero nodes, the wave just starts and ends from one side to the other; you have one node, it's exactly in the middle; you have two nodes, they cut it exactly in thirds. If you kept on going, each wave that's generated has a symmetry where all the nodes cut the system into equal parts. There is a similar restriction on symmetry once we have a cyclic system of p orbitals. In one of these cyclic systems, one of the requirements of symmetry is that the nodes must pass all the way through the center of the ring. If you have multiple modes, they all pass through the center of the ring; there's no easy way to prove that [without] more advanced quantum mechanics. Let's see how that changes or influences the type of molecular orbitals that we're going to end up with.

If we have a molecule like cyclobutadiene, just to prove to ourselves that there's something unusual going on, let's draw a SMOG first. In this case, each of those carbons is sp^2 -hybridized, so we'll end up with something like this. There's our four sp^2 -hybridized carbons; there are of course hydrogens on each of those positions, and you have p orbitals. All the p orbitals overlap with each other, in theory, because all of them would be potentially close to each other that they should overlap. I've already told you that in real life, this is a structure that's distorted, where the two double bonds are trying to pull away from each other, so there's not an equivalence across the structure; that's what we need to now discuss why.

In the linear system, when we had something like the allyl carbocation, there were three atoms involved, so we had three molecular orbitals. When we got to the 1,3-butadiene, there were four atoms involved, so we had four molecular orbitals. Same thing here: we're going to have four p orbitals, four orbitals involved, so once you delocalize, that makes four molecular orbitals. Let's see if we can rationalize what the representation of those four orbitals is going to look like. In real life, we've got the four orbitals, and they happen no matter how we describe it. We describe it, though, by using this picture and taking those p orbitals and shading them in in a way that makes something that looks like the real molecular orbitals. What way of shading the p orbitals would be the most energetically favorable possibility? There is one and only one lowest energy level; what would that look like for the cyclobutadiene system, in terms of shading in p orbitals? When they're all in phase, which mean they're all shaded exactly the same way. Here's our energy level, and here's our orbital description of it. This would be a case where we have no nodes, which is also generally the case for the lowest-energy system, one that does not have any nodes in it. What would be the absolute worst-case scenario, in terms of using shading? Every other one is opposite each other, which in an even-numbered system like this, only four atoms, you can do that easily; I'll shade every other one. How many nodes does this system therefore have? [Remember that] the node must pass exactly through the middle of the molecule; this is one of the things that just happens when you have cyclic symmetry. For one node, it has to pass through the middle of the molecule. If I draw one node, it makes the two halves opposite each other, which is exactly what's going on. But then the two halves also have an opposition within themselves, so if I draw another node like this, now I've got all the flips between signs accounted for. There are only two nodes in this system.

Why am I making a big deal out of this? Because there is no such thing as $1\frac{1}{2}$ nodes, or $3\frac{1}{4}$; the nodes are always whole numbers, and they're always zero or greater. If I have zero, and I have two, and I have two more molecular orbitals, then how many nodes are going to be in those two molecular orbitals? If two is the maximum and zero is the minimum, and they're only one way to do the two and there's only one way to do the zero, then how many nodes must be left in the other orbitals? One. The important thing about there only being one node is that this is going to generate what are called degenerate – which means equal energy – orbitals. What will this look like? One way we could cut through a system with just one node is to do just that: put one node between the two pairs of atoms. That means one half will be colored one way, one half will be colored the other; that means that we'll have two favorable interactions, we'll have two unfavorable interactions. The number of favorable equal the number of unfavorable, so what kind of orbital do you think I just made, energetically? A non-bonding orbital. The one where every other sign is opposite, what kind of orbital do you think that is? Antibonding. The one down here, where everything is lined up the same way is going to be bonding.

We already had one way that I cut through with just one node. Another one of these things that you just have to believe is that another level of symmetry that occurs is that nodes have to be mathematically orthogonal to each other, which doesn't always mean 90° . In this case, the only way to generate something that doesn't look like this orbital at all is to have the node cut instead through the atoms themselves. Wherever the node cuts through, that means the value of the function is zero. If we're trying to represent this function using p orbitals, we're not even going to use the p orbitals where the node cuts through, because if the function is zero, why represent the function with anything that's not zero. The fact that I'm not shading either side of them means they're not used at all; I would normally draw this picture leaving those p orbitals out. The point of this is that the two p orbitals that are part of that representation are far enough apart that they don't interact with each other, so they're neither good nor bad, which means it's again a non-bonding orbital.

Let's put this on an energy diagram. Zero means the energy of the atoms as if they had never been bound. In this case, we are only talking about the pi system, we are ignoring what happens to the sigma bonds. We have the one orbital that's bonding, we have the one orbital that's antibonding, and the two orbitals that are non-bonding. How many pi electrons are there? Four, because whether or not there really are double bonds there, on paper when we write it down, it does correctly account for the number of electrons that are there. If we have two pi bonds that we're writing, that means there's four pi electrons, even if they're not really bonds, even if it is one of these delocalized systems. What's the point of showing that we have four electrons? They've got to go somewhere. Aufbau principle, the electrons go to the lowest energy level possible, so they're going to go into the bonding orbital. The Pauli exclusion principle, you can only fit two electrons in one orbital, so then, the next electron, by the Aufbau principle, has to go to the next energy level up. Since we didn't get to apply this before, because we have degenerate energy levels, two energy levels that are equal, then after we put one electron in one, the other electron's that left has to go into the other. The most immediate consequence is if we calculate bond order. Bond order is the number of bonding electrons minus the number of antibonding electrons, that whole thing divided by two. We have two bonding electrons, we have not antibonding electrons, and notice the non-bonding electrons don't even get figured in here cause they don't help and they don't hurt; they don't do anything, that's why they're called non-bonding. We end up with a bond order of one, split across four atoms. Can four atoms be held together by one bond? No, that's why this molecule's unstable.

Why does the molecule try to pull apart, then? What's the driving force for that to happen? Let's shift back a little bit and imagine that I have two molecules of ethene, two separate molecules of ethene. Why does that matter? Because ethene has only a pi bond and a pi antibond to it. If these are separate, they don't interact. So the two electrons that are shown in that pi bond, they only go into a bonding orbital, so the total bond order equals two. By taking the two double bonds and keeping them completely apart, the four pi electrons are able to all exist in bonding orbitals.

As soon as you connect those p orbitals, you try to make a circle out of them, it changes the type of nodes that exist, it changes the system of molecular orbitals, and it creates a new set of orbitals in which electrons that used to be bonding have now been pushed up in energy into a non-bonding orbital. It's not favorable, so the molecule does what it can and tries to distort, the double bonds try to pull back apart, cause then electrons start going more into a bonding orbital. But the single bond that connects them is only so strong, can only stretch so far. The destabilization caused by pushing these electrons up into a non-bonding orbital is enough that it causes those single bonds to stretch enough that, with a little heat, the whole thing just falls apart. That's the story of antiaromaticity; that's what antiaromaticity is – an unusual destabilization of the pi system caused by the pi system being fully, cyclicly conjugated.

Cyclobutadiene – or even the butadiene system, if we looked at the linear system, used that as a comparison – these are not isomers, so you can't make a direct comparison, but the point still works in this case. When linear 1,3-butadiene is forced to cyclize, two bonding electrons are forced into higher energy non-bonding orbitals, which is energetically unfavorable. To avoid this situation, the molecule attempts to distort to prevent full cyclic conjugation. This is why cyclobutadiene is not a square, and why it cannot be isolated at room temperature. When we have the linear system, there's one set of nodes that are there, and they just work out the right way so you get two bonding and two antibonding orbitals. When you make it a circle, think of this: if you have some shape that's responsive to sound, imagine that you change the shape of that object, you're going to change what sounds it may respond to. If you have a wave that has to correctly overlap itself, if you have a line, there's one set of restrictions on what wave can exist. When you make it a circle, you add an additional level of restrictions. That's what changes the node patterns; that's what changes the type of molecular orbitals that you've got. In this case, this particular example with four atoms, you end up with a system where it's only got one bonding orbital, one antibonding orbital, and then two non-bonding orbitals. Going from the linear to the cyclic system, that's an increase in energy that must occur in order to get those electrons into now non-bonding orbitals.

For benzene, we're about to see, the opposite happens. If we looked at the linear system, it is actually more favorable to go into the cyclic system. What do these molecular orbitals in benzene look like? We have six carbons. We could draw a SMOG, but really no need; it's similar to the cyclobutadiene, where you've got every carbon being sp²-hybridized, which means every p orbital interacts with every other p orbital. Except, they do this time; it's favorable for the p orbitals to interact, which is why all the bonds end up being the same length. If we have six atoms, that means we have six molecular orbitals. We're only going to end up with one case where you have the worst combo possible. Since we have six atoms, you can go even-odd, every other one, up and down; that gives us our highest-energy orbital. Our lowest energy orbital will again be the one where all the p orbitals that we use to represent it are in the same phase. Let's draw those two orbitals first. Lowest energy system would be similar to what we saw in cyclobutadiene. In fact, no matter how many carbons you've got, whether they're an even or odd number even, you're always going to have the lowest-energy orbital being the one where all orbitals used to represent it are shaded the same way. Since there's only one way you could do it with all of them shaded the same way, there is never more than one lowest orbital in these cyclic systems. The highest energy orbital is the one where every other p orbital is shaded the opposite way. Remembering the restriction on nodes, how many nodes would there be in this highest-energy orbital? Three. You see that I have zero nodes and three nodes; what must exist between? One and two.

In these cyclic systems, we'll never have more than two degenerate orbitals for any one level. We can have as many atoms as we want, and we'll end up with a whole bunch of orbitals, but we'll never end up with more than two that have the same energy. Having said that, if I've got six total orbitals that I need, and I've only got two on paper so far, that means I've got four orbitals left. You can't have more than two of the same energy, which means we are going to have two and another two that have the same energy; we're going to have two pairs of molecular orbitals that are degenerate. Notice that I've already shown what the end result's going to be: in this case, no non-bonding orbitals, there's only bonding and antibonding. Even though I've drawn that zero line there, there's no non-bonding orbitals. Now it just remains for use to draw the representations for these four remaining orbitals. We're going to end up with orbitals where a node passes through atoms again; if it passes through the atoms, that means we're not even going to use that orbital. The one-node system, there are two unique ways to do it. One case, the node goes between atoms; just like in the cyclobutadiene, one node goes through the atoms. On the one one the left, three of the p orbitals are shaded one way. These are two allyl interactions, so if you count up the total number of favorable versus unfavorable interactions, there's more favorable than unfavorable; that's why it makes this a bonding orbital. In the cyclobutadiene case, because of the number of atoms involved, when we got to the one-node case, the number of favorable and unfavorables are equal. There is something to do with the number of atoms that are in the ring. There is a way we can predict what the energies of the orbitals are without having to draw all of these pictures out every time. We're doing it the long, painful way for just two cases, cyclobutadiene and benzene, because they're such classic cases in molecular orbital theory. Let's look at the other one-node system. You have favorable interactions on either side, and the two sides are too far apart from each other for them to have an unfavorable interaction, so it's as if you had two isolated pi bonds – which are bonds, so that's a bonding orbital.

Let's get to the two trickier orbitals to draw. When you have two nodes in a cyclic system, then must be 90° to each other, so there's two possibilities here: one of the two nodes passes through atoms, or neither of the two nodes passes through atoms. It will help if you remember how many nodes are around, and in the two node case remembering that they have to be 90° to each other. Notice that we have just unfavorable interactions left.

Within an orbital, there's not bonding and antibonding; there's constructive and destructive interference. We have only unfavorable interactions. On the other side, we have both favorable and unfavorable interactions, but the favorable is going to be outnumbered by the unfavorable; we have two favorable interactions, but four unfavorable one. We already know that the top one is just all unfavorable, so it's the highest-energy orbital.

How many pi electrons in benzene? Six. Notice that they all only go into bonding orbitals, so this is already one difference from the cyclobutadiene case. What we haven't seen in this diagram is the fact that these electrons are lower in energy than if we had three independent pi bonds. There, all of the electrons are just in bonding orbitals; that's why cyclobutadiene is bad, cause you end up with two bonding electrons versus four. Benzene has six bonding electrons; three individual double bonds have [six] bonding electrons. In the individual double bonds, you'll never get as good an overlap as what we've got here in the lowest-energy level of benzene. Benzene's lowest energy level is lower than the bond of a pi bond. Overall, this system is lower in energy than you could ever get from individual pi bonds. That's why benzene is aromatic, because we end up with this very unusual stability. [Frost circle and Hückel rules] For aromaticity, something has to be cyclic; it is the cyclization of the system that causes that unusual stability. On top of that, it has to be planar, because if the p orbitals don't overlap, even if it's cyclic, you wouldn't have interaction. It has to be cyclic, planar; all the p orbitals – or every atom in that system that's in the ring – has to be conjugated. The last one of these rules is known as the $4n + 2$ rule. What I've shown us is the groundwork for proving why is it that this $4n + 2$ is the magic number of electrons we must have.

cyclobutadiene – can only be isolated @ sub-zero temperatures; extremely reactive

- The single bonds are unusually long and weak.

benzene – easily isolated across a range of temperatures; can only react with strong electrophiles or nucleophiles

- There is no difference between any of the C-C bonds in benzene; all of the bonds are between a single and double bond in length.

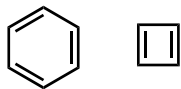
antiaromaticity – A significant destabilization of a pi system caused by the full cyclic conjugation of that pi system.

When linear buta-1,3-diene is forced to cyclize, two bonding electrons are forced into higher-energy non-bonding orbitals (energetically unfavorable). To avoid this situation, the molecule attempts to distort to prevent full cyclic conjugation. This explains why the shape cyclobutadiene is not square and the molecule cannot be isolated @ RT.

Hückel

Structures

02/27/12 lec • 1



02/27/12 lec • 2

