

Lecture 16B • 02/28/12

Let me briefly summarize the two molecules we did discuss last time, and then move into a wider discussion of how do we recognize when is something aromatic and when is something antiaromatic. Here are the two molecules we had: benzene.... notice that we've never had the phrase 1,3,5-cyclohexatriene (or cyclohexa-1,3,5-triene) that is another potential name for benzene, but that would be as if you really did have those double bonds there. I'm just pointing out that even the fact that we don't name it systematically is an indication of its unusual reactivity. That's versus cyclobutadiene, which is not a stable molecule. In fact, if you compare one to the other, benzene, there's something unusual going on because all the bonds in the circle, all the carbon-carbon bonds, are equal to each other, whereas in cyclobutadiene, even though it's the same situation, where it's a cyclic compound where every carbon's sp²-hybridized, unlike benzene, where that kind of structure makes for something that's really stable, in the cyclobutadiene case, it turns out to be really unstable, due to the fact that you cyclize it. Benzene is unusually stable due to cyclic conjugation. All the carbon-carbon bonds are equal. That's versus [cyclo]butadiene, which is unusually unstable due to cyclic conjugation. There's a definite distinction between the single and double bonds.

I want to introduce this thing called a Frost circle, which is an extension of the results that we get from looking at the benzene and cyclobutadiene cases. When we were trying to construct those molecular orbitals, the lowest-energy molecular orbital we modeled each time as if we had all the p orbitals the same phase as each other. If you think about it, there's only one way you could have all the orbitals the same phase [and thus zero nodes]. No matter whether we have five carbons or eighteen carbons, no matter how many carbons may be there, there only going to be one lowest-energy level every possible. Due to a really strange coincidence, it turns out that, if you know how many atoms in the ring are involved, there will always be that many energy levels. Geometrically, it works out this way. The example that I'm going to use to construct a Frost circle is this molecule: COT for short, cycloocta-1,3,5,7-tetraene [should know from name it's not aromatic]. This again looks like it should be similar [in] reactivity to either benzene or cyclobutadiene, because every carbon is sp²-hybridized, it's cyclic. But, do you think this is a planar molecule? Because every position is sp²-hybridized, and sp²-hybridization, that usually produces something that's planar. If every single carbon is planar, then shouldn't the whole darn molecule be planar too? It would make sense; but it's not. If you tried to make the whole molecule planar, it ends up being less stable than if it distorts so that the double bonds don't interact with each other. That sounds exactly like the story for cyclobutadiene, doesn't it? Cyclobutadiene distorts because it's trying to avoid that destabilization. Cyclooctatetraene has a sort of boat-like structure, where two of the double bonds flip up to avoid the other two double bonds. That's so it avoids this extended conjugation. How could we explain why this is happening? It's going to be based on the molecular orbitals, but we don't want to have to try to write the shade-in diagrams for all the eight cyclooctatetraene molecular orbitals.

We don't need to, because here's the really freaky coincidence that happens – this would be the Frost circle. You start with a circle, put an origin in it, and that origin represents zero energy. If we end up with an orbital on that line, that means it's going to be non-bonding; anything above is antibonding, and anything below is bonding. As I had said before, there's always only exactly one lowest energy level in any of these cyclic systems, so I'm automatically going to put an energy level there. The strange coincidence that occurs is if you inscribe an octagon. Why an octagon? Because there are eight carbons in the circle. It turns out that the relative energy levels that we get exactly match the energy levels that we get in real life. If we knew what, quantitatively, the energy of going from zero down to that lowest energy level, and then were to measure the energies in real life for the other orbitals, it matches this. It just this crazy coincidence that occurs from cyclic conjugation.

We've eight energy levels. Notice three of them are bonding, three of them are antibonding, and then there's two non-bonding orbitals; we know that because an octagon's going to even cut the circle into quarters. How many electrons total are going to go into here? There are four double bonds on paper, that means eight electrons. Where are the eight electrons going to go? They're going to follow the normal filling rules, which means two electrons are going to end up in non-bonding orbitals – again, the same situation as the cyclobutadiene. If we allowed all the double bonds to be separate from each other, like what the structure really does, then all those pi electrons would be in bonding orbitals instead. So, when we try to flatten the structure, we destabilize it because we're pushing electrons into non-bonding orbitals. It avoids being planar so that all of the electrons can be in bonding orbitals. It's just another example of when something bad can happen. The point of this example is to show that we could use a Frost circle to correctly predict those relative energy levels, to correctly predict how many are bonding, non-bonding, and antibonding. If cyclooctatetraene was forced to be planar, two pi electrons that otherwise would be in bonding molecular orbitals are instead pushed into higher-energy non-bonding orbitals, which is not favorable. As such, the structure of cyclooctatetraene is distorted, so that the four double bonds avoid each other.

I'm going to do one last example, in which I'm going to use the Frost circle again, so that I can justify the results that occur. This is cyclopenta-1,4-diene. [Its] pK_a is far, far smaller than what a standard hydrocarbon should be. It turns out, in fact, it is the hydrogen right at this position. [16], [its] pK_a value, is certainly a lot lower than 50 or 60, which is typically what you have for an alkane. That means that, for just a plain hydrocarbon, no oxygen or anything else in it, this is an extremely acidic compound. Can anybody come up with a rationalization of why this would be acidic? It's as acidic as an alcohol that's got an electronegative group on it to make it electron-withdrawing and make it more acidic – but why? What would it look like if it were dissociated – take an H⁺ off. We make this anion. What is the hybridization of the carbon at that lone pair? It looks like it's sp³, doesn't it?

Is it? Cause now it looks to me like it's sp^2 . So which one is it? Beyond that, what about these other carbons that used to be sp^2 but now looks sp^3 ? Which one is which? It turns out I could write three other resonance structure. You could push that lone pair three other places and end up so that each carbon has the lone pair at some point. If every carbon has the lone pair, then every carbon can't be sp^3 , cause the only way this could occur is if this is delocalized, which means every position is sp^2 . The cyclopentadienyl anion, which is what this is, is completely delocalized. Although its written structure appears to contain a carbon that is sp^3 hybridized, this is only because it is a resonance structure that fails to properly show the true structure of the molecule.

What if we were to write one of these Frost circles for it? What's the rules for constructing a Frost circle again? One vertex of a polygon is automatically located at the bottom of the circle. Two – the number of sides of the polygon is equal to the number of atoms in the ring. Imagine this – if I put an ethyl group on benzene, is that ethyl group going to have any effect on benzene itself? Are there any p orbitals on the ethyl group that could affect the conjugation going on on the benzene ring? No. When I make a Frost circle of that compound, then, I'm not going to have eight points in the circle, because in the [ring] itself, there's only six atoms. The polygon being inscribed only has as many points as the number of atoms in the ring itself. If the farthest part of it was an alkene, it wouldn't be conjugated at all, it would still have no effect. If you made the whole ethyl group an alkene to make the molecule styrene, the extra double bond, it turns out, does not interfere with the benzene portion of it. That ends up being a very reactive molecule because you have aromaticity and conjugation between that ring and the double bond. But, unless you make another loop, it doesn't have an effect. The number of vertices in the polygon equals the number of atoms in the ring. Notice I said atoms instead of carbons: [one example I will show] doesn't even have any carbon in it, but still has this same sort of stabilization. The polygon is inscribed in a circle. The vertices that are at the same level as the origin represent non-bonding orbitals; below represents bonding; above, antibonding. If I had five carbons in that cyclopentadienyl system, it's a pentagon that I'm going to inscribe now. I put one point down at the lowest position, cause that represents that one lowest-energy molecular orbital. Because I've had some experience doing this kind of problem, I just happen to know that three of the points of this pentagon are going to end up below the middle line and two of them are going to end up above. We have an unequal distribution of molecular orbitals; that happens this time because we have an odd number of points in that circle. We could at least use this to describe what happens.

How many electrons am I going to put in here if this represents the cyclopentadienyl system? How many total pi electrons? Six, cause you have two double bonds, and they you've got the lone pair, so $4 + 2$. That lone pair, remember, it's not in an sp^3 -hybridized orbital, cause it's in this completely delocalized system. This has six pi electrons. Notice that those six pi electrons are going to exactly fill the bonding orbitals. What are some generalizations? If you had the smallest system, then you'd have one bonding orbital. If you had, for example, a three-atom system, that you had conjugation, you'll end up with one and only one bonding orbital. That means there's always at least one bonding orbital. No matter how many atoms are in the system otherwise, no matter how large or small the ring is, when we start adding any other orbitals to it, there's always going to be, if there are more bonding orbitals, an even number of orbitals around, because if you look at some of these Frost circles or look at the diagrams we've constructed [before], all of those cases had one lowest orbital and then pairs of bonding orbitals. You put these two things together, and this is the explanation for what is known as the $4n + 2$ rule – that if you count up the number of pi electrons, that's the magic number that you've got to have if you're going to have this stabilization occur. If you looked at all of the systems where we have destabilization – for example, cyclobutadiene, there were a total of four pi electrons. Four doesn't fit this formula $4n + 2$. If you look at the cyclooctatetraene, that would be 8 pi electrons; 8 doesn't fit this equation of $4n + 2$. If, instead of that cation, the triangular cation, what about being an anion instead? That would have been four pi electrons, and from this diagram, you would see that some of those electrons would automatically go into antibonding orbitals. It's more symmetry, more coincidence. This is the rule that's developed. Aromatic systems will only have bonding electrons, which means the total number of pi electrons equals $4n + 2$, where $n \geq 0$. That's not entirely correct; the better way to say this is that all bonding orbitals are filled. This is the origin of this $4n + 2$ rule, which is part of what are known as the Hückel rules – rules for predicting whether a compound will be aromatic or antiaromatic.

A compound will be aromatic when it is cyclic. The stabilization, the unusual stabilization only occurs when you pull everything into a circle. Just think of it this way: if you had a linear system, just a line of p orbitals, the two end orbitals don't interact with each other. As soon as you pull that around, they, on top of all the other orbitals, interact. That changes the types of molecular orbitals that are available. All of this only happens if there's full conjugation around the circle. I showed you an example up above where I put an ethyl group on benzene. The ethyl group doesn't have any effect, it doesn't prevent conjugation, so we ignore it. So it's cyclic, it's fully conjugated. For something to be fully conjugated, which means those p orbitals really do overlap with each other, it's gotta be planar. Then, the last restriction is that we can only have $4n + 2$ electrons.

Shall we look at some examples of aromatic versus antiaromatic versus non-aromatic systems. Non-aromatic would mean neither stabilized or destabilized. This is the molecule naphthalene. Aromatic or non-aromatic or antiaromatic? Aromatic? Why? Is it cyclic? Ignore the double bond that's bisecting the compound; just focus on the fact that you've got a p orbital here and a p orbital here, and there's a larger ring system involved. Is it cyclic? Yes. Is it fully conjugated? Yeah, every position is sp^2 -hybridized. Is it planar? It turns out in this case, yes, it is, because those six-membered rings, they're both locked in, and because it's all full of double bonds, it is planar. Does it have the right number of pi electrons? How many total pi electrons are there? 10, cause there's five double bonds.

The reason I said ignore that double bond in the middle of that ring cause realize that I could write another resonance structure that doesn't have the double bond in the middle, but instead has it going just around the system; let me write that one to make it a little clearer why it is aromatic. For that resonance structure, it looks like the double bonds are only going around the outside. So yes, it is cyclic, it is fully conjugated, it's planar, and it's got 10 electrons, which works of $n = 2$. n is any number it has to be, as long as it fits that equations, and as long as it's a whole number. As long as you can match it to a value of n , then it's ok.

How about pyridine? Is it aromatic? Is it cyclic? What's the hybridization on each atom in the ring? sp^2 , so they all should be fully conjugated. Is it planar, therefore? Yes, in a six-membered ring, it's the only choice it has is to be planar if they're all sp^2 -hybridized. How many pi electrons are there? What about the lone pair on nitrogen? Is it part of the pi system? No, it's not. We could write a portion of a SMOG to justify this. If I have the nitrogen and [a] carbon on either side of it R stand stand for our variable name, but in this case it also means the rest of the ring; at the moment, I'm only concerned what's going on around nitrogen. Nitrogen is sp^2 -hybridized, which means it does have a p orbital available to undergo conjugation. But if that's true, that means that the lone pair is not in the p orbital; it's in an sp^2 orbital which is perpendicular to the pi system. It is aromatic, since there are only six electrons that are in a planar, cyclic, conjugated system.

Shall we see another example? This is the compound pyrrole. Is it aromatic? Is it cyclic? Is it planar? Is is fully conjugated? What is the hybridization on the nitrogen? sp^3 ? No, it's not, it's sp^2 . Why would it be sp^2 ? There's two stories to tell behind this. One, it's the fact that nitrogen auto-inverts. If you look at the structure of [ammonia], it's three hydrogens pointed one way, a lone pair pointed the other – except that, a few billion times a second, the lone pair and the hydrogens switch places; it's called the auto-inversion of nitrogen. That process used to be used as the basis of atomic clocks, cause it was predictable, the frequency. But if that's inverting all the time, that means that there is, in theory, one moment where the whole system is planar. Remember, the hybridization matches geometry, not the other way around, so if you can pause for a moment and have that nitrogen planar, you have a p orbital. If you have a p orbital, it all of a sudden overlaps with the other p orbitals that are around it. There's a lone pair there. I'm about to draw a SMOG to prove that lone pair, unlike [in] pyridine, is part of the pi system. If it's part of the pi system, then, with the two other pi bond's we've got, we've got a total of six electrons in a cyclic, planar, fully conjugated system, which is why pyrrole – and the other heterocycles like it: thiophene, where you put sulfur instead; furan, where you put oxygen instead – all of those are aromatic system. Although the nitrogen appears to have sp^2 -hybridization, it is energetically far more favorable for it to be sp^2 hybridized, since it would then become part of an aromatic system. If someone asks what's the hybridization of nitrogen, it's sp^2 , no matter what it looks like on paper, because remember what things look like on paper don't necessarily match the true molecular structure. Geometry determines hybridization.

We do end up with areas where there's deviations. For example, cyclooctatetraene, you don't have planarity there because it'd be unfavorable to, so that's a distortion, that's a deviation from the ideal. In this case, it's also geometry, but it's also the stabilization, because whether or not that nitrogen was planar, the bonds with carbon could still be coplanar; the hydrogen would be pointed off at one angle, the lone pair would be pointed at another. Bring the lone pair up where it's parallel with the other p orbital, it gets trapped into that system. Because it's more favorable, it happens; things roll downhill. Since it's favorable because it's aromatic, that's why the structure's going to adopt the configuration that it has. We should draw a portion of a SMOG here to show that. The only way to explain [for example] for pyrrole and pyridine, whether they are or not aromatic, is if you can concretely say where the lone pairs are in these systems, which you can only do if you can draw a SMOG. Notice, it is the hydrogen itself. Pyridine didn't have a hydrogen, it just had a lone pair. Here, there's an actual hydrogen where it is the thing going to end up perpendicular to the plane of the ring. The lone pair just becomes part of that pi system.

Let me show you a couple more common examples. Is it aromatic? It's cyclic. What's the hybridization of boron? sp^2 automatically. That means there's p orbitals there. Because of that, what's the hybridization of each nitrogen? It is also sp^2 , for the same reason that it is in pyrrole. When it's sp^2 hybridized, every nitrogen and boron is conjugated with each other. The lone pairs on the nitrogen, that adds up to six pi electrons. That means it's aromatic – cyclic, planar, conjugated, has the right number of electrons.

One last molecule. This is cyclic, isn't it? It's got 10 pi electrons. What are the other restrictions? It's fully conjugated, which it looks like it might be. And it is planar – which it's not. To see why, let me redraw it larger, so that I could draw the two hydrogens in that must be pointed at each other in this structure. They must be pointed directly at each other, in line with each other. The two hydrogens can't exist in the same place, so the molecule has to twist, one hydrogen going lower, one hydrogen going higher. But that means it's not planar, which means it's not [fully] conjugated, which means it's not aromatic. Due to steric hinderance, the fact that two hydrogens are pointing at each other, the molecule gets distorted and non-planar, so it's not fully conjugated.

benzene – unusually stable due to cyclic conjugation; C-C bonds are equal

cyclobutadiene – unusually unstable due to cyclic conjugation; definite distinction between single & double bonds

Frost circle

If COT was forced to be planar, two pi electrons that otherwise would be in bonding MOs are instead pushed into higher-energy non-bonding orbitals (not favorable). As such, the true structure of COT is distorted, so that the 4 pi bonds avoid each other.

The cyclopentadienyl anion is completely delocalized. Although its structure appears to contain a carbon that is sp³-hybridized, this is only because it is a resonance structure that fails to properly show the true structure of the molecule.

1) One vertex of a polygon is automatically positioned @ the bottom of the circle.

2) # of vertices in the polygon = # of atoms in the ring.

3) The polygon is inscribed in a circle; the vertices that are at the same level as the origin represent non-bonding; below, bonding; above, anti-bonding.

Generalizations:

– There is always at least one bonding orbital

– Aside from the lowest-energy orbital, bonding orbitals appear in degenerate pairs.

4n + 2 rule - Aromatic systems will only have bonding electrons, which means the total # of pi electrons = 4n + 2, where n ≥ 0.

Hückel rules – A compound will be aromatic when:

– It is cyclic; it is fully conjugated (in the circle); it is planar; it has 4n + 2 e-

naphthalene: cyclic; fully conjugated; planar; 4n + 2 = 10, n = 2

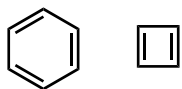
pyridine – lone pair is in sp² orbital, which is perpendicular to pi system – aromatic, since there are only 6 pi e- in a planar, cyclic, conjugated system

pyrrole – Although nitrogen appears to have sp³ hybridization, it is energetically far more favorable for it to be sp² hybridized, since it would then become part of an aromatic system.

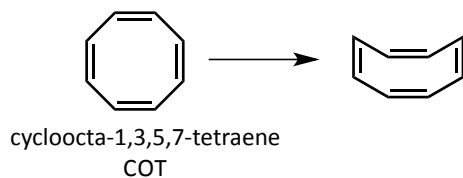
cyclodecapentaene – cyclic, 10 pi e-, not planar – not aromatic – Due to steric hinderance (the two H being pointed @ each other), the molecule is distorted and non-planar, so it is not fully conjugated.

Structures

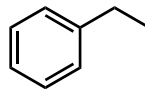
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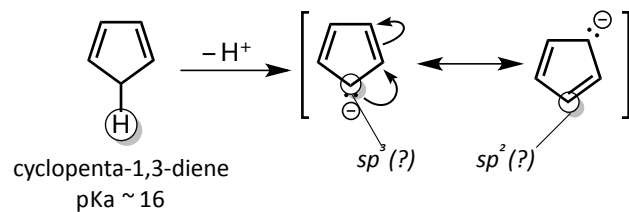
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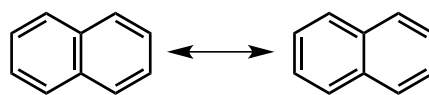
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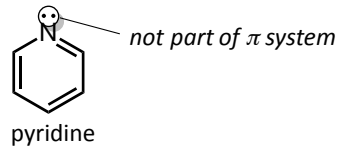
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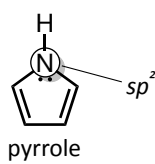
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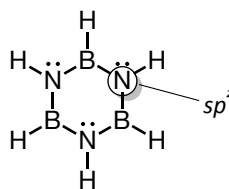
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2/28/12 lec • 9



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