Course on Stereochemistry
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Mod05 Lecture 20
Conformations Cyclobutane and Cyclopentane

Okay, welcome back to this analysis of conformations of cyclic systems, okay. So we have just completed the analysis of cyclopropane and you have seen the concept of banana bond and then the concept of unequal hybridization, okay. Now we will go to the next higher homologue of cyclopropane and that is cyclobutane, as I said in cyclobutane if it is planar, if it is flat molecule then what happens? It suffers from angle strain. It also suffers from what is call the torsional strain, because the adjacent bonds are eclipsing each other, okay I put two red bolls here, just to show it in a better fashion. So they are eclipsing each other.

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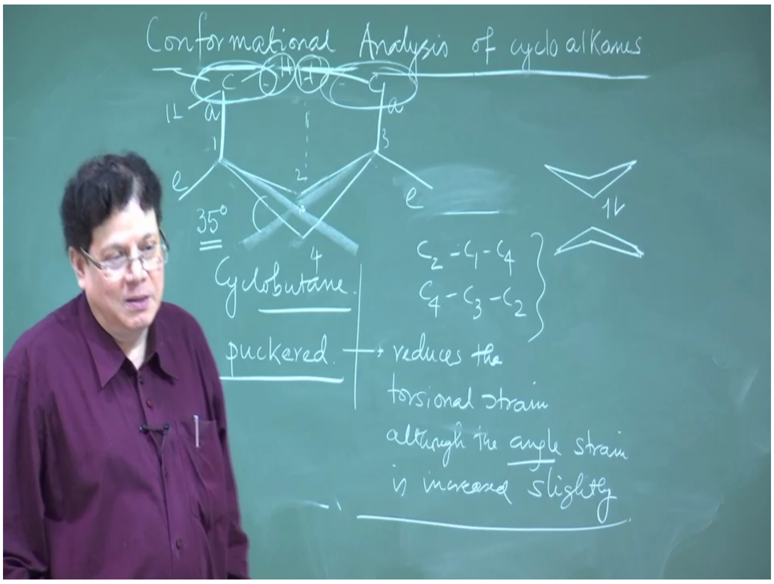

Now the question is in order to reduce the torsional strain what this molecule has to do? This molecule may push these two carbons upwards you see. Now these two red bolls are no longer eclipsing each other. So as I move these two, so that will happen with all the adjacent atoms, but just we are specifically concentrating on this red balls. So if you move it upwards they now, suffer from less torsional strain okay, again I repeat if they are planar then it has torsional strain then I eclipsing each other if you push it upwards then the torsional strain decreases, but at the expense of increase in angle strain. The angle strain increases, because these angles decreased while you try to push it upward. So question is which is the better option to reduce the angle strain.

to maintain the angle strain whatever it was there or to increase it or at the expense of the torsional strain which is decreasing and what happens ultimately it was found that cyclobutane likes to reduce the torsional strain. So it gains more by reducing the torsional strain at the expense of increasing the angle strain and it actually takes a shape like this. A popular kind of shape, so in I can show it in the board. So it takes a shape, which looks like this. So this is what is cyclobutane.

So this is no longer flat this is a puckered molecule, puckered means again I tell puckered is non-planar molecule, oaky. So here why it adapts a puckered form, because this reduces the torsional train, although the angle strain is increase slightly, but overall it gains more by reducing the torsional energy at the expense of increasing the angle strain. So this is the shape of the cyclobutane. So how much puckering is taking place?

So that depends on that what is the angle between the plane containing suppose this is 1, this is 2, this is 3, this is 4. So the plane containing C1-C2-C3, so this is plane and the other plane is, sorry C1 may be you can consider in this fashion that will be better, C1-C4-C3 that is okay, C1-C4-C3 that is what (())(4:42) or C1-C2-C4 the better is C1-C2-C4, so C1-C2-C4 that means these three carbons, you should write in s continuous way. So that should become C2-C1-C4. So erase this one, so C2-C1-C4 that makes a plane like this and then C4-C3-C2, so (these two planes divide) these two planes are no longer in the same plane. So there is an angle between them and the angle is so if you have this plane and extend it backward and if you have this plane extend it backward. So there is an angle that is generated. This angle is about 35 degree.

So the amount of puckering is about 35 degree if I take the model that will make it clear. So this is what is the shape? So the amount of puckering as you take this plane and take this plane and then the angle between this, so you extend this plane backwards. So there is an angle between these two planes which is about 35 degree. So the amount of puckering is 35 degree, okay.

Now the interesting point is while doing so, now you have these two look at these two bonds. This is a bond which will be almost pointing upwards and the other bonds other two bonds at C1 and C3 will be pointing towards this direction. So they are, so if you take an axis like this, see this molecule will have a C2 axis that goes through here, because if you turn it, so this will come here that will go there, C2 have a C2 axis provided these substituents are all same.

So these bonds are parallel to the C2 axis and they are called axial. They are co-axial with the C2 axis and they are axial and these are equatorial bonds, in case of cyclobutane, okay.

So what we learn from cyclobutane that it is no longer. So the deviation from planar, it is starts right from the 4 membered system. There is no way that again I repeat, three membered systems it is a triangle, triangle has to be planar. So no question of deviation come (())(7:20) planarity, but whenever an opportunity came for these system, it immediately started to adapt non-planar and the reason for adapting non-planarity comes from the fact that reduces the torsional strain, okay.

So number longer the angle strain is a dominant factor, okay. The torsional strain becomes more and more dominant, okay as the angle strain decreases, the torsional strain becomes more and more dominant, okay. In cyclopropene nobody bothers about torsional strain, because the angle strain is very high. In cyclobutane, now we have to bother, because the angle strain is not that high. So torsional strain or becomes the dominant factor to adapt a conformation which has got less energy, okay. So this is the conformation of cyclobutane, okay.

Now if this the conformation then you see that these if there is an atom here and if there is an atom there, so now there quite close to each other. So there may be steric interaction between these bonds. If these see these are occupied by the methyl suppose, suppose there is a methyl here, methyl means very big. So there is hydrogen like that and this carbon there is hydrogen. So now there will be clash between these hydrogens. So you can compare now the relative stability of say Cis and Trans, so this is the geometry, see other another interesting point is that it is not fixed in this geometry, there is these two carbon atoms are laying in a plane which are below the plane containing these 3 carbon atoms, but that is not fixed. What happens? This carbon 4 and carbon 2 can go up and C3 and C1 can come down that means this is one conformation. It immediately goes to the other conformation. So that happens and the energy barrier for this two is **is** not very much.

So this happens at the room temperature. So these two conformations equilibrium between each other, okay. So that is an important point that this is not the only conformation. So you can have a kind of this is called flipping, so you can flip this bring this 4 up 2 up and bring this C3 down and C1 down, okay. So we have identified this flipping we have identified what are called the axial bonds and the equatorial bonds.

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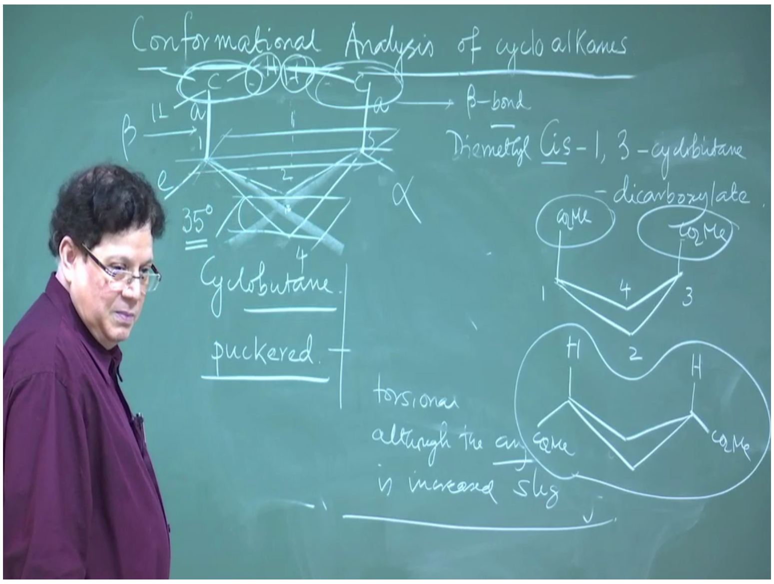

Now let us try to compare or try to draw different derivatives of cyclobutane. Suppose I like to draw Cis-1,3- dicarboxylate or you can say actually in proper nomenclature is suppose dimethyl Cis-1,3-Cyclobutane dicarboxylate, okay that is the correct nomenclature, okay. So that means what I have? I have a cyclobutane first of all, so write the cyclobutane. This is cyclobutane and now it says Cis 1, 3-cyclobutane Cis. Now what does Cis means here? Cis and trans in case of cyclic systems, comes from the it is **it is** different from Cis and trans, in case of double bonds. In case of double bond, so if they are opposite to each other we call them trans and later on this is modify to E and Z, okay.

In case of cyclic systems, it is basically that whether the bonds are above the average plane of the molecule, average plane means there is I can see two planes, one is this one and another plane containing these two carbons, okay and there is plane which contains these two carbons. So the average plane is somewhere in between (if you consider the average) if you consider suppose this is the top plane. So if I take the top plane, I see that this bond is above the plane of above that plane and this bond is below that plane. This bond is above this bond this above. So something above we already known that how to designate that, that is called a beta bond, right. So this will be in addition to axial this will be a beta bond, because it is above the plane containing the C1 C3 and this is also that beta, because this is above that plane and this is alpha and the alpha.

So when I call something Cis that means I have to put the groups, first of all one 1, 3. So there are two ester groups ester groups are Co2Me, because dimethyl dicarboxylate Co2Me. So what will happen now? The question is where to put, suppose this is 1, this is 2, this is 3, this is 4, so where to put these groups? These two groups are such that they are Cis to each other. Now there two ways to put that ring, one is I can put the Co2Me here and Co2Me there that is one possibility. The other possibility is that I can put one here and another there, okay.

Now out of these two obviously this will be unstable, because as I said that if you put bigger groups here at the axial position. So there will be interaction between these two and which will be call 1,3-diaxial interaction. This will be more clear when you go to cyclohexene system, but this one sees the axial Cis interactions starts from cyclobutane itself. So due to this 1,3-diaxial interaction, this molecule will adapt this conformation, okay.

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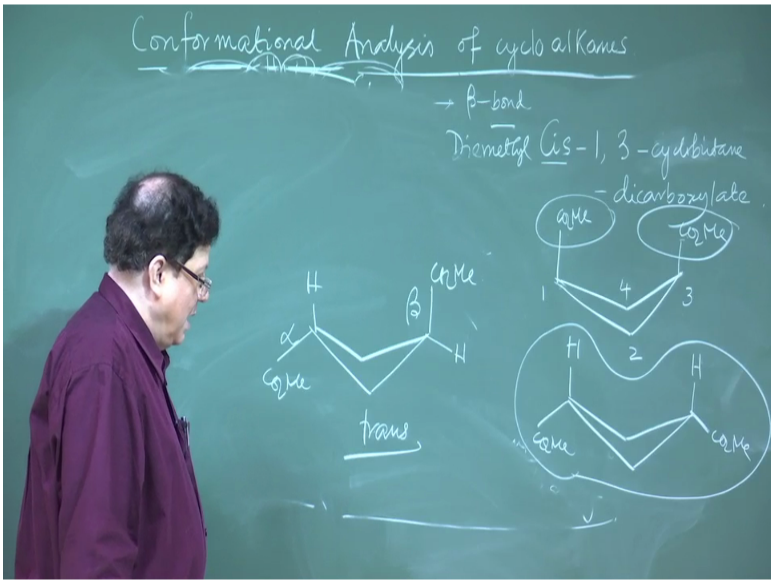

In case of trans you do not have any option, one has to be axial and the other has to be equatorial. So trans do not have any option, one has to be axial, one has to be equatorial. So this is the Cis compound and if I want to draw the trans compound and I can also tell about their stability the trans compound is this. One has to be axial and the other will be equatorial. So this is the Trans compound why it is Trans, because this is beta and this is alpha, okay.

So that is the different derivatives at the stability. So which one is more stable obviously, this one is more stable, because in this case one of the Co2Me is occupying in axial position. So this is more stable that the other one, okay and these are all experimentally verified and that suggest that yes really cyclobutane otherwise if you think, it is flat molecule, it will be difficult to explain the difference in stability of the substitute disubstituted cyclobutane, okay. So from the stability concepts stability measurements of the different disubstituted cyclobutane. It has proven that yes, it is really exist in the puckered conformation.

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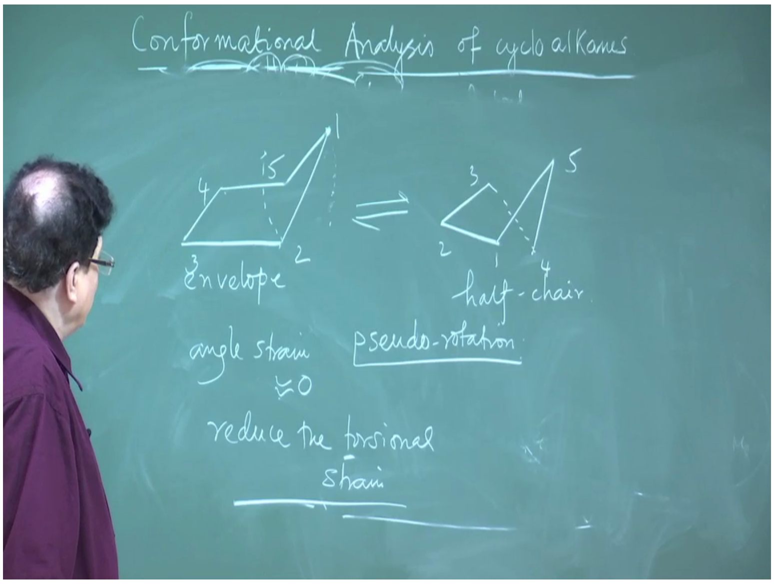

Now let us come to Cyclopentane, so that is cyclobutane, let us come to cyclopenten. In case of cyclopenten, as I said the angle strain is almost zero, close to zero, because this is if it is a flat system. So this is 108 degrees than the actual angle is 109.5. So it is almost zero angle strain, but it does not stay in the planar form. Simply because as I said that if it is a flat molecule then it suffers from what is call the torsional strain. These bonds are adjacent bonds eclipsing each other. So it will now try to rotate, so that this eclipsing interactions or the torsional strain decreases and that is what happens in cyclopropene.

So in cyclopropene what happens is that one of the atom if you take it up, it actually adapts two types of geometries, one is what is called a envelope geometry. One is called an envelope geometry, so envelop is basically 4 carbon atoms are in the plane, I hope you can see it, 4 carbon atoms are ins the plane and one carbon is up. So this is like an envelope, so we can draw this. Now this is the flap of the envelop, so this is the what is call envelop conformation and it also can adapt another conformation, where there is also less angle strain and that is what is call half chair conformation. Half chair conformation is such that 3 carbon atoms are in the plane. One carbon is above that plane and the 5th carbon is below that plane. So again I repeat what is the half chair form?

In the half chair form, suppose these three carbon atoms are in the plane. So one carbon goes up and other carbon goes down, but these 3 carbons remain in the plane. So that is the half chair conformation and how do you draw it the half chair. The half chair we draw it this way. So this is the half chair, so what I am saying that these 3 carbons atom carbon atoms are in a plane, one carbon goes up and another carbon is below that plane of (())(18:35). So this is what is called half chair conformation?

One interesting aspect very similar to cyclobutane is that this envelop conformation where there are 4 carbon atoms that are I the plane , it here also the carbon which at the flap of the envelop, the top most corner the top most point of the flap, there is a carbon , it also fluctuate that means this carbon is now at the top at the flap, the next time this carbonyl go up and that carbonyl come down and we will make all the 4 carbon these 4 carbon atoms like if this is 1, 2, 3, 4, 5, so this is one envelope (())(19:23) conformation, but it equilibrates between another envelop of conformation in which this one goes down and 2 goes up, okay. 1 goes down to up to certain level, so that 1 then 5, 4 and 3 are in the pentene.

So another envelop conformation then then 2 goes down and the 3 goes up then 4 goes down and 4 goes down and 5 goes up. So basically what I am saying that this is not fixed this goes down and then the other remains in the plane and one of these atom will go up, so that means this flap position is not fixed, it is continuously fluctuating between all these 5 atoms, same is true here that suppose this your 1, 2, 3, 4, 5. So what happens here also the this 5 carbon will go down and then one of these 1 carbon will go up again, then the next time C2 will go up and C3 will go down. So that continuously, so there is no fixed carbon atom which is occupying the flap position or which is occupying this top position or the bottom here. So this is continuously happening in the molecule, I can show it in the in this. So what I am saying in the envelop form that this is at the top now, but this goes down and this goes up.

So now what is you have a new envelop, so where this is up and then this goes down and this goes up. So we have another new envelop. So this is what is happening continuously in the system, so also in the half chair and this process is what is called pseudo rotation. This is what is call pseudo rotation, okay pseudo rotation, so these are the we will not go any further with cyclo cyclopenten, but you should remember that this is; this adapts again a puckered conformation. Why because there is by doing that it does not, it reduces the torsional strain and anyway in this case, the angle strain is almost zero. If it adapts puckered conformation, the angle strain is nearly zero, it was it just its the start with it was almost zero and even it adapts puckered conformation that is also zero. So unlike cyclobutane where puckering leads to increase in angle strain. Here that does not happen, angle strain remains almost zero, because you can see it is so flexible I can immediately rotate it very easily, but that I cannot do for cyclobutane. It is i**t is** still more rich it okay.

So the flexibility tells you that actually, there is no angle strain here, but you can easily make up and down of these carbons, okay. So that is , so it is having the pseudo rotation and it is having a puckered conformation and the reason for having puckered conformation is that to reduce the torsional strain, okay. So that is what is all about cyclopropene you can think over it. This is a problem for you if you when you go through this lecture, that between these two which one you think is more stable, the half chair or the envelop always think of the torsional strain and then you can get the answer that in which case where is the torsional train mold. So that will the little bit (())(23:23) torsional strain less means more stable.

So as per torsional strain you can come out with an answer of this that which one more stable envelop or half chair, although the difference is not much, but still there is energy difference between them, okay but that is a thought provoking question, I will not give the answer you try to find it out what I said, the torsional strain, which happens because the eclipsing of the hydrogens between the vicinal carbon atoms, okay.

So once you calculate that once you see that in a molecule how many carbons are in the plane you can get the answer, okay. So this is all about cyclopropane, cyclobutane and cyclopenten. So next one is cyclohexane. So we will start the next lecture from cyclohexane, which by the way is the most stable of all the cyclic systems, okay. Thank you.