

Lecture 12A • 02/15/12

We're going to continue our discussion of conjugation.

If we go back and talk about electrons and how they act like waves, [there's] something known as the particle in a box. You've got some kind of box where imagine that the walls are infinitely tall. It's a one-dimensional system, where the electron, all it can do, is go left and right between the two walls of the box. The electron's a wave; it can't exist outside the box, so whatever function, whatever wave we use to describe the electron, has to have a value of zero at one end of the box and zero at the other end of the box. Graphically, what do the solutions look like? We have something like this, where we're talking about energy potential; it's infinite at either end of the box, and zero in between. We have an electron that's bouncing around inside of it. An electron's a wave, and there's function that describes that wave. The only way it can fit in this box and physically make sense is if the wave starts and stops at the ends of the box. It turns out that – long, long, long story short – one of the solutions for the Schrödinger equation is just a sine function – actually, it's part of an exponential version of a sine function. It's something, at least, we can draw a pretty picture of. That's why you'll start with this problem in a discussion of quantum mechanics, because it is solvable, it is only on in dimension, and it's more humanly possible to discuss.

One of the other things that comes out of it, though, is that there is not just one equation that has these endpoints matching the ends of the box. What we could do is imagine that we had a function like this, $\sin \omega x$, where x is the x coordinate. There are multiple values of ω that would satisfy the conditions of y being zero at one end and the other. If you were to see all of those possible solutions, it looks like this: that you have a series of waves. If I separated these out and drew them individually, the first four waves, which correspond to the first four energy levels, which is the same n as the principle quantum number in your four quantum numbers for describing an electron; same n is involved here. First energy level, the wave looks like that; first, second, third, fourth. You notice that these correspond to waves that have zero nodes, one node, two nodes, three nodes. Remember a node is a place where you have a function whose value is zero; that means that that's a place where the electron does not exist. Notice, automatically these functions and nodes are symmetric; it just works out as one of the coincidences of all of this, that wavefunctions must be symmetric about the systems that they are in. You don't have a node all the way to one side versus the other, cause sine functions aren't lopsided like that.

What does this have to do with conjugation? If we looked at a double bond, versus allyl, versus a conjugated diene, versus a conjugated allyl, all these different systems, these are like one-dimensional systems, in a sense. Imagine an electron crawling up and down the carbon backbone and that's what it's restricted to. Then you have one end of the molecule, past which the electron would fall off, and then you have the other end, so this is a little bit similar to the particle in a box problem. We've got a pi system that's got an electron that's got a wavefunction that's got clear boundaries; the electron's not going to fall off the molecule. But otherwise, it's like you've got this clear line across, because you get all of this conjugation. The conjugation part of it, that's the point of doing SMOGs, so that you could see structurally that the electron, it's like it was crawling along a wire. Once we establish that that's what's going on, then that's how I arrived at those waves that I was superimposing on those orbital diagrams to explain how do we shade those different p orbitals to come up with a representation for the molecular orbitals. That's why I did the phone cord demonstration, because that's exactly the same situation: one fixed physical point, another fixed physical point, a sine wave that bridges the two, and there physically, the wave can't be anything but zero at the two ends. If you have a sine wave, but you have restrictions on what kind of sine wave, that means you only have a limited number of values of ω that would fit that, which gives you a limited number of waves, which gives you exactly the ones that you see in real life. This is all fundamental to the way that bonds vibrate, because bonds vibrating also have quantized energy levels – quantized means only very specific values. Transitions between energy levels, that's what spectroscopy investigates. [story about p-chem]

What I'm trying to say is that imagine the two ends of the box are the two ends of the molecule. Then if the electron is trapped in that box, it has to have wavefunctions that match that, that when you put it into this extended pi system, it's got barriers it can't cross. That causes it to have a certain set of equations which are these molecular orbitals that we're trying to draw pictures of.

We drew a picture of the bond and antibond for ethene, when you have two p orbitals. Then we drew the molecular orbitals for the allyl system. I want to do the next one, which is what happens when you have four orbitals, what happens if you have buta-1,3-diene. There is another butadiene: this is buta-1,2-diene. One of those two molecule has conjugation, one of them doesn't. Why? That dot is orthography, it's a way of writing this structure to show that you have a carbon there. Otherwise, if you had a double bond and then another double bond, if you were sloppy about it or if it didn't get printed well, you'd think it's just one big long double bond, so the dot shows there's a break there which means there a carbon at that point. These are sp²-hybridized. Do you think it would be helpful to draw a SMOG for that molecule? In buta-1,3-diene, all of the carbons are sp²-hybridized, which means the way that we represent this molecule [is to use] p orbitals on each of the carbons. We're in the same situation that we were with the allyl system: which set of p orbitals do we connect? Yes. All of them. There's experimental evidence for that, that shows there's something unusual about this molecule that you wouldn't expect if you just looked at it as two independent double bonds.

If there is conjugation going on, what do you think that's going to do to the single bond, the single bond that's connecting the two double bonds? Do you think it's the same length as a regular single bond? What causes bonds to be longer versus shorter? What's one of the main aspects of a bond that's going to tell you whether it's going to be shorter or longer? Energy is related. The type of nucleus – but also whether it's a single, double, versus triple bond. If you have a double bond, that's almost always shorter than the same two atoms if they were just in a single bond, cause there's more electrons that are bridging between the two nuclei, which if you have electrons between the two nuclei, it's lower in energy, wants to form a bond in the first place, that helps to bring the nuclei together. So, a carbonyl is a shorter bond, for example, than a carbon-oxygen single bond. Most carbon-carbon single bonds have roughly the same length to them – but not this one. This one is much shorter than a standard single bond, which is evidence that there's something going on between the carbons' p orbitals on either side of that single bond. In other words, if you didn't have conjugation, why would there be anything to bring the two halves of the molecule closer? But there is conjugation, which is causing that single bond to shrink.

Bond length can be established through x-ray crystallography. How do you figure out what the structure of a molecule is? How do you take a picture? How did the structure of DNA get discovered. You take x-rays, which are high-energy light. You bounce it off of a compound; it turns into a pattern of dots that you can mathematically analyze to backtrack and figure out where did the atoms have to be to create these diffraction patterns that got created. The fact is that the single bond is shorter than it should be. This is just a stepping stone to benzene; that's where we're really headed.

Due to conjugation, the single bond in buta-1,3-diene is shorter than an average carbon-carbon single bond. Linking this to benzene, all six carbon-carbon bonds in benzene are equal. Conjugation entirely explains benzene's unusual behavior. On paper, this has double bonds in it; if you've learned alkene reactions, then, if you didn't know better, I could say let's do oxymercuration-demercuration, let's do hydroboration-oxidation, let's do all the things we would do with alkenes – except most of them don't work with benzene. That's where all of this is leading to: to explain why doesn't benzene react that way. Benzene can react.

I need to come back to this other molecule to ask why is there no conjugation even though we've got two double bonds. The question was: why is buta-1,2-diene not conjugated? That dot, what's the hybridization there? It's sp hybridization, isn't it? Let's write out a SMOG for that. The carbon with the dot has the two sp orbitals; we have an sp²-hybridized carbon on either side; then we have an sp³, a methyl group at the end. I'm drawing everything but the p orbitals. What are the p orbitals on the sp hybrid? What is their relative geometry to each other? They're perpendicular. Do you remember the diradical we drew a SMOG of? Think of that. In a system like this, you've got a p orbital pointing one direction, but the other's perpendicular to it. One of the two pi bonds involves one of those p orbitals; the other pi bond has the other. If you're looking from the side – I use that stylized eye to show how I'm observing a molecule – this means look along the molecule that direction. The reason there's a little line up top is because it matters totally your orientation, the way that you're looking at it, so this is your eyebrow, the line on the top. So what would it look like from the side? Like this, to oversimplify. There's a 90° angle between the two pi bonds. Since the two pi bonds are perpendicular to each other, there is no conjugation. This is what is known as a cumulated diene. It happens any time you have one carbon that's shared between two double bonds. There's no hyperconjugation, even; well, there is, from this pi bond with that sp³ hybrid. Hyperconjugation is always between different types of orbitals; conjugation is going to be between multiple p orbitals. Hyperconjugation is a partial donation of electron density to a neighbor; conjugation is the full delocalization of electron density. A pi bond would be non-conjugated; it would just be a bond. Put another orbital that it complete overlaps with, that's conjugation. Put another orbital it kinda overlaps with, it gets a little density from, that's hyperconjugation. It's called hyper because you don't have complete delocalization.

Hyperconjugation is the partial donation of electron density to a neighboring orbital through a interaction that does not involve a bond. [avoiding term non-bonding] Conjugation is the full delocalization; if you not sure what that term means: local means right here, delocal means not right here, delocalize means to make not right here, delocalization is the act of making it not right here – in other words, you spread the electrons all across the molecule, how's that? The full delocalization of electron density across multiple orbitals due to full bonding overlaps. The hyperconjugation would be what happens between the p orbital here and the sigma bond. What happens is that sigma bond, it has electron density, and every once in a while as that sp³ carbon rotates and the sp³ orbital becomes almost parallel with the p orbital, they'll overlap a little bit. It's the idea that they only overlap a little bit that makes it hyperconjugation. If they don't fully overlap, it's not a bond, but they're doing some kind of interaction, so it's not nothing. Hyperconjugation, where it shows up more frequently, is to explain why it is that tertiary versus secondary versus primary carbocations are stable. If we look at a primary carbocation, for example, the ethyl cation, draw a SMOG for it, it looks like this: one sp³ carbon, one sp² carbon, a p orbital on the sp² carbon. It [the p orbital] interacts with the neighboring sigma bond. It doesn't matter that it's hydrogen or what that's attached over there, it's just the fact that you've got a sigma bond. That electron density, it's negative, it's an electron. You've got a positive charge sitting there; negative charge in any way interacting with positive charge is favorable, that's why hyperconjugation can have [an] effect on reactivity.

Let me draw this, because this is the more advanced version of the diradical problem. What you're asking is what you would get if you had this – a diradical. If you had a pi bond, that's because two p orbitals are parallel to each other; if you twist the p orbitals, you break the bond, but you've still got one electron in each p orbital. That's how you get a diradical.

The only way that you could end up with that p orbital is to have a system like this, because all of the hybridizations would still be the same. There's the pi bond; here's the perpendicular p orbital. This is an interesting problem, because if you did have a diradical, you'd actually have conjugation that way.

Let's move on now to this; let's draw molecular orbitals for that. The whole point of all of this stuff before – other than to show you the difference between conjugated and non-conjugated systems – is to show you've got this line – yeah, it kinda zigzags, but pretend for the moment that it's a line, and we have this wave that's bouncing back and forth between the two ends of the molecule. There's this rule of symmetry – the number of molecular orbitals in a pi system is always equal to the number of p orbitals in that system – which really has to do with how many nuclei there are. You put two nuclei together, you make two molecular orbitals; you put three nuclei together, you make three molecular orbitals; four nuclei, four orbitals. Why? Because that matches the number of possibilities of distributing electrons that end up in functions that match the boundaries of this system. We have four molecular orbitals that we're going to generate. Each of those four molecular orbitals, we use four p orbitals to represent them. I'm going to superimpose on top of them these phone cord waves. Look at the fact that there's no nodes in this lowest structure. If I'm going to color in orbitals, a make all of the signs of the p orbitals the same to match this function that exists across it. It should make sense that this would be the lowest energy possible. P orbitals don't really add together this way; this is a way of representing. But still, this corresponds to a wave that would span all the way across; it puts the most electron density between nuclei, and so it's going to be the lowest energy orbital possible. To use the sophisticated notation that we developed, all we have is good interactions going on there.

What about the next level up? Notice that there's one node. Let me write that one node in on the diagram here. A node means that you flip sign, so two of the p orbitals on the left and two of the orbitals on the right would be opposite each other. That means you have a good interaction, another good interaction, but one bad interaction. It's still, overall, is favorable, but not as favorable. For an even number of p orbitals, zero energy is always between the middle two; it's another consequence of symmetry – zero energy meaning if none of this bonding ever happened in the first place, if you had four independent atoms – in terms of their p orbitals. Yeah, there's the sigma bonds that are underneath all of this, but that's a separate story. As far as the p orbitals, zero energy always in between for an even number of p orbitals. That's because the node does not pass through one of the atoms. If we had an odd number of orbitals – just like the allyl system – then half of, the orbitals minus one, will be bonding; an equal number will be antibonding; and you'll always have on non-bonding orbital in between.

Coming back to these other examples. The two-node system; the nodes are right on either side, they're just on the outside of the middle two orbitals. How could you figure that out? If you're really good with drawing and you measure out exactly what a third versus a quarter is – realize that's what's going on, we've got two different types of divisions going on here. Other than that, you just memorize. Let's fill them in. Notice now that the number of unfavorable interactions outweighs the favorable interaction; that means it's an antibonding orbital; it is higher in energy than if these things never interacted in the first place. The last orbital is one where you've got nodes in between everything. To fill in here, we had two nodes then three nodes. There were three nodes; that means every other one's pointed the opposite direction, which means you have nothing but poor interactions, deconstructive interactions, so that's yet again an antibond.

How many electrons do we fill up in this molecular orbital diagram? You know that answer by looking at the molecule that's involved. Notice that we have two pi bonds – that means we have four pi electrons. Even if we end up saying that they're not really pi bonds; even if we end up saying it's a conjugated system, we could still use it on paper to count the number of electrons that are there. We have a total of four electrons in this butadiene. Aufbau principle – fill up the lowest energy level first. Pauli exclusion principle – you can squeeze two electrons into an orbital, as long as they're opposite spin. Hund's rule doesn't apply cause we don't have degenerate orbitals; we don't have orbital with equal energy. So then we got back to the Aufbau principle, which is go to the next energy level up and fill it up. We only fill the bonding orbitals. You might remember that there's this equation, bond order, which is number of bonding electrons minus number of antibonding electrons, whole thing divided by two. There's no non-bonding electrons that you put in this equation because they don't bond or antibond; that's why they're non-bonding electrons.

[electrostatic potential maps] The blobs [for buta-1,3-diene] would look something like this. For the four orbitals, you'd have something that looks like this. For the first two energy levels, the lowest and the next one up, the next one up would look like this, and the next one up would have four blobs, corresponding to no nodes, one node, two nodes, and three nodes. Notice how those match these pictures that we're generating with the p orbitals. What we could indirectly observe in real life are just the electron patterns; this is our way of coming up with a model that matches it. When using our writing system, whenever you have conjugation, the molecule doesn't really look like what you're drawing.

Spectroscopy comes in at this point often because in conjugated systems, to move an electron an electron to one energy level up is usually accessible using UV light. How do most chemical reactions occur in these conjugated systems? Think of it like valence electrons. What are valence electrons? The most energy electrons in an atom; they're the ones in the outermost shell. We don't have shells where, but we do have different energy levels. The highest energy level is going to have the electrons that are most likely to react. This orbital is the highest occupied molecular orbital (HOMO). Where do these electrons go?

If you were going to put electrons in this molecule, the only place they could go is the empty orbital, the antibonding orbital, or in general, whichever is the lowest-energy orbital that has space, which is referred to as the lowest unoccupied molecular orbital. This is a bit of molecular orbital theory called HOMO-LUMO interaction, cause the highest energy electrons go into the lowest energy space.

The photon that hits it has just right energy that exactly matches this gap between energy levels; to completely rattle your cages, remember NMR theory: the reason that light gets absorbed in that case is you have nuclei that are flipping back and forth between two energy levels. This is the same thing; it's just that NMR's radio waves and this is UV – that that photon has the right energy amount to kick the electron from one energy level to the next.

Particle in a box

Due to conjugation, the single bond in buta-1,3-diene is short than an average C-C bond.

Since the two pi bonds are perpendicular to each other, there is no conjugation.

hyperconjugation – the partial donation of electron density to a neighboring orbital through an interaction that does not involve a bond.

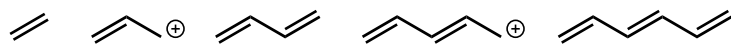
conjugation – the full delocalization of e- density across multiple [atoms] due to full bonding overlaps.

The # of MOs in a pi system is always equal to the # of p orbitals in that system.

Bond order = (# bonding e- - # antibonding) / 2

Structures

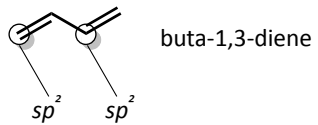
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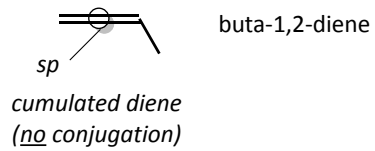
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buta-1,3-diene



buta-1,2-diene

cumulated diene
(no conjugation)

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