

## Lecture 18A • 03/08/12

Imidazole. Why is it aromatic? Because it's a combination, structurally, of both pyridine and pyrrole, because the nitrogen that has the double bond, you can't have a pi bond and a p orbital both pointing at the same time the same direction, so the nitrogen that has the double bond, the lone pair automatically has to be perpendicular, which is exactly the same as pyridine. The other nitrogen, the one that had that hydrogen on that, that's exactly like pyrrole – that the lone pair is able to be in a p orbital, and because it's so favorable energetically to be aromatic, it is going to end up in a p orbital, so that puts the hydrogen perpendicular. So, one lone pair is part the cycle, one lone pair is not part of the cycle; therefore, there's only six electrons, it's cyclic, planar, conjugated, it's aromatic. Both nitrogens are sp<sup>2</sup>. One nitrogen's automatically sp<sup>2</sup> because it's already got the pi bond, and the other one is sp<sup>2</sup> because the lone pair ends up part of the ring, which is just like pyrrole. Imidazole has the same structural features as both pyridine and pyrrole.

The other question. That ethyl group was just to throw you off. That ethyl group had nothing to do with that second molecule, so we don't show it. You only count the things that are part of the ring. So yes, the compound has seven carbons, but you're only going to put a pentagon in that [circle]. It's not aromatic to begin with because it's not fully conjugated. That eight-sided figure, is it non-aromatic or aromatic? It depends. Because if you force it to be flat, of course it's antiaromatic because that's when you end up with that eight-sided figure and the orbitals and all that nonsense. But it doesn't do that because it's unfavorable, so in real life, it has that distorted structure. So is it non-aromatic or antiaromatic? Do you mean when you force it to be flat, then yes, it is aromatic; or do you mean when it is distorted, so it doesn't have that conjugation, and so it's neither aromatic nor antiaromatic. What does aromatic mean? Stabilization cause you make a circle. What does antiaromatic mean? [Destabilization cause you make a circle.] So what is the only difference, in terms of the Hückel rules, between aromaticity and antiaromaticity? The all have to be conjugated; if you don't have conjugation, you won't wind up with antiaromaticity. Antiaromaticity is when you make something that's cyclicly conjugated that's destabilized – so if it's not conjugated, it can't be aromatic or antiaromatic. It has to be conjugated; it has to be cyclic; and it has to be planar. So what's the only thing that determines whether something's aromatic or antiaromatic? Number of electrons, period.

If you fill up that Frost circle.... A Frost circle, how do you construct it? One point goes at the bottom automatically. You have a polygon that has the same number of sides as the number of atoms in the ring, and then you chop a line straight through the middle of the circle. Any orbital that's on the line is non-bonding; any orbital below it is bonding; any orbital above it is antibonding. How do we use that in this problem? There's six pi electrons; the exactly fill the bonding orbitals, which is why it's aromatic. All of this  $4n + 2$  nonsense, that's just the quickie way to memorize the rule, but otherwise, it's the fact that you fill the bonding orbitals. If you think about the cases that have ended up being antiaromatic – at least when we force them to be antiaromatic – we take that cyclobutadiene, not when it's totally stretched, but when it is symmetric and it's perfectly antiaromatic; we take that eight-membered cyclooctatetraene and we force it flat. Notice that we have more electrons that what will fill into the bonding orbitals, which is why it's antiaromatic.

[There is one carbon that] does start with sp<sup>3</sup>, which blocks the conjugation, which is why the molecule starts out non-aromatic. It is planar, because if you have five things in a ring, and four of them force the molecule to be planar, it is impossible to make the fifth one non-planar – unless it's something like cyclooctatetraene where it's a big enough molecule that it can distort. The five-membered ring too small for four things to be one in position and last one is out in space somewhere. It starts out non-aromatic, cause it's not fully conjugated cause you do have one position that's sp<sup>3</sup>, but then once you lose the hydrogen, the lone pair becomes delocalized, it becomes aromatic, it becomes sp<sup>2</sup> hybridized.

[If you don't fully fill the bonding orbitals] it's still not that favorable. You might have, for example: take that five-membered ring and put a plus instead of a minus. It's more favorable than an average carbocation, cause you do have that delocalization, but it's not truly aromatic, because you don't have the right total number of electrons.

[exam review – activators versus deactivators; ortho/para versus meta substitution; why are those separate considerations] It's because directing ability is entirely due to resonance, it's entirely due to delocalization. We found that, for ortho-para directors, there was a lone pair that could delocalize onto the ring to provide electron density, but in specific places on the ring – versus the meta director which caused a bad interaction between whatever carbocation you formed and that position, that substituent, so meta directors want to avoid that, which is why the go meta. The reason that's different as far as activation and deactivation, is that's due to activation energy. It turns out that halogens, which have lone pairs and therefore can do resonance, they cause ortho-para substitution because they put more electron density certain places due to resonance. But in the case, of fluorine, it's more electronegative than the density it provides through resonance, it takes more than it gives, so it causes a higher activation barrier which slows the reaction down; it's still ortho-para, but slower. For chlorine, it's the reverse case. Chlorine is not as electronegative, but it has bad orbital overlap with carbon, so it never provides as much electron density to begin with; it does provide it through resonance, which is why it's ortho-para, but it takes more than it gives, which is why it's a deactivator.

## Structures

No structures for this lecture.