Course on Stereochemistry
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Mod05 Lecture 19
Conformations of Cyclic Systems (Contd.)

Okay welcome back, we will just again, start from where we left last time, we have introduced the another new type of strain to you while discussing the conformation of cyclic systems and we have seen that these molecules specially the small member rings, they suffer from a strain which is called the angle strain.

Now according to modern day theory, because if we look at cyclo, again I show the cyclopropene ring, you see the bonds are I had to struggle to connect these two, two hands okay. It is so much bend and the the model is almost coming apart ruptured at this point. So the question is whether the molecule really looks like this or not or there is some alternative way of thinking the conformation of cyclopropene, okay.

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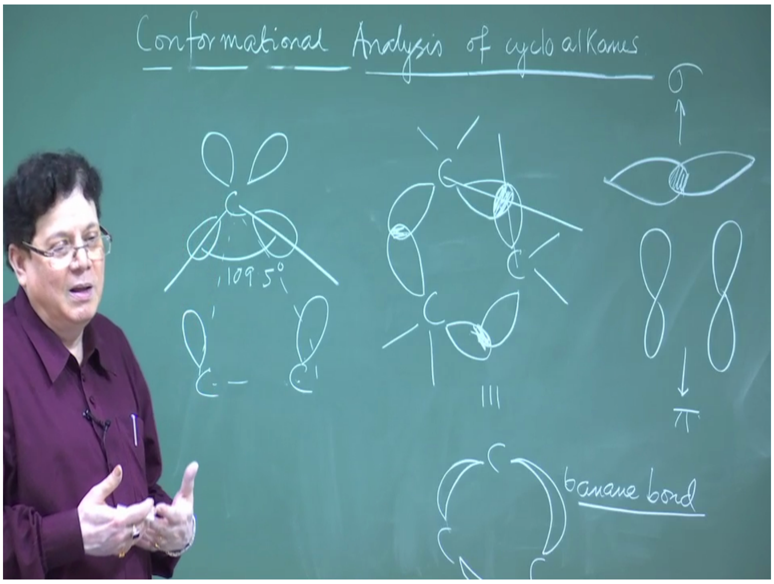

Now according to the modern day theory when you draw the orbitals say, you have the sp3 orbitals of the carbon and this angle is we know it is 109.5 degrees. If you write another carbon here to make cyclo another say two carbons here, to make the cyclopropene. So what is happening now, this orbital is pointing towards this direction see and this orbital let us just concentrate on these two carbons, the connection of this carbon with that carbon, so what happens? These orbitals are no longer pointing towards each other in a head on fashion means in a linear fashion, which forms the strongest sigma bond.

So in a sigma bond the orbital should approach in a linear fashion, okay in a coaxial fashion. So that the overlap is maximum when they come close to each other, so there will be overlapped the orbitals. This is the overlap portion. The extent of overlap will determine the strength of the bond. In case of cyclopropene what happens? As these carbons come closer the orbitals are no longer approaching in a linear fashion. So this is one orbital at this carbon the orbital will be like this and for this carbon, so another carbon is here. So here also very similar situation, this is pointing towards that direction, this is pointing towards this direction and for this also, so in no case the orbitals are unlike in a sigma real sigma bonding situation seen arrow, the carbon atoms are no longer have the orbitals pointing towards each other in a linear fashion or in a head on fashion.

So if you do that that means they actually approach in an angular way. In sigma bond they should approach in a linear fashion. In pi bond we know that they approach in a lateral fashion. So this leads to sigma bond and this leads to pi bond and we know that the pi bonds are less stable than the sigma bond, simply because the extent of overlap is much more here rather than the extent of overlap with they approach laterally and this is a seen arrow which is in between this. They are not lateral; they are not head on also. So what happens?

They actually approach in an angular fashion. So this is the angular fashion that what I am saying. So the extant of overlap, now will be less if the two carbons approach head on then the amount of overlap that you get among between the orbitals that will be much more. Here the extant of overlap will be less. This is the extant of overlap; this is the extant of overlap, okay.

So another way to look at this system cyclopropene is to tell that the bonds see, when they joint each other when these orbitals combine with each other in a in phase the orbitals are in phase, then ultimately the molecular orbital that will be generated. They will look like this. Now this are what are called you see the bonds by, these are now orbitals, these are no longer very mechanical concept of bonds. This is the orbital concept. So they will look like, these are called banana bonds or bend bonds, okay you can all it as bend bonds. The bonds will be bends or you can say that this looks like a banana overlap ultimately the molecular orbital that is generated that looks like a banana.

So that is called a banana bond and this banana bond will be much weaker than a carbon-carbon single bond in a linear alkane, because as I said, because they do not approach in a linear fashion. They approach in an angular fashion and that is why the extant of overlap will be much laser (())(6:23). So this is the molecular orbital concept of instability of cyclopropene. So what is the answer if somebody asks you?

According to Bayer strain you say that they suffer from angle strain, but the real structure, because molecular orbital theory came much later and this is the accepted version of to explain the structure of molecules. So what happens in the molecular what is a theory according to that the extant of overlap that forms the carbon-carbon bond in cyclopropene is much less, because the orbitals approach in an angular fashion and that makes the bonds are no longer, perfect sigma bonds.

So it is in between the sigma and pi, it is not a pi, because they are not approaching in a lateral fashion. It is not a perfect sigma, it is a sigma bond by till it is (())(7:14) a much weaker than a sigma than normal sigma bond.

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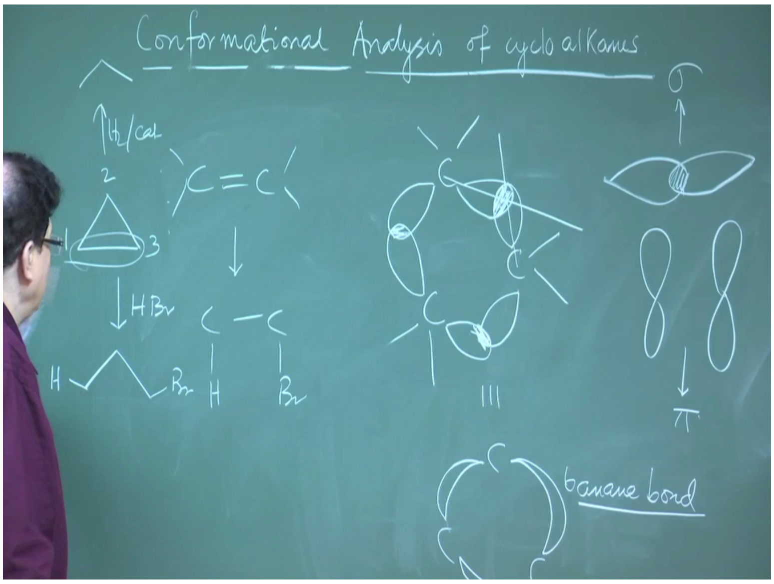

And how do you know it is weaker, because you can do a many reactions on cyclopropene, which is looking like as if it is possessing a double bond, like in ethylene if you add H Br we know that the bromine add Cr and H Br whereas in ethane nothing happens if you add H Br it does not break that one side bromine goes another side hydrogen goes, because this is a very strong bond you cannot break this bond okay, but this happens with cyclo with ethylene, because the pi bond is very weak.

Similar things happen with cyclopropene. So if you take cyclopropene and add H Br. So as if one this bond is like a pi bond, it is a weak bond, so on one side bromine is added and the other side hydrogen added. The difference between this and that that this is a 1, 2 addition and that is a 1, 3 addition okay, but the similarity is there. That this bond is weak and you can break and there is a 1, 3 reaction. It is a addition reaction, okay. Similarly, if add hydrogen in presence of the catalyst then you will get the normal propene. If you add bromine, you will get 1 3-dibromo propene, okay. So that shows that these bonds are weaker, okay. Now there is a, so that is the how it is describe this banana bond.

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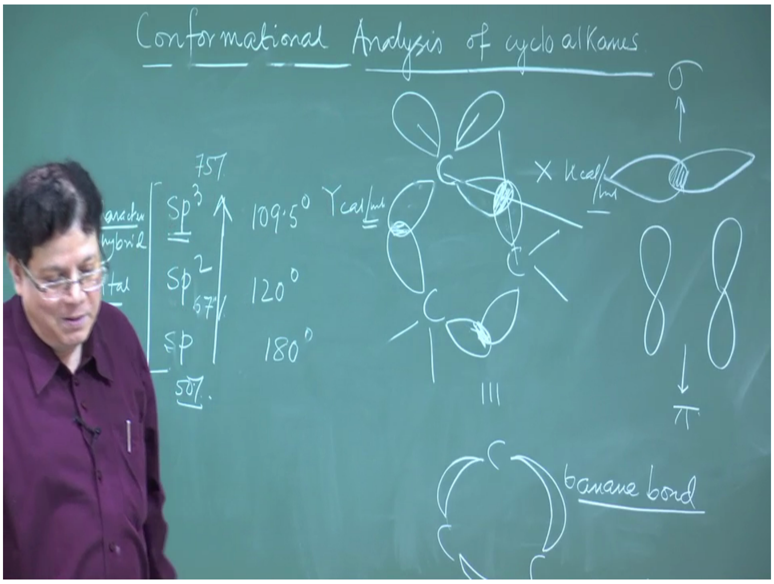

Now there is another concept that also that that came up little later. Once the banana bond was that theory was put forward then people started looking at this molecule again and you will calculated you can calculate that what will be the strength of these bonds, if they are perfect the perfect banana bonds and if the carbon is **is** sp3 hybridized then what will be the extent of overlap you can calculated that. So this bond strength can be calculated, okay and during the calculation what they found that cyclopropene bonds as per calculation, (the) whatever be the strain, this as per the overlap. If you if you whatever the strength (())(9:52) comes out actually the strength of the carbon-carbon bond is slightly higher than that means as per calculation, quantum mechanical this calculation this orbital overlap, you can calculate.

So as per calculation you get a bond strain suppose X kilo calorie per mol and actually you can also by combustion experiments you can or by hydrogenation you can tell what is the strain of this carbon-carbon bond and suppose this is Y kilo calorie per mol. So what they found that Y is little larger then X. So where was the problem, because this should match then there is something problem with this calculation, but quantum mechanics is based on a sound (())(10:45). So that you cannot challenge. It is very difficult to challenge that concept.

So something extra must be happening to this molecule so that the carbon-carbon bond is slightly more stable than what is expected out of calculation from molecular orbitals. So the then it was revise the little bit. This is the modern day concept of cyclopropene that you know that if a carbon is sp3 hybridized then the bond angle becomes 109 degree 109.5 degrees if it is sp2 hybridized then it is 120 degree the bond angle and if it is sp hybridized the angle becomes 180 degree. So what does it tell that the as the percentage of, so the percentage of p character is highest here, okay.

So the percentage of p character as it p character percentage of p character in the hybrid orbital**.** So if the percentage of p character goes down p character is increasing on this side. So this is 50 percent p character, 50 percent s character. Here it is 1 third that means this is 33. This is the sp2, so s has 33.33. So this is about 67 percent p character, I am talking about p character and this is 75 percent p character. So as the p character increases, the bond angle decreases, okay as the p character increases the bond angle decreases. So with this presumption now, the modern day theory is that this carbon is no longer perfectly sp3 hybridized, see what was the concept of hybridization. The concept of hybridization was that you take orbitals and orbitals of different energies, some may be same energy, but at least one has to be different like sp3, 3 p orbitals of same energy and one s of different energy, you mix them and you generate, because 4 orbitals are combining you generate 4 new orbitals, which are called hybrid orbital and the extent of these hybrid orbitals have all of identical energy, okay identical energy that is the important thing and that means they are degenerate.

So you **you** generate a set of degenerate orbitals and the percentage of the character, the s character in all the 4 orbitals like this is one orbital hybrid orbital. This is another hybrid orbital. So there will be here, there will be hybrid orbital. So this is the sp3 situation, okay and the percentage of s character or p character will be same in all these 4 orbitals. So that was the concept earlier.

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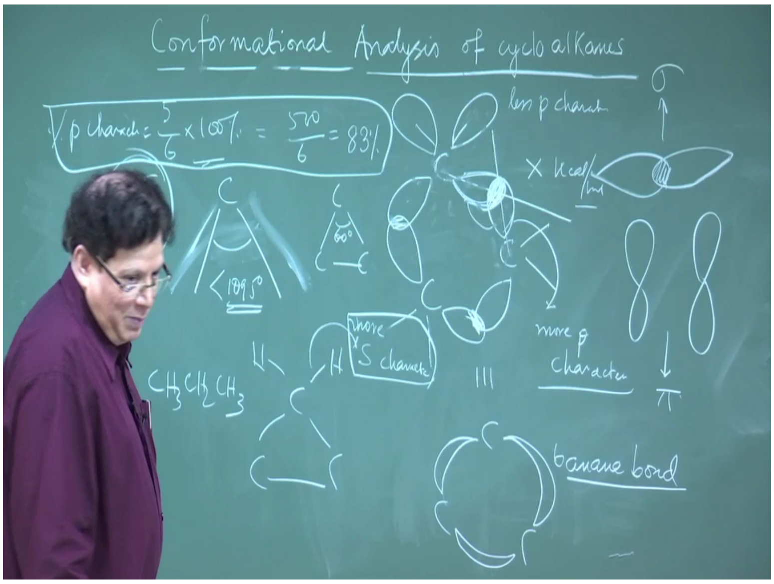

Now in case of cyclopropene, once they found that actually this bond is little bit more stable than what is coming out of calculation. So they revise these hybridization concept a little bit. So what people are saying that the percentage of we know that as the percentage of p character goes up the angle decreases, okay. So if the percentage of p character goes above 75 percent then the angle will further decrease and if the angle further decreases then according to Bayer strain theory, see there is a angle strain here, the normal angle should be 1096 degree 109.5 degree, but if you think it has the rigid system, it is 60 degree, okay and in terms of molecular orbital theory, this is there is less overlap if they approach this as per the hybridization concept, okay.

Now if you increase the percentage of p character here, in this orbital and percentage of p character in this orbital then what will happen? This angle what you are seeing here that angle will further will decrease, because you are increasing the percentage of p character in this orbitals, you can also see it, you can also explain it in here, if this bond the normal valency angle is 109.5 keeping the p character as 75 percent, but if the p character say goes up to 90 percent, then what happens?

This angle will no longer be 109.5, so the angle suppose, the angle what is required in a hybridization say sp5 hybridization, we have never heard of sp5, but sp5 if it is sp5 hybridization then the angle will be less than 109.5, I do not know what will be the angle, suppose this is 100 degree then the effect of that the overall angle strain, which was the earlier 49.5 divided by 2 that means 24.75 that will be less now, because now you have to have 10 minus 60 divided by 2 so that becomes 20. So the angle strain decreases.

So now this carbon, is inelegant one (())(16:54) that there is a problem if I have a perfect equality amongst the hybrid orbital. So it will what it will do? It will put more p character in the bonds which are making the cyclic system and, but you have to compensate that if you put more p character here, so you will have to have a less p character on the outer bonds which are outside the ring, which are not making the ring bonds.

So the bonds which are not making the ring bonds you make more s character or less p character here and here you introduce more p character and now the rough calculation people have calculated that what is the extent of hybridization of this side and what a extent of hybridization on this side. They found that the this can be explained this inequality of bond strain can be explained. If you think that this carbon is sp5 hybrid hybridization on this side and the rest is outside that means the rest the outside bonds again I repeat, they have less p character this has more p character and the p character is about what is required? What is present in sp5, so that will be about what 5 by 6 into 100 percent?

So the percentage of p character, in the inside bonds will be 5 by 6 into 100, so that comes around 500 by 6 that means 8, so around 83 percent. So around 83 percent p character in the inside bonds, okay that explain so many things, because if we increases the p character the difference the bond becomes little bit stronger, because now this they approach in a more linear fashion. This is not linear exactly, but earlier the extant of overlap what was there as per sp3 hybridization.

Now the extant of overlap will be more. So this bond becomes stronger. Now it matches with (the) whatever is the experimental value. It also matches with the reactivity of cyclopropene, because as the p character increases the bond become weak, because the s electrons are closer to the nucleus. So greater the s character, the bond becomes stronger. So this bonds become weaker and these bonds in turn should become stronger that means in cyclopropene, the C-H bonds becomes stronger compared with a linear system and the C-C bond become weaker, because this has got more p character and this has got more s character as present in the in a linear system. So this has got more s character, okay. So today we have learn that hybridization does not always follow democratic rules that everything has to be equal, okay. So there is in equality in hybridization also, especially when it is required, okay.

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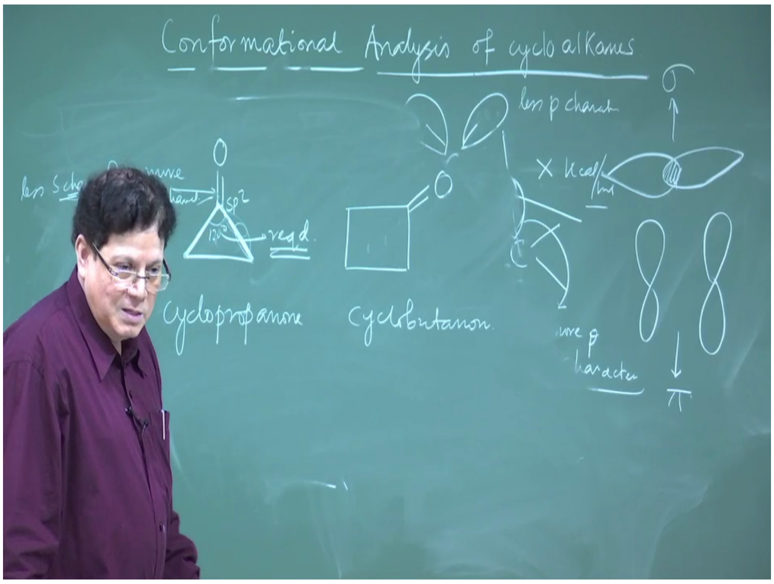

So that is well explained in case of cyclopropene and the question is what is the proof is there any real experimental proof that yes, there is the outside bonds in a cyclic system like cyclopropene is stronger, so people have done this. So they made this is what is called cyclopropanone. So they put a ketone here, okay. Now this molecule will suffer from more angle strain, because this is now sp2. So this is 120 degree as per normal hybridization, but actually this is required as per hybridization, but actually the angle is 60 degree, because this is this is 3 membered ring, okay. So it will suffer from more (())(21:36) angle strain. So again what will happen? The percentage of p character here, in these 2 bonds will be increased so that the angle strain is minimized or the other way the bond strength is more, so that the overlap is more when the orbitals approach each other (())(21:56), so the there will be more p character here. So there will be more s character on this point.

So this carbonyl should be stronger than if you take cyclobutanol or forget about cyclic system. This carbonyl should be stronger than acetone, because in acetone, there is no such strain there is no such problem, the angle is perfectly maintained. So this will have more s character and this will have less s character. So which carbonyl is then stronger, because as I said the s electrons are closer, so this carbonyl is stronger than this carbonyl that you can measure?

There are spectroscopic ways to measure that what is the energy required to stretch this carbonyl bond that if you want to stretch the carbonyl bond you require (())(22:58) more energy for this than that and this is what is measured in what a spectroscopy called higher spectroscopy (())(23:04) and people have shown that the (()))(23:08) gives the stretching frequency that is required that means the energy the frequency corresponding to the energy which is required to stretch these bond verses to stretch this bond and it was now perfect edge is established that this requires more energy to stretch than this one and so also if you come to cyclobutane. So it will be easier to stretch compared to cyclopropanone, coclobutenone carbonyl is will be easier to stretch than in case of cyclopropanone, okay.

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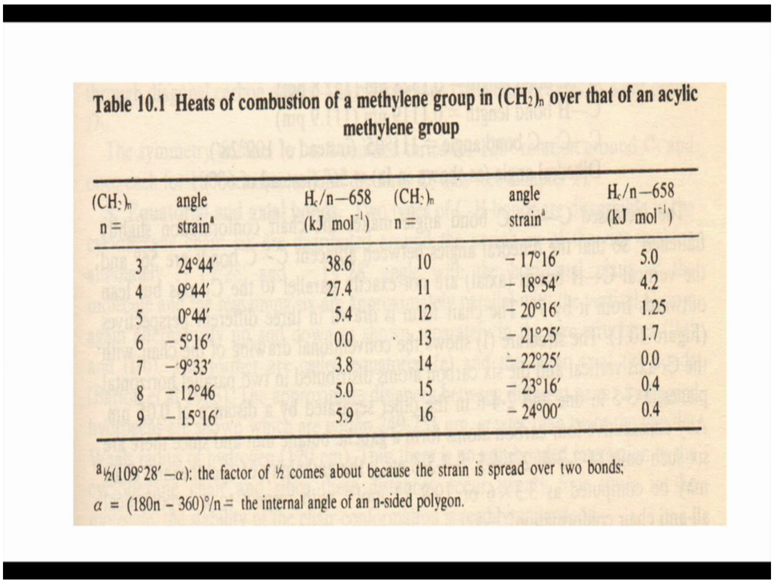
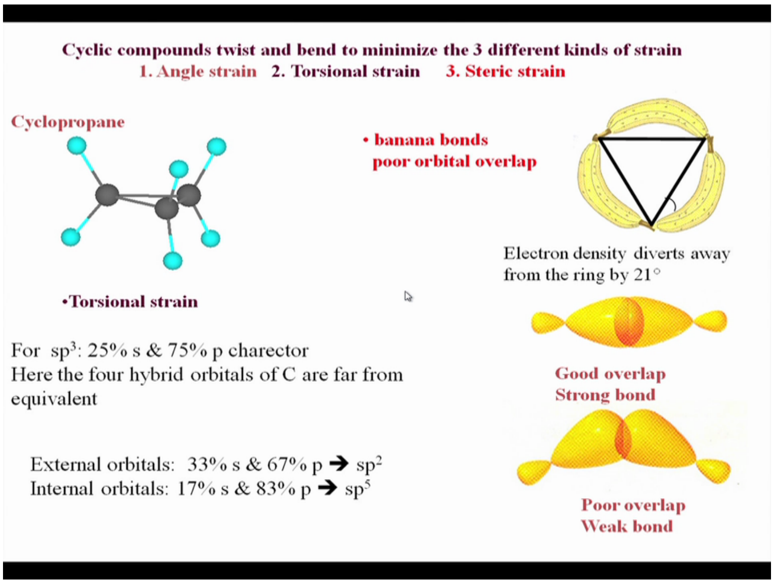


Table 10.1 Heats of combustion of a methylene group in $(CH_2)_n$ over that of an acyclic methylene group

$(CH_2)_n$ n =	angle strain[a]	$H_c/n-658$ (kJ mol^{-1})	$(CH_2)_n$ n =	angle strain[a]	$H_c/n-658$ (kJ mol^{-1})
3	24°44′	38.6	10	− 17°16′	5.0
4	9°44′	27.4	11	− 18°54′	4.2
5	0°44′	5.4	12	− 20°16′	1.25
6	− 5°16′	0.0	13	− 21°25′	1.7
7	− 9°33′	3.8	14	− 22°25′	0.0
8	− 12°46	5.0	15	− 23°16′	0.4
9	− 15°16′	5.9	16	− 24°00′	0.4

[a] $\frac{1}{2}(109°28' - \alpha)$: the factor of ½ comes about because the strain is spread over two bonds;
$\alpha = (180n - 360)°/n =$ the internal angle of an n-sided polygon.



Cyclic compounds twist and bend to minimize the 3 different kinds of strain
1. Angle strain 2. Torsional strain 3. Steric strain

Cyclopropane

• banana bonds
poor orbital overlap

Electron density diverts away from the ring by 21°

•Torsional strain

For sp³: 25% s & 75% p charector
Here the four hybrid orbitals of C are far from equivalent

Good overlap
Strong bond

External orbitals: 33% s & 67% p ➔ sp^2
Internal orbitals: 17% s & 83% p ➔ sp^5

Poor overlap
Weak bond

So that is the modern day, first I said that there is this existence of what is called banana bond that the orbitals are approaching in an angular fashion, so that case what is call banana bond and then I said that to further add the strength of the bond to further reduce the strain that is present in cyclopropene or to try to strengthen the carbon-carbon bond, there is unequal hybridization. So what the people said that there is the hybridization the unequally the hybridization are not equal in all the hybrid orbitals. So some orbitals have more s character and some orbitals have more p character. It is the inward bonds that means the bonds, which make the ring those bonds will have more p character, because more p character means less angle and less angle means less angle strain, okay and I can show you here, there will be some pictures here for. So I started with this that cyclic that we have known what is called torsional strain? What is call steric train? Those are introduced in while discussing the acyclic systems.

Now what we have a what is called angle strain that is what also known as Bayers angle strain and if I completely show the slide, this is what is the slide that in case of cyclopropene, I should have also mention this that there is angle strain that is true and there is another strain that is the what I said the bond oppositions strain, because these two bonds the side wise they are eclipsing each other. So there is what is called eclipsing strain or you can call bond opposition strain.

So they are their dihedral angle is zero, okay. So there will be that bond of position strain that is present here, but the major contributing factor for instability, it is not this bond opposition strain. This is present definitely, but the major contributor is the less overlap according to molecular orbital theory less overlap while forming the carbon-carbon bonds, okay and here the picture it says that it suffers from torsional strain.

Torsional strain is the one that when you lie in a energy maxima, you will try to go to the a minimum point close by, okay. So it suffers from this torsional strain, okay. Torsional strain is absent in case of staggered form, but this is in the eclipse form. So will suffer from torsional strain and this will suffer from another strain that is what is the angle strain or Bayer strain and this whatever I said, these are all explained here that actually the hybridization generally is **is** democratic that means the percentage contribution of each orbitals each orbitals in the hybrid orbital is usually same, but that does not happen in cyclopropene.

Before that people said that there is this type of bond, I told you about the banana bond. This comes, because they approach in a angular fashion. This is a sigma bond perfect sigma bond when they approach in a coaxial fashion. This is the bond, which is in between a pi and the sigma, okay and so poor overlap and that is why this is a weak point and the next what was suggest is that, in order to strengthen the bond little bit more or in order to reduce the angle strain reduce (())(27:41, so the angle strain.

So the hybridization, the internal orbitals that means the orbitals which make the carbon-carbon bonds the hybridization, I already told you, it is about sp5, so it has got the 83 percent p character and 17 percent s character, okay so that is the modern day concept of cyclopropene.

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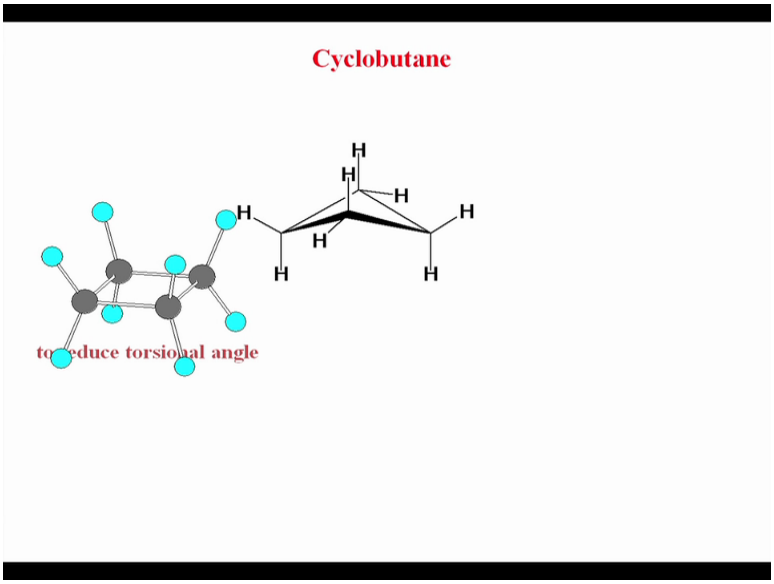

Cyclobutane

to reduce torsional angle

Next we come to cyclobutane. Now in case of cyclobutane, Bayer considered it as a flat molecule okay and flat molecule and then the angle strain was calculated, I already in the earlier lecture I told you about how much how to calculate the angle strain. It is 109.5 minus 90 divided by 2; however later on, it was observe like I was telling that these molecules if you make it flat, they will suffer from not only from angle strain, but they will suffer from what is called the torsional strain or the eclipsing stain.

These are same thing, eclipse in strain some people call it pitjar (())(28:51) are strain, because it is the scientist pitjar who first described introduce this concept of strain. So this strain is called when the bonds are eclipsed, they suffer from a strain and that is called pitjar strain that is also called eclipsing strain and today, we can early call it torsional strain. So they suffer from when you make a flat system the adjacent bonds will be eclipsing each other. So it will suffer from the torsional strain. So apart from angle strain that is present it will suffer from torsional strain.

The interesting point is even if we reduce it to zero the angle strain like cyclopenten, it is almost zero, because it is 108 degree now, regular pentagon and, but you still suffer from this torsional strain, because these eclipsing to each other, okay. So the question is whether it will now remain in this form or not, because it is suffering from torsional strain and it is suffering from angle strain.

Now the torsional strain uh can reduce little bit if you make it not flat if you make it little bit puckered, puckered means non-planar then what will happen? So if I try to move this carbon now a little bit and this carbon you see that the torsional strain, the bonds are no longer eclipsing each other. So there will be slight dihedral angle. It is not go here, but the torsional strain will decrease as you move these two carbons upwards, but what happens if you move these carbons upward the angle these two angles now become less than 90 and if it becomes less than 90, so it is it the what increases is the angle strain. So now you have a tread off. So if you rotate it a little bit if you make it little bit non-planar then it will reduce the torsional strain, but on the other hand it will increase the angle strain. So the question is which one it prefers, okay. So that will be in the next lecture.