Lecture 15A • 02/29/12

We found two contrasting effects of cyclization: 6-carbon compound with three double bonds, if it were linear, that exists; four-carbon compound with two double bonds, if it were linear, that exists. What we found out is that there's some unusual stability that occurs by bringing the six-membered system into a ring, that the bonds between different carbons are all the same length, so there's something unusual about the structure of beznene. The opposite happens with cyclobutadiene. It is unusually unstable; the two pi bonds try to get as far away from each other as possible. But yet, if we look at the two molecules, they're both cyclic systems, they both have sp2-hybridized carbons at every point in the system, but we have these contrasting effects – one of stability, one of instability.

Cyclobutadiene is anti-aromatic; cyclization causes instability. Whereas for beznene, it is aromatic – which does not directly relate to the fact that many of these derivatives do have a fragrance. The word aromatic might have come from the fact that these compounds are fragrant, but the term itself refers to this stabilization – the fact that cyclization causes notable stability.

To make the arguments that I did as to why is one stable and one is unstable, we had to write these molecular orbital diagrams – not SMOG diagrams, we did these diagrams where we used p orbitals that were shaded different ways to represent the bond, non-bonding, or antibonding orbitals that would form. For benzene, what ends up happening is by cyclizing, the total energy released by putting bonding electrons in the bonding oribtals, there's a greater amount of energy released for benzene than there is in a linear molecule. That is that extra stabilization that occurs. For cyclobutadiene, because of the cyclization, we went from a system that had – if we were in a linear system – only bonding orbitals, but by making it a ring, we forced two electrons into an antibonding orbital, which is what caused it to be destabilized and why the molecule tries to pull apart, so that it's not fully cyclicly conjugated. In theory, this same approach we could use for any sized molecule with any number of atoms, but you could imagine that if we have a nine-sided figure that it might get kind of scary to rationalize what might those molecular orbitals look like.

But, we don't need to know what they look like in order to predict their energies because of this crazy coincidence known as a Frost circle. If you look at the diagrams for benzene, the energy diagrams, for both benzene and cyclobutadiene, there is only one lowest-energy level. If you think about it, think of the particle-in-a-box example, think of the phone cord example, think of the fact that these conjugated systems we imagine as a line of carbons. There's this lowest-energy wave that would cross it. There is only one way to have that lowest-energy wave, so no matter what size the circle is, there will only be exactly one lowest-energy level. Due to this symmetry that occurs, in the cyclic systems, for every other energy level – except possibly the top one – all those other orbitals occur in even numbers of [orbitals]. What we would find if we did every possible cyclic combination is that, beyond that first lowest-energy bonding orbital, you always have, for bonding orbitals at least, pairs that would appear.

Here'z the way that a Frost circle works. Let's take a particular example molecule that I have in mind: another classic case for discussing aromaticity or anti-aromaticity. This is the molecule COT, which stands for cycloocta-1,3,5,7-tetraene. Let me explain the rules for creating a Frost circle. Obviously, you start with a circle. Put the origin in the middle. That line that passes through the origin that cuts the circle in half, that is the zero-energy level. The first thing that you do is inscribe a polygon, with the number of sides equal to the number of atoms in the ring. If we have a molecule like this, ethylbenzene, that ethyl group is not in conjugation with the benzene ring, it's just sp3-hybridized. There might be hyperconjugation, but there's no conjugation, which means the ethyl group doesn't really stabilize or destabilize the ring terribly much (it does actually have a small beneficial effect). In other words, if we're worried about whether this is an aromatic compound or not, we don't look at the ethyl group, we only look at the ring portion of it. So, when doing this Frost circle, that polygon you're going to inscribe has the same number of sides as the number of atoms in the ring. The one restriction to this is that one vertex of the polygon must be located at the very bottom of the circle. Then, vertices on the midline represent non-bonding molecule orbitals; above the line, we have antibonding, and below the line, bonding. Where this comes from is that any interaction between a pi system, a conjugated pi system, could be modelled using a series of matrices, where the different elements in that matrix represent the different interactions that occur between atoms. In a cyclic system, we restrict that so the interaction only occurs between one atom and its immediate two neighbors. In turns out that, in solving the system of equations that comes of that matrix, the solutions always have this form where the lowest-energy orbital, there's only one of it, and that for the bonding orbitals, the would otherwise occur in pairs.

Let's see how that would work in this cyclooctatetraene system, because we have eight carbons in the ring, and because there's 8 atoms in the ring, we're going to inscribe an octagon into the circle. The fact that molecule has an octagon shape is a coincidence; it's because there's only 8 carbons in the ring that we're going to inscribe an octagon. Again, if we look at the case of ethylbenzene, we would not put 8 points in that polygon, because we've only got six carbons in the ring. Cyclooctatetraene, let's inscribe that octagon. We end up with a set of molecular orbitals that have these energies. For our purpose, we don't even need to know quantitatively what those energies are; we just know that we have a certain number of antibonding, nonbonding, and bonding orbitals. In cyclooctatetraene, how many pi electrons are there? 8, because each pi bond – whether it's real or not, whether it's just on paper or not – does represent two electrons, so four pi bonds, eight electrons.

Let's fill these up [with 8 electrons]. Notice that two of the electrons go into non-bonding orbitals. How would that compare to the linear case? In the linear case, you're going to end up with four bonding and four antibonding orbitals. For an even number of linearly-arranged p orbitals, half of the molecular orbitals that result are bonding, half are antibonding. There's still 8 pi electrons, but now they only go into bonding orbitals. Here, in the case of the linear, we have eight bonding electrons; here, only six bonding electrons.

The true shape of cyclooctatetraene is line this: where two of the double bonds kinda pucker up like a boat shape to avoid the other two double bonds, cause when the double bonds avoid each other, all of the electrons end up in bonding orbitals. If you were to force the pi bonds to be flat, then you're going to force two of the electrons into non-bonding orbitals, which would be higher in energy, and it's not favorable. Even though there might be a cost to distort the molecule, it ends up being beneficial to do that to avoid this anti-aromaticity. In cyclooctatetraene, when the molecule is forced to be planar, two pi electrons are forced into non-bonding molecular orbitals. If cyclooctatetraene distorts, the four pi bonds are no longer fully conjugated, so the pi electrons would exist only in bonding orbitals instead. Part of the reason this is a classic example is if we looked at the structure and that's all we knew about it, it's just the way it's written on paper, we might guess that it should be planar, because sp2-hybridization, that is planar geometry, and if every carbon is sp2-hybridized, why wouldn't it all be planar? The problem is, though, it won't be planar, because if it was, then you'd have this destabilization because of the change in molecular orbitals that would result.

Next example, where I'm again going to use a Frost circle. The two things about a Frost circle that I care about right now are that, one, we don't have to know how to write the pictures of the molecular orbitals to argue whether they're bonding or antibonding, and, [two], it does give us the relative number of bonding, non-bonding, and anti-bonding orbitals. Here's another very classic case: cyclopenta-1,3-diene. It has a pKa value of 17; the hydrogen that I've drawn in is the hydrogen that that pKa value is referring to. It is acidic for a compound that is just a pure hydrocarbon. Alkanes, if we didn't know any better, that would look like an alkane proton. They usually have pKa values in the 50s and 60s, alkenes around the 30s, alkynes in the mid-20s. An alcohol with a nice electronegative element on it is going to have a pKa of around 16, but only because it has that electronegative element. How is it that we have a pure hydrocarbon that is, by comparison, really acidic? Why is it able to get deprotonated, because a pKa of 17 compared to 50 means there's a whole lot of stabilization going on due to something. Resonance.

Let's look at that resonance. An H+ comes off, which is going to leave an anion. Leaving out the bond numbers for short, this is called the cyclopentadienyl anion. What is the hybridization of this carbon that I've circled, with the anion on it? Sp3. Are you sure? Because, if there's resonance going on here, let's write a resonance structure. We could write another resonance structure; if fact, there's a total of 5 of them for this molecule. If you look at any one point where the ion temporarily gets localized, you could say each one is sp3-hybridized. But you look at any other structure, that same carbon's sp2-hybridized. This is because these are resonance structures, so on paper, yes, it looks like the anion stops in one place, but the point of resonance structures is none of these [is] right. So although the cyclopentadienyl anion is written with a localize lone pair, which makes that carbon appear to be sp3-hybridized, the written structure fails to correctly reflect the shape of the cyclopentadienyl anion, due to delocalization.

Why would it do this at all, though, because yes, it's resonance stabilized, but there isn't just resonance going on here, because it's cyclic. Let's draw a Frost circle for this. I just happens again to work out that we're going to inscribe a pentagon in here, because there are five atoms in the ring. If we had extra atoms, thing that were not in the ring, they wouldn't be inscribed as part of this polygon. We inscribe the polygon, and what do we get out of it? In terms of orbital energies, we end up with five molecular orbitals, three of which are bonding, two of which are antibonding. How many pi electrons are there? Six. Why? Two pi bonds, and then the delocalized lone pair; since the lone pair's delocalized, it's part of the pi system, so we count those electrons. Six electrons total, which, notice, they happen to exactly fit in just the bonding orbitals, so there's only bonding electrons, which means stabilized. If we take what looks like a pretty extreme case of a molecule, the cyclopropenyl cation, this is going to have the same type of stabilization. If we draw a Frost circle – it's as minimal a one as you can get – it shows us that we'll end up with one bonding orbital and two antibonding orbitals, but only the bonding orbitals will have electrons. In this three-carbon system, there's one bonding orbital. In the four-carbon system, there['s] still only one bonding orbital, and then there were the non-bondings. In the five-membered system, we have three bonding orbitals: the lowest one, and then pairs. If you look at benzene, you have the lowest one and [a] pair. If you look at the cyclooctatetraene, we had the lowest one and pairs.

There are some generalizations that can be made about aromatic systems. These are the Hückel rules for aromaticity – when is a system going to be aromatic. It only happens if the molecule is cyclic, if the portion that you're trying to identify is aromatic is cyclic, because whatever strange thing that happens that makes it stable or unstable only occurs when you make the cyclic molecule. Along with that, you have to have full conjugation around the ring – every point has to be conjugated, otherwise you don't have delocalization. Along with that, though, it has to be planar, because if the orbitals used to represent these are not all aligned with each other, then there's not the conjugation.

And then there's this last rule, which is normally [just] memorized, but the Frost circles actually give some justification to this: that the number of pi electrons must equal 4n + 2, where n is any number it needs to be in order to make that expression true, the only restriction being that n has to be greater than or equal to zero, but only using whole numbers. In other words, if you have two electrons, 6, 10, 14, 18, those are all valid numbers. The reason that last part of the rule works is, if you have something like the cyclopropenyl cation, you're only going to have one bonding orbital; there's your two [electrons], n = 0. The cyclopentadienyl [anion], we have six, n = 1. If we look at cyclodecapentaene, then you're going to have 10 bonding electrons, two more orbitals – in general, 4n + 2 [electrons].

WIth that definition in mind, let's look at a few common example molecules and try to figure out whether they are aromatic or not. What's the name of that molecule? Naphthalene. It has a resonance structure. The reason I show the resonance structure is that it more clearly shows the fact that, ignoring the single bond that connects the two sides together, if we look just at the pi system, it looks like we have this track going all the way around the outside of the molecule. So if we were to make a Frost circle, we would make a decagon, even though this is not the shape of a decagon. We don't even need to do that because that's what the Hückel rules allow us to do – instead of having to draw those diagrams out, we can just plug-and-chug. Do we think this going to satisfy all of the conditions of the Hückel rules, though? Is it cyclic? Of course it is. Is it fully conjugated? It sure appears to be; every point around the circle is sp2-hybridized. Is it planar? Yes, it is planar. There's no other option, especially because you've got that connection between the two sides of the molecule. Does it have the right number of pi electrons? Yes, because 5 pi bonds written means 10 electrons, so if n = 2, 4n + 2 gives is 10. So, it is aromatic. That's because it is cyclic, it's fully conjugated (each carbon is sp2-hybridized), it is planar, and has 10 pi electrons (which equals 4n + 2 of n = 2).

Shall we see another one? How about its close cousin. Is it cyclic? Is it conjugated? Is it planar? No, it is not planar. How could it be, cause you have a hydrogen pointing down this direction that's bumping into the hydrogen pointing up from the other direction. Because of the size of the ring, they would pretty much have to be right on top of each other if not, in fact, overlapping each other, which is not physically possible. So, the structure has to distort to accomodate those two hydrogens, which means it's not planar, which means it's not fully conjugated, which means it's not aromatic, even though it looks like it should be. So, due to steric hinderance, the molecule distorts, causing it not to be planar, causing it not to be aromatic. If the ring is locked into this configuration, then each carbon is sp2-hybridized, because we've got hexagons going on, so the carbon-hydrogen bond coming up from the bottom, for example, really would put the hydrogen right about here. The same would be true in the opposite direction. It can't physically happen, so it bends.

Let's see another couple of example molecules. What's the name of this one? Pyridine. Is it cyclic? Yes. Is it planar? Sure it is; you've got all pi bonds here, and it's only one ring, so it is planar. Is it fully conjugated? Does each position have a p orbital. Another way of asking it, will each position be sp2-hybridized? Yes. Does it have the right number of electrons? Yes. Why? Maybe if we drew a SMOG we could figure that out. I'm only going to draw it for part of the molecule. Each position is sp2-hybridized, which means there are p orbitals at each position. Yes, they all overlap each other. Off each side, I'll say 'R', which is going to mean the rest of the ring in this case. But, if you have a pi bond between carbon and nitrogen already, can that lone pair be in the same orbital? No. The lone pair is in the sp2-hybridized orbital and is perpendicular to the pi system. The lone pair does not delocalize, so it is aromatic. That lone pair can't be in the same place as the pi bond, so it can't be part of the pi system.

How about the other close cousin of this molecule, pyrrole. Is it cyclic? Yes, of course it is. Is it planar? Yes, because even if we think the nitrogen has got trigonal pyramidal geometry, then the two bonds that are part of the ring are still going to be coplanar with the ring, so yes, it is definitely planar. So, it is cyclic, it is planar; is it conjugated? What is the hybridization of that nitrogen? sp3? No, it's not; it's sp2. Normally, you count lone pairs and sigma bonds and that tells you the hybridization – most of the time. Geometry determines hybridization. This is planar, and so it's sp2-hybrdized, because when it's planar, if it's sp2-hybridized, it's got a p orbital that delocalizes with the other p orbitals. That lone pair would be in the p orbital, because as I'm going to show in the SMOG in a moment, the hydrogen is now pointed out of the ring. If that lone pair joins the other orbitals, you have six pi electrons – that's exactly the number that you need to fill the bonding orbitals of the equivalent-to-the-cyclopentadienyl-system set of molecular orbitals that we would generate. In other words, it's aromatic.

Another part of that story is that nirogen autoinverts. If you look at the structure of nitrogen, it's got a trigonal pyramidal geometry to it – three bonds making the base of a pyramid, one lone pair pointed the opposite way. That structure inverts zillions of times a second. In fact, that used to be the foundation of certain types of atomic clocks – ammonia-based atomic clocks. If that things always inverting, that means at some point it's transitioning between the two, which means it really does act, for a moment, like it's sp2-hybridized – the moment it is, you've got a p orbital, which is conjugated, and it never leaves it. So, this is aromatic. The nitrogen in pyrrole is sp2-hybridized, due to the fact that energy is released by the lone pair on nitrogen delocalizing with the neighboring pi bonds. If I did a SMOG just for this portion of the molecule, we'll see on the nitrogen and the two carbons neighboring it – on all of those atoms, on every atom, every part of the ring is going to have one hydrogen coming off at a 90° angle. Since the hydrogen is perpendicular to the pi system, that makes the lone pair part of the pi system, so it becomes aromatic.

[Between pyrrole and pyridine, you can't ask which one is more stable because they're two completely different molecules with two different molecular formulas]. What you could ask is: what is the resonance or the aromatic stabilized present in each compound. That might be answerable, but you can't answer directly: which compound is more stable.

Where would you have acidic protons on pyridine? What would the pKa value you guess would be for pyridine? Because there is an effect of aromaticity on acidic, but if we just looked and saw those were double bonds, we could guess the pKa is somewhere around the mid-30s, for example. Nitrogen, yes, this has a hydrogen on that nitrogen, but nitrogen compounds are bases. There is a large difference in the basicity of these two compounds, because for the top one, pyridine, if you react that with an acid and you have protonation, it doesn't affect the aromaticity of this system, because the pi part of that never has to interact; it's just the lone pair. But down here, if you force that lone pair to react with an acid, you break aromaticity, which is unfavorable. So, the top compound's a base, but this bottom compound really isn't.

We have time for one more example – one of my favorite examples. Count the number of sides. 7, which is part of the reason this is fun. Is this compound aromatic? Is it cyclic? Yes. Is it planar? Yes. Is it conjugated? No, because there's actually two hydrogens here, not a lone pair. This is a special molecule, because it loses hydride, H-. It's not acidic. [what would you call it?] It loses a hydride instead, and it forms the cycloheptatrienyl cation, also known as the tropylium ion as its common name. Why might the tropylium ion be favorable, and therefore losing hydride from that parent compound be favorable?

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benzene – aromatic – cyclization causes notable stability
cyclobutadiene – antiaromatic – cyclization causes instability

Frost circle – Rules for creating a Frost circle
– Inscribe a polygon that has the same number of sides as the # of atoms in the cyclic system.
– One vertex of the polygon must be located at the very bottom of the circle.
– Vertices on the midline represent non-bonding MO; above, antibonding; below, bonding

In COT, when the molecule is forced to be planar, two pi e- are forced into non-bonding MOs. If COT distorts, the 4 pi bonds are no longer fully conjugated, so the pi e- would exist only in boning orbitals instead.

Although the cyclopentadienyl anion is written with a localized lone pair (which makes that carbon appear to be sp3 hybridized), the written structure fails to correctly reflect the shape of the CPD anion due to delocalization.

Hückel rules for aromaticity:
1) cyclic
2) full conjugation around the ring
3) planar
4) # of pi e- = $4n + 2$; $n \geq 0$; n must be a whole #

napthalene – aromatic – cyclic, fully conjugated (each carbon is sp2 hybridized), planar, 10 pi e- => $4n + 2$, $n = 2$

not aromatic – Due to steric hinderance, the molecule distorts, causing it not to be planar, causing it not to be aromatic.

pyridine – cyclic, planar, conjugated, $4n + 2$ – aromatic
lone pair is in a sp2-hybridized orbital and is perpendicular to the pi system; the lone pair does not delocalize.
pyrrole – cyclic, planar, conjugated – The nitrogen in pyrrole is sp2-hybridized due to the fact that energy is released by the lone pair on N delocalizing with the neighboring pi bonds. – aromatic

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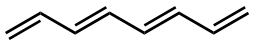
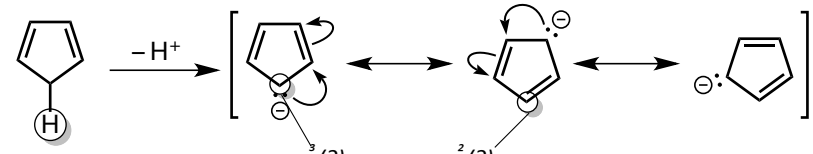
Structures *(remaining structures identical to lecture 16B)*

2/29/12 lec • 1



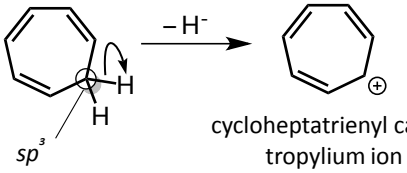
2/29/12 lec • 2



pKa ~ 16

cyclopentadienyl anion

2/29/12 lec • 3



cycloheptatrienyl cation
tropylium ion