Introductory Organic Chemistry

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Lecture - 51
Aromaticity

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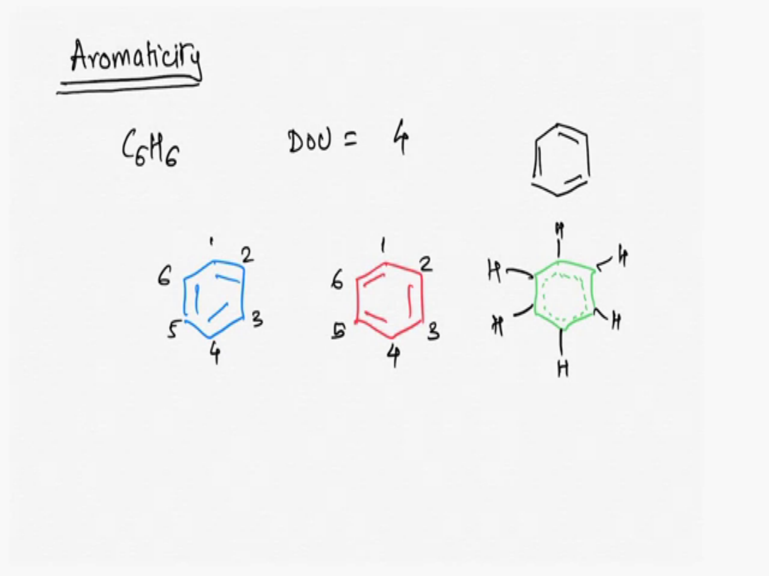

Welcome. This week we will be discussing Aromaticity and the first molecule that we think of when we think of aromatic compounds is really benzene. So, benzene is a colorless compound, it has a melting point of about 6 degrees and it is liquid at room temperature. Benzene was really first isolated by Michael Faraday and he isolated it from gasoline around 1800s. So, you can imagine that from 1800s we have really started looking at the chemistry of aromatic compounds. And benzene has a molecular formula of C_6H_6.

So, chemists were able to figure out that this is a molecule, colorless liquid, has a molecular formula of C_6H_6 which really suggests that it should have a high degree of unsaturation. So, if I figure out the degree of unsaturation for this compound it comes out to be 4, right. Now, we know that the degree of unsaturation is because of the 3 pi bonds and the ring that exists in benzene; but really at that point when there was no other way or no other spectroscopic techniques to figure out the structure of molecules it was difficult to come up with this molecular structure.

And in fact, chemist struggled a long time to come up with the right chemical structure for benzene. You must have heard about the story of Kekule, a chemist who dreamed about a snake eating itself and then he thought of benzene could be a ring structure. Initially chemists were just trying to fit the structure of benzene to linear alkenes or alkynes and none of it could really satisfy the chemical properties of the molecule. And when Kekule came up with this ring structure it was evident that this kind of structure fits the chemical reactions of benzene and thus chemists went on with this formula.

However, if you really look at this particular structure here, we can see that it has 2 resonance structures. So, one is this, but it can also have a resonance structure that looks like this. As you can see if I label the carbons here the double bonds in the first structure or alternative to the double bonds in the second structure and then it was thought that these are really resonance structures of benzene. So, it should really exists as a resonance hybrid and in fact, it does exist as a resonance hybrid that looks like this. And how do we know that?

Now, with the help of newer techniques we are able to figure out that benzene really exist as a regular hexagon with all C-C-C bond angles to be 120 degrees and all the H-C-C bond angles also to be 120 degrees. So, there is a hydrogen on each one of these carbons which we typically do not show, but each of the carbons is really bonded to 2 other carbons and 1 hydrogen.

In fact, each carbon is sp^2 hybridized such that it forms the sigma bonds with the sp^2 hybridized orbitals and there is a pi bond that gets formed which is by the overlap of 2p orbitals. So, each carbon has a 2p orbital that goes above and below the plane which has a single electron which overlaps to form this pi bond.

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In fact, I have a model of benzene here and as you can see that the molecule is planar; all the carbons lie in the flat plane and all the hydrogens are also in the same plane, what you see going above and below the plane is really the 2p orbital. If we really calculate the bond length of each carbon-carbon bond it comes out to be 139 picometer. So, all carbon-carbon bonds experimentally figured out that the bond length is 139 picometer.

This is kind of in between single bond and a double bond indicating that what this resonance hybrid we have drawn really exists. In the sense that the molecule is not in the first conformation or the second conformation, but really a hybrid of these two, existing as this particular resonance hybrid.

Now, a way to describe the pi electrons in benzene is to call them delocalized; what it means is that the electrons or the pi electrons are no longer localized on the carbon-carbon bond. So, for example, in the first structure the carbon-carbon double bond just does not exist on only carbons 1 and 2 or 3 and 4, and 5 and 6, instead the electrons are delocalized on the entire molecule that is they are spread out on the entire molecule and all over the 6 atoms in this ring. Each carbon also has this unhybridized 2p orbital that goes above and below the plane and really contributes to the formation of the pi bond.

So, this is really an important characteristic that we should look at when we are thinking of aromaticity. So, considering the high degree of unsaturation in benzene chemists initially thought that it should react like an alkene or an alkyne, right. Because it has carbon-carbon double bond, so it should really do all the reactions that alkenes do. So, these include reactions with acids, electrophilic addition reactions with HBr, HCl, reactions with bromine, oxidation reactions, reduction reactions really all the characteristic reactions of alkene should be really done by benzene because it has three double bonds.

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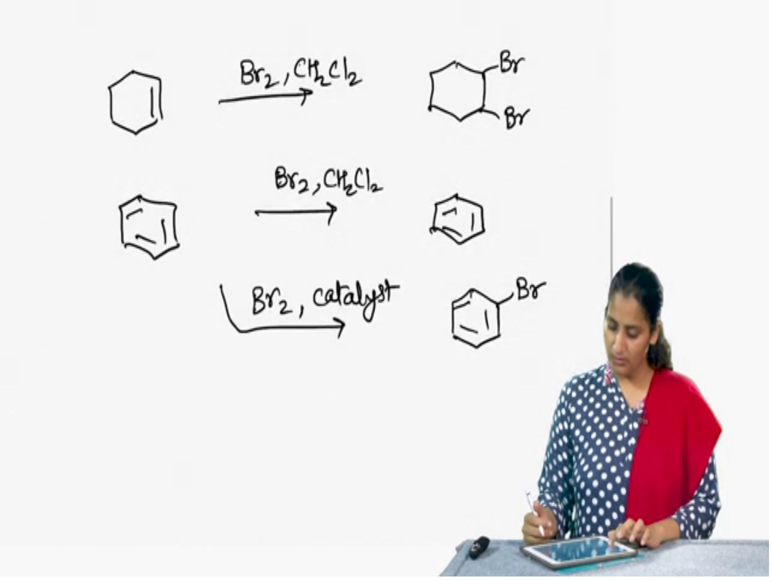

However, when chemists tried doing the same reactions on benzene it was turned out that it does not react so. In fact, let us take the example of addition of Br_2 and if I take cyclohexene and we add Br_2 in presence of let's say dichloromethane as the solvent, we know that it results into addition of these two bromines on the carbon-carbon double bond such that it is an anti-addition; we have seen this reaction. However, if I tried to do the same reaction on a benzene molecule with Br_2 and dichloromethane, it does not really give me a product in fact, benzene remains unreacted.

However, if I add Br_2 in presence of catalyst to this same reaction, then we can substitute a hydrogen on that benzene ring. So, this is not really doing an addition reaction, it is doing a substitution reaction, right a hydrogen is getting replaced with bromine. So, this really puzzle chemist like why is benzene not reacting the same way as that of any other alkene or for that matter when we take hydrogenation reaction this is a well known reaction for alkenes wherein you can add hydrogen in presence of palladium on carbon as a catalyst. Such that the two hydrogens get added on the carbon-carbon double bond.

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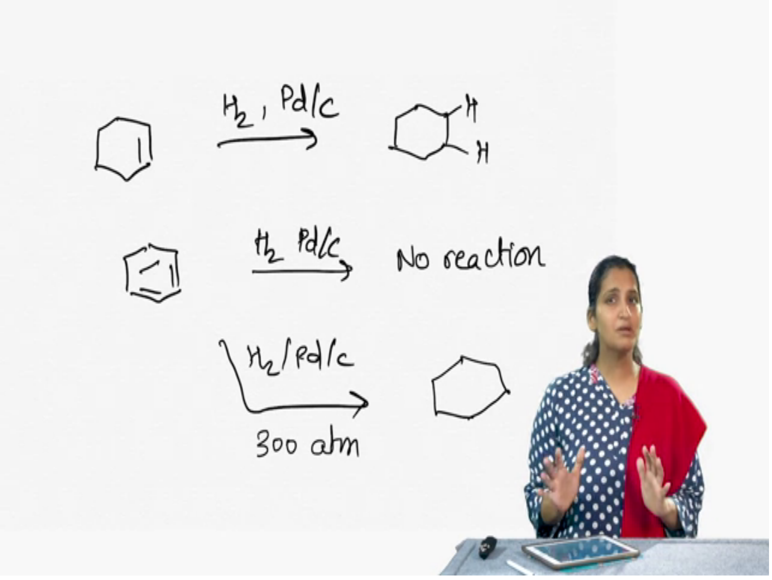

However, if we try to do the same reaction with benzene as the starting molecule, hydrogen and palladium on carbon does not really react with benzene and you get no reaction. On the other hand if you do this reaction at a really high pressure so around 300 atmosphere pressure, then we can get benzene to react such that it gives you cyclohexane. So, all of these reactions that did not fit the reactivity of alkenes puzzled chemists and then they tried to reason why benzene does not react the same way as that of alkenes.

Let us look at one of these reactions in detail. We know that the catalytic hydrogenation of an alkene is an exothermic reaction and the heat of hydrogenation per double bond really varies based on the degree of substitution. However, we also know that the heat of hydrogenation is corresponding to the number of double bonds present in the structure.

So, for example, if you have one double bond and if it gives you a heat of hydrogenation to be x, then if we change the number of double bonds to 2 double bonds then it should give you approximately 2x amount of heat.

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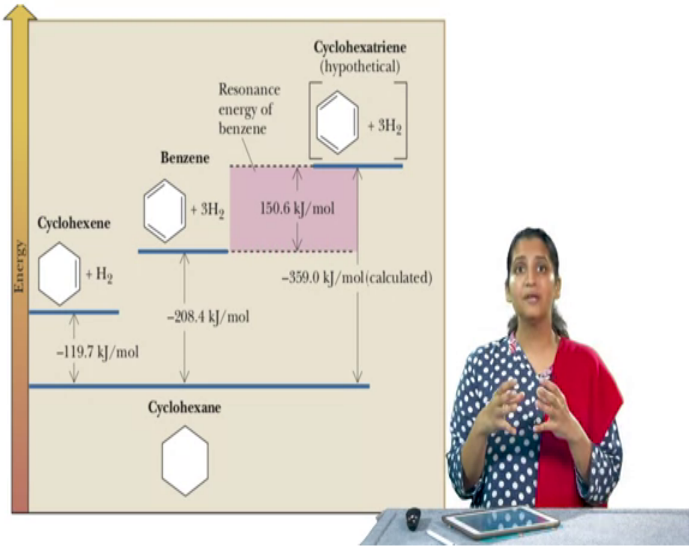

So, now let us look at this graph, when we calculate the heat of hydrogenation for cyclohexene we get it close to one 120 kilo Joules per mole. So, if we imagine benzene to be 1, 3, 5-cyclohexatriene that is it has 3 double bonds, then the heat of hydrogenation should be 120 into 3. So, it should be around 360 kilo Joules per mole.

So, that is about the calculated heat that is what we expect benzene to give out as benzene reacts in the hydrogenation reaction; however, when chemists calculated the heat of hydrogenation for benzene it was figured out to be close to 208 kilo Joules per mole. So, this is about 150 kilo Joules per mole different from the approximately calculated heat of hydrogenation.

So, what really gives benzene this kind of stability? Right; because if we really look at this diagram it tells us that benzene is about 150 kilo Joules per mole more stable than the hypothetical 1, 3, 5-cyclohexatriene. So, the difference between the amount of energy that we expect to get out and that is around 360 and the one that is observed is 208 is 150 kilo Joules.

And this 150 kilo Joules really represents the crude measure of just how extra stable benzene really is relative to the compounds that we expect to be with 3 localized carbon-carbon double bonds. So, when we expect 1, 3, 5-cyclohexatriene to have 3 localized double bonds we are kind of neglecting the fact that in benzene really the carbon-carbon double bonds are delocalized.

And what really is happening is that the individual atomic orbitals on these carbons are combining to form the molecular orbitals in the case of benzene. And when we think of 1, 3, 5-cyclohexatriene we are really neglecting these biomolecular orbitals that are resulting as a combination of the six p-orbitals.

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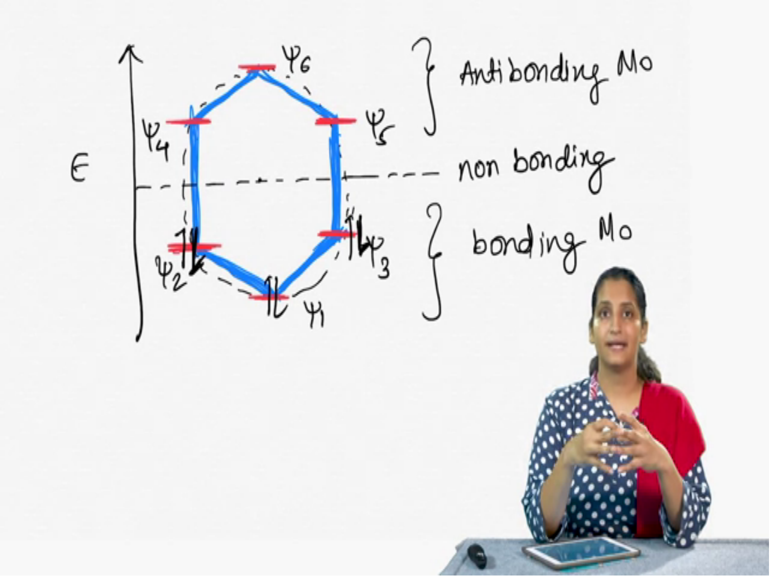

In order to draw the molecular orbital diagrams of benzene or really any regular cyclic arrangement of p-electrons there is a particular method and these diagrams are called as Frost circles. So, now, let us look at the molecular orbital diagram for benzene and we are only drawing the molecular orbitals that are resulting from the combination of these six p orbitals that is the formation of the pi bonds in benzene, we are not really looking at the other bonds in benzene.

So, the way you draw a Frost circle for benzene is that first you draw a circle and then you draw the regular hexagon of benzene such that one of its vertex points down and you fit this particular polygon in this case a hexagon such that it fits into this circle. Since we know that there always exists a circle for all regular polygon such that it can be fitted on the circumference of this circle.

So, in this case we will draw the benzene ring such that it fits the circle with one of its vertex pointing down and the y-axis will represent the energy of this particular molecular orbital diagram. Now, the molecular orbitals by the combination of atomic orbitals that are formed are such that wherever the hexagon cuts the circle that is where we will see the molecular orbital form.

So, for example, I have 6 atomic orbitals combining. So, it should form 6 molecular orbitals. So, I should have psi 1 (Ψ_1), psi 2 (Ψ_2), psi 3 (Ψ_3), psi 4 (Ψ_4), psi 5 (Ψ_5) and psi 6 (Ψ_6), resulting as a combination of 6 atomic orbitals. This is somewhat different for the linear molecular combinations that we have seen. So, for cyclic molecules this kind of procedure is followed.

Now, what we do is we will start placing the 6 atomic orbitals that are combining or the 6 pi electrons that are really combining. So, the first two electrons go in psi 1, the next two will go in psi 2 and psi 3, one-one electrons because they are at the same energy level and then the other two will go in psi 2 and psi 3 and really fill up the 3 molecular orbitals psi 1, psi 2 and psi 3 such that all of them are completely filled, okay.

Now, the thing is that the horizontal diameter of this circle represents the energy of carbon p-orbitals, okay. So, any energy levels that are on this line are kind of non- bonding whereas, all of those who are below the diameter are bonding molecular orbitals and the ones that are above this line are the anti-bonding molecular orbitals. So, let us draw that line which goes through the center of this circle and this becomes our non- bonding orbitals whereas, the ones below are bonding molecular orbitals and the ones above are anti-bonding molecular orbitals.

Now, it so turns out that benzene has this amazing stability as compared to other molecules and really is categorized as an aromatic compound is because all the electrons that are combining to form these molecular orbitals lie in the bonding molecular orbitals, okay. And none of the electrons are existing in the non-bonding or the anti-bonding molecular orbitals and this kind of stability gives it the aromatic nature.

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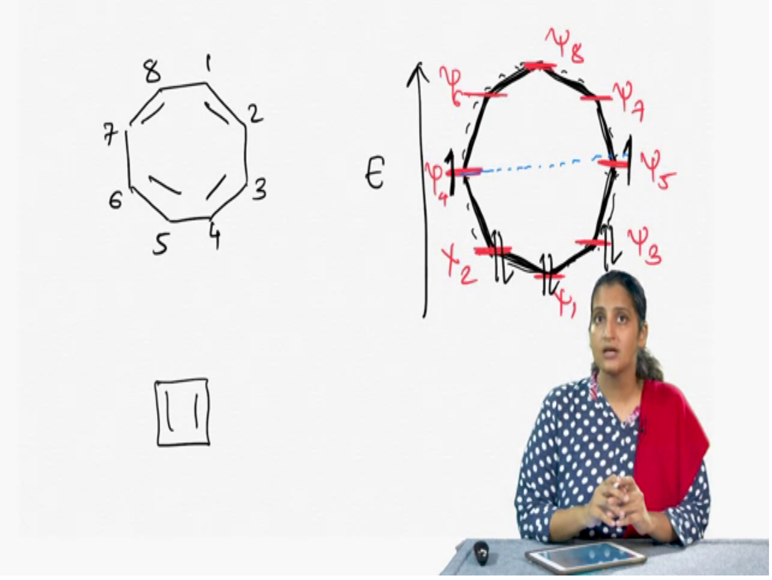

So, now let us look at one more molecule and see if our hypothesis holds true; what I have here is 1, 3, 5, 7-cyclooctatetraene, okay. So, it has a very similar structure to that of benzene; it has a ring structure, it also has pi bonds that are alternating inside this ring. So, this is very similar to that of benzene and in fact, chemists thought that cyclooctatetraene should also be equally stable as that of benzene and when they tried to fit this to the molecular orbital theory that they had come up with, let us see what happened.

So in order to draw this cyclooctatetraene's molecular orbital diagram, the first thing I will do is I will draw the circle and then I will draw this octagon such that, it fits into this circle. Now, we are combining 8 electrons from the p orbitals, so 8 atomic orbitals are getting combined. So, I should form 8 molecular orbitals and those are given by these. So, I should have psi 1, psi 2, psi 3, psi 4, psi 5, psi 6, psi 7 and psi 8 getting formed. We also see that the line that goes through the center of the circle that is the diameter is the non-bonding molecular orbitals and psi 4 and psi 5 lie on that diameter.

In fact, now let us start filling those 8 electrons into this molecular orbital diagram. I should have the first two electrons go in psi 1, the next two will go in psi 2 and psi 3; the next 2 will go again in psi 2 and psi 3 such that all psi 1, psi 2, psi 3 are filled. And now what I have is 6 pi electrons really are taken care of and I need to fill the next 2. Now, these next 2 electrons one of them will go in psi 4 and one of them will go in psi 5, right. And that really means the two of the electrons of cyclooctatetraene are really in psi 4 and psi 5; those are the non bonding molecular orbitals.

And so for cyclooctatetraene it really does not follow the same molecular orbital diagram as that of benzene wherein all the electrons should be in the bonding molecular orbitals. In this case 6 of the electrons are in the bonding molecular orbitals, but 2 of the electrons are in the non-bonding molecular orbitals and that really gives us the difference in the reactivity of benzene and cyclooctatetraene.

So, in fact, when chemists tried to see the reactivity of cyclooctatetraene, turns out that cyclooctatetraene really does not follow the same reactivity trends of benzene. It reacts like any other alkene and it can do all the reactions of alkenes that we have seen before. So, molecular orbital theory which is really a tool to explain the reactivity of molecules tells us the difference between the reactivity and kind of explains this difference in the reactivity based on the fact that for a molecule to be aromatic all the electrons for the pi molecular orbitals should be lying in the bonding molecular orbital zone.

One thing to remember is that the molecular orbital theory or really the resonance theory is a powerful tool which really chemists use to understand the unusual stability of benzene or the corresponding derivatives. So, chemists have tried to use these two theories to really explain the reactivity of various compounds. One of the compounds we have talked is cyclooctatetraene, right which we have seen really reacts as a regular alkene, the other compound that chemists thought of was cyclobutadiene.

So, cyclobutadiene is a cyclic molecule; it also has alternating double bonds. So, chemists imagine that it should also be as stable as benzene, turns out it is exactly opposite of that. Cyclobutadiene cannot be synthesized at room temperature such that it can be isolated. In fact, multiple attempts to isolate cyclobutadiene have failed and really what happens is as soon as you synthesize it, it reacts quickly with itself to form a dimer and really until 1965 cyclobutadiene synthesis was not successful and it took us a long time to come up with the successful synthesis of cyclobutadiene.

Now, what make cyclobutadiene this really-really unstable compound and it does not show the chemical and physical properties we associated with the aromatic compounds. So, chemists thought of cyclobutadiene as an anti-aromatic compound, okay. So, it is exactly opposite to that of aromatic compounds, it is extremely reactive and cannot be isolated really and what chemists thought was to come up with a theory of what are the fundamental principles that really give a molecule aromatic character, that really give a molecule an anti-aromatic character or that really give a molecule is non-aromatic character.

So, benzene we saw is an aromatic molecule, cyclooctatetraene really behaves like any other alkene, it can be synthesized and it is really a non-aromatic compound whereas, cyclobutadiene which is highly reactive is an anti-aromatic molecule. So, one of the questions as we said is what are the fundamental principles that are underlying this aromatic character?

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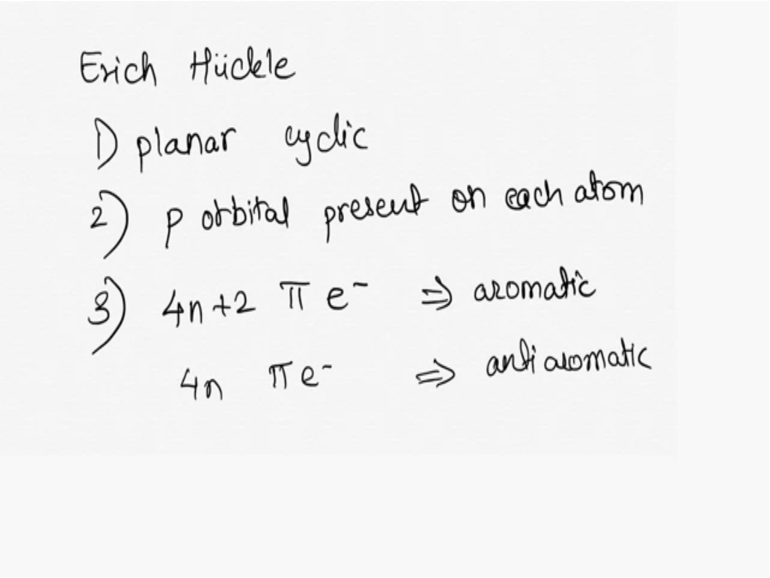

Erich Hückle

1) planar cyclic

2) p orbital present on each atom

3) $4n+2\ \pi e^-$ ⇒ aromatic

$4n\ \pi e^-$ ⇒ anti aromatic

And the answer was given by Erich Huckel around 1930s, where he came up with a set of rules that really can figure out if a compound is anti-aromatic, aromatic or non- aromatic. So, he was a chemical physicist really and he calculated a lot of molecular energy calculations for mono cyclic planar molecules and based on these calculations he has come up with a set of rules. So, let us look at this set of rules; the first set of rules is that the molecule should be planar, okay. So, it's a cyclic molecule, it should be a planar molecule for the molecule to be aromatic in nature, for it to have that extra stability.

The second rule is there should be a p-orbital present on each atom. Now, it's so turns out that the p-orbital can be empty, the p-orbital can be filled, but there should be one p- orbital that is going above and below the plane of this planar molecule. And the third rule is it should have 4n + 2 pi electrons, if that is the case then the molecular is aromatic and we will look at this rule in detail. However, if it has 4n pi electrons, it is anti-aromatic, okay. So, now, let us look at the three molecules that we have seen before.

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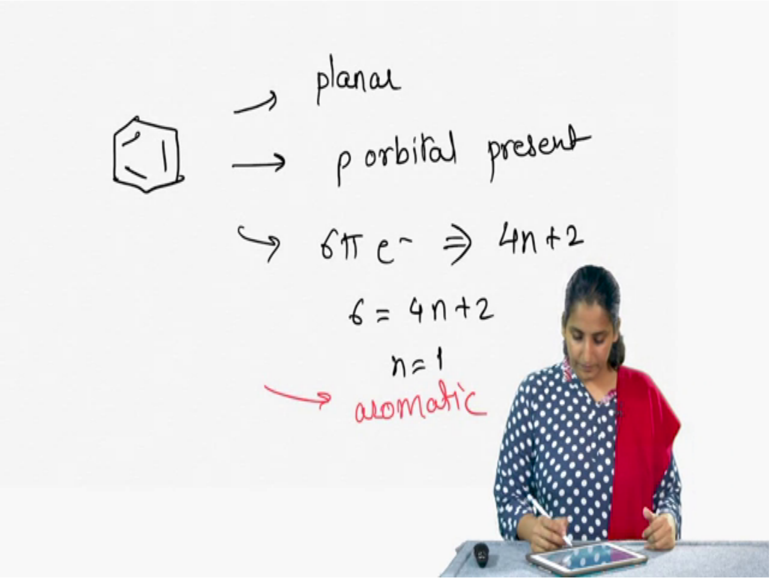

→ planar

→ p orbital present

↪ $6\pi e^-$ $\Rightarrow$ $4n+2$

$6 = 4n+2$

$n = 1$

→ aromatic

Let us look at benzene, okay; benzene is planar it has all the carbon atoms in the same plane as that we saw whereas, it also has a p-orbital present on each carbon. So, that criteria is also satisfied. It has 6 pi electrons in the p-orbitals. So, looking at this I am not looking at all other electrons we are only calculating how many pi electrons are present and the answer is 6; 6 resulting from the 3 double bonds and it has 6 pi electrons, then it fits this 4n + 2 rule; how do I know?.

So, when I say 6 equal to 4n + 2, n comes out to be 1. So, if the value of n is such that it is a whole number that it goes from 0 1 2 3 4 so on and not really a fraction, right. So, then it fits this 4n + 2 rule. So, in this case the molecule is aromatic because it fits all the 3 rules that we talked about.

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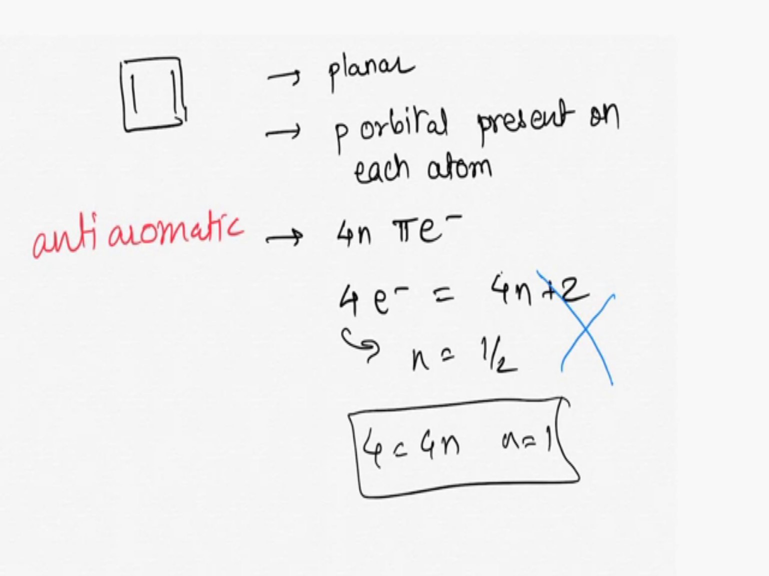

If we think of cyclobutadiene, then the molecule is planar then the molecule also has a p-orbital present on each atom and the molecule also has 4n pi electrons, how do I know that? Because I have 4 electrons, 1 2 3 4, resulting from the two double bonds. 4 electrons is equal to 4n + 2, it does not really give me a whole number because n will be equivalent to half and that is not a whole number. So, it does not satisfy 4n + 2, in fact, it satisfy 4 equal to 4n, where n equals 1; this kind of equation is satisfied, so it becomes anti-aromatic molecule, right.

And that really explains the unstability of this particular compound that it does reactions very-very vigorously in fact, it cannot be isolated on its own. Now, let us look at cyclooctatetraene as one of the molecules. Now, in the case of cyclooctatetraene we have seen that it reacts like just any other alkene. So, it is not really unstable, it is not extremely stable it is somewhat in between, right. So, it should fit all the characteristics of a non-aromatic molecule.

Turns out that cyclooctatetraene, if we imagine it to be planar, if we imagined that there is a p-orbital present on all carbons and if we see that it has 4n pi electrons because it has 8 electrons, it should really fit the anti-aromatic character, right. However the reason why it is not anti-aromatic is because the first rule such that the molecule should be planar is getting violated in the case of cyclooctatetraene.

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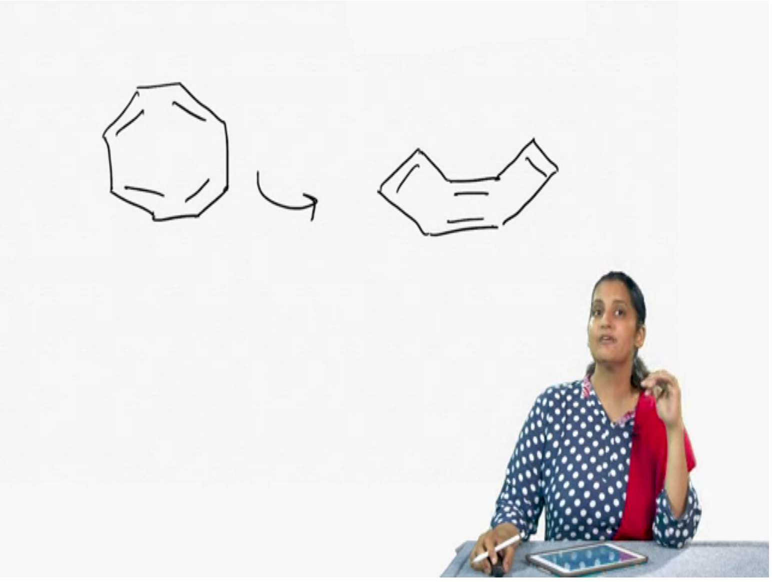

So, if we look at the molecule and if you really try making the model of cyclooctatetraene. So, turns out that you will be unable to keep it flat and planar. In fact, what turns out is that it tries to form this tub-like structure such that the molecule does not remain planar and two of the edges of the cyclooctatetraene really form a tub-like structure. And that really makes the molecule non-planar and so it does not fit all the characteristics of anti-aromatic molecules as well and remains a non-aromatic molecule; just like any other alkene it will remain non-aromatic molecule.

So, what we need to do in order to decide if a molecule is aromatic, non-aromatic or anti-aromatic is that we need to look at each one of these criterias very carefully and see if they are being followed or not.

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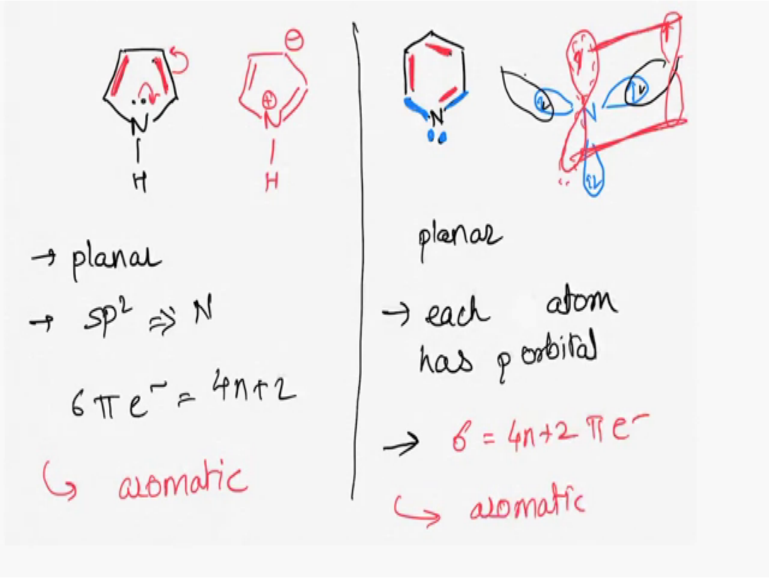

The next two molecules that we want to talk about are really heterocyclic molecules. So, the first one is pyrrole and the next one is pyridine. In fact, we have talked about these molecules when we have thought about which nitrogen in the case of pyrrole ring versus pyridine ring can really function as a base and attack in an acid-base reaction. So, now, let us look at whether aromaticity can explain this reactivity of these two molecules.

So, let us take the first one, pyrrole, it's a planar molecule, so I have the model made here, right. It also has a pi electron on each atom and how is that? So, we can see that the two carbons here have a pi electron, right or p-orbital really that is present and the other two carbons also have a p-orbital each on them. Now, what about the nitrogen? If we see that the nitrogen is sp^3 hybridized, then it will not have a p-orbital that goes above and below the plane just like other carbons.

However, if the nitrogen is sp^2 hybridized, then we can say that the nitrogen has a p- orbital. So, let's imagine this to be the nitrogen, if it is sp^2 hybridized then the 3 sp^2 hybridized orbitals go such that they are in the plane of this molecule, right. And the lone pair is situated such that it goes above and below the plane of the molecule. Now, if that is the case then we can say that all the atoms in this particular molecule really have a p- orbital that goes above and below the plane of the molecule.

So, one of the other ways that you can figure out that the nitrogen is not sp^3 hybridized is because of the fact that it can show resonance structure. So, I can also draw resonance structures such that this becomes a valid resonance structure for this molecule. Now, we have seen that the molecule has a p-orbital that is present on each atom and also that when we have to calculate the number of pi electrons that are present, remember that there is one-one pi electron present on each of the carbon. So, that makes it to 4 and then there is the lone pair that is present on the nitrogen. So, that makes it to total of 6 pi electrons, right.

So, that fits 4n + 2 and in fact, pyrrole rings are seen to be aromatic. They react such that they follow all the trends of aromaticity; that means, they are extremely stable, they will not be reacting like an alkene, okay. In fact, this particular pyrrole ring is also seen in biological system indicating that it is quite stable.

Now, let us look at the next molecule that is pyridine. In the case of pyridine again the molecule is planar and if you really look at this structure, then it is clear that the nitrogen is sp^2 hybridized because it is forming a pi bond to begin with. Now, in an sp^2 hybridization for nitrogen; nitrogen has to form 3 bonds with the 3 sp^2 hybridized orbitals and it forms the 2 sigma bonds with the sp^2 hybridized orbitals.

And the pi bond really results because of the p-orbital that remains unhybridized during the sp^2 hybridization. So, the lone pair in this case is also present in the sp^2 hybridization. So, the nitrogen here is having 3 sp^2 hybridized orbitals that are flat and planar; it has one-one electron in each of these two and a lone pair in the one that is outside the ring. These two orbitals will overlap with the carbon's sp^2 hybridization to form the nitrogen- carbon sigma bonds.

The pi bond in this case really results because of the p-orbital that lies above and below the plane of this sp^2 hybridization and there is a presence of a pi bond between nitrogen and carbon. So, that is how the structure of pyridine is. So, when we have to consider if each of the atoms in this particular molecule is sp^2 hybridized, then we can say that each atom is sp^2 hybridized and there is a presence of p-orbital on each of them.

Now, let us also look at whether it fits the 4n + 2 pi electron rule and in the case of pyridine we have to calculate the electrons in each of the double bonds 1 2 3 4 5 6, right. So, there are 6 pi electrons; one of the questions is should the lone pair be counted as the number of pi electrons in conjugation? The answer is no because if you think of it, let's say this is the nitrogen and the lone pair is going in this direction, right. So, let's imagine that my hand is the lone pair.

Then the number of pi electrons that are in conjugation that means, the number of electrons that can overlap with each other to form the molecular orbitals is still 6. These two electrons cannot overlap because of the geometry they cannot overlap in this plane or this plane to really be counted in the pi electron system.

So, in this case the number of pi electron is still 6 and it fits the 4n + 2 pi electron rule and thus the molecule remains aromatic. In fact, again pyridine is one of the molecules that is seen in biological systems and really is stable and does not do the reactions of alkenes to begin with. So, with this let us stop the discussion of aromatic, anti-aromatic and non-aromatic molecules. And in fact, in the tutorial we will be going over lot of these molecules such that we get to choose whether it is aromatic, anti-aromatic or non-aromatic.

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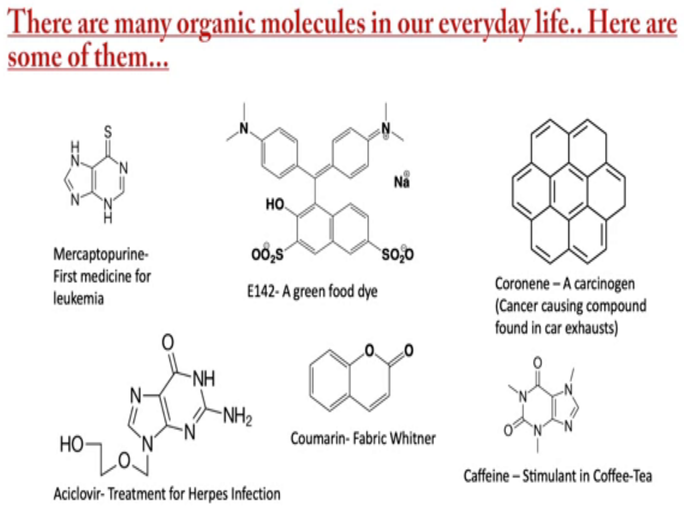

There are many organic molecules in our everyday life.. Here are some of them...

Mercaptopurine- First medicine for leukemia

E142- A green food dye

Coronene – A carcinogen (Cancer causing compound found in car exhausts)

Aciclovir- Treatment for Herpes Infection

Coumarin- Fabric Whitner

Caffeine – Stimulant in Coffee-Tea