Introductory Organic Chemistry

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Lecture – 07
Alkanes and Cycloalkanes Part - 2

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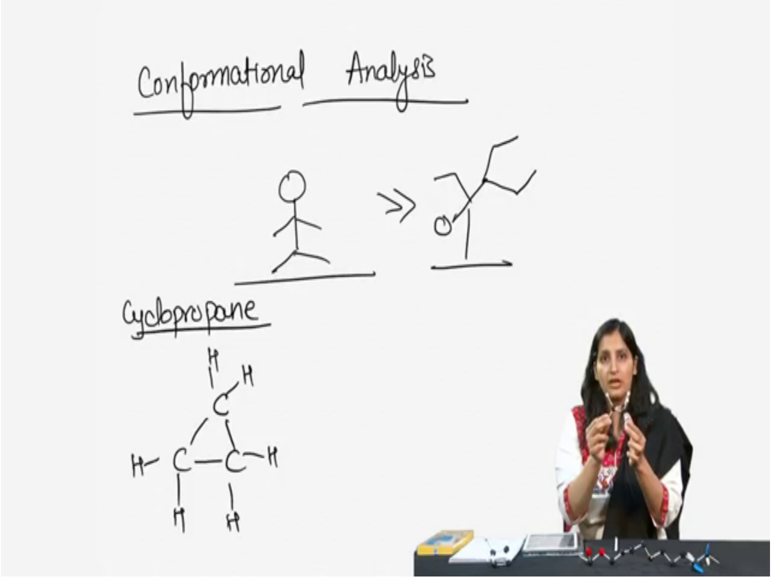

So far, we have looked at how carbon-carbon bonds can rotate along the axis and give rise to multiple conformations of the same compound via this rotation. So, one thing to remember is that even though we give rise to multiple conformations, we are still talking about the same compound with the same chemical formula and what we are really changing is the arrangement in the 3D space of this molecule. So, for example, I have this Pea moth pheromone model here and you can see that these two carbons; for example, here have a double bond in them.

So, I have denoted the pi bond with the p orbitals and rest of them is just a carbon and hydrogen chain. So, each of these linkages is a CH_2 linkage and it is a long chain and at the end we have an ester group. So, this same molecule can be folded multiple ways and I am still talking about the same chemical compound, but remember each of these conformations is a different conformation. And as the carbon chain goes on increasing in number, you can imagine that the number of conformations will also go on increasing for this particular molecule right. So, I am currently making really many many conformations of the same molecule.

One thing to remember is that in biological systems, the conformation plays a very important role. So, for example, this particular pheromone may not be active when it is the kind of this open chain form and in order for it to be biologically active, it needs to be kind of in a particular conformation let us say like this, right. So, the conformation is going to play a very important role when we have to assess whether a molecule is biologically active or not. We also looked at how particular conformations are more stable than other conformations.

So, in the case of butane for example, we looked at how the anti-conformation was very much more stable, approximately 5 kilo calories per mole more stable than the eclipsed conformation where the 2 methyls were eclipsing with respect to each other. So, I can kind of denote it with this cartoon wherein the two conformations; one of them is a man standing like this and the other man is kind of just trying to stay stable on one of his hands. So, clearly this confirmation even though the man is the same, this confirmation is way more stable than this one as you can see and that is how the molecules are two. So, in for example, in molecules we saw that how eclipsing interactions lead to torsional strains and they give rise to the strain in the molecule resulting in lower stability.

So, one of the questions you might want to ask is how fast are these molecules inter converting between the two conformers. So, if I take ethane molecule for example, how fast is it going from the eclipsed to staggered and back to eclipse, how fast is this rotation? And the true answer to that is actually dependent on how much energy the molecule has. So, in order to give a good analogy, you can imagine an egg box that has a marble inside it. So, at low energy the marble will be in any one of the wells right. But if I now start shaking this box slightly, the marble will have some energy to jump on one of the peaks and go into another well, right.

If I start shaking this box even more vigorously, what is going to happen is that the marble is going to move from one well to the another continuously such that it has enough energy to kind of travel in all these wells. So, in reality in the case of ethane as well or any molecule for that matter, depending on how much energy that molecule has you are going to see that the molecule will go from one conformation to another and will sometimes even be achieving the higher energy conformations depending on how much energy, it gets from the surroundings.

So, if I just calculate for ethane which has the energy barrier of 3 kilo calories per mole going from the eclipsed to staggered and staggered to eclipse that energy barrier is around 3 kilo calories per mole. And you also have the room temperature to be around 25 degrees centigrade so, which is corresponding to 298 Kelvin. Now if I want to calculate the equilibrium constant to go from staggered to eclipse, the equilibrium constant comes out to be very close to 6 into 10 raised to 10 per second ($6 \times 10^{10} s^{-1}$).

So, you can imagine that at room temperature, the ethane molecule is constantly moving around from one of the staggered conformation to eclipsed and back to staggered. It has enough energy to go from one conformation to another such that its it is moving in this or buzzing in this kind of a crazy fashion, the molecule, the carbon-carbon bond is rotating so vigorously with the Keq of about $6 \times 10^{10} s^{-1}$.

Now, if you are able to stop this rotation from staggered to eclipse and back to staggered, we are able to stop this rotation by lowering the temperature to a really low temperature. We may be able to see that the rotation goes on slowing and at some point, you maybe able to really trap the ethane molecule in one conformation or the other. But this is very difficult to do and we may have to go to a really low temperature in order to achieve this. When we go to cyclohexane; for example, I will show you how these different conformations are kind of captured with the help of spectroscopy.

So, you can see that hydrocarbons or alkanes, the very simplest of molecules are exceedingly complex as we start imagining their rotations and vibrations and in fact, when we start imagining how they behave in solutions. So, it is good to imagine molecules not as a static structure, but as a dynamic structure that keeps on moving, rotating and vibrating in order to understand their reactivity. So, the ability to imagine this molecules in dynamic fashion is way more important when we start looking at cycloalkanes.

We are going to begin looking at the conformational analysis of the very first cycloalkane which is cyclopropane and as you can see that the conformations a particular cycloalkane can have really depends on the size of its ring. So, we are going to begin with the first cycloalkane which is cyclopropane. Now cyclopropane on paper looks like three carbons forming bonds with each other in a ring fashion; so, somewhat like this, right. So, we are going to talk about cyclopropane, but remember that a 2D representation is never really the clear representation for a molecule. So, I have made a 3D model of cyclopropane. So, as you can see even in this model which is really a representation with the help of some plastic balls and sticks, you can see that the bonds are kind of bent; they are not straight bonds. And you can also observe that the C-H bonds on each of these carbons are such that the eclipse with the other C-H bond on another carbon.

So, for example, these two C-H bonds are eclipsing and the same way these two C-H bonds are eclipsing and so on. So, I really have 6 eclipsing pairs of C-H bonds in a cyclopropane molecule.

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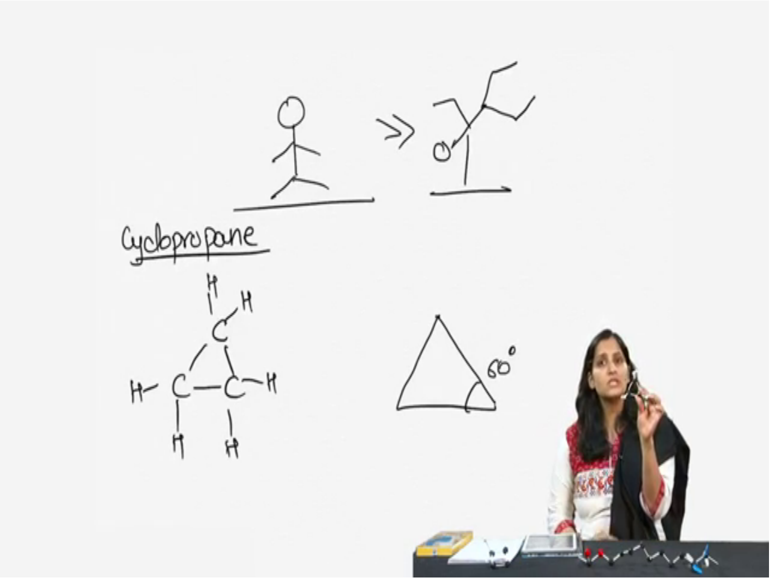

So, if you really see the observed bond angle between a carbon-carbon and carbon bond for a cyclopropane molecule; if I want to keep it such that all the 3 carbons are in the same plane the bond angle is close to 60 degrees, right, which is that of any equilateral triangle right. So, this is close to 60 degrees which is very much deviated from the ideal bond angle for an sp3 hybridized carbon.

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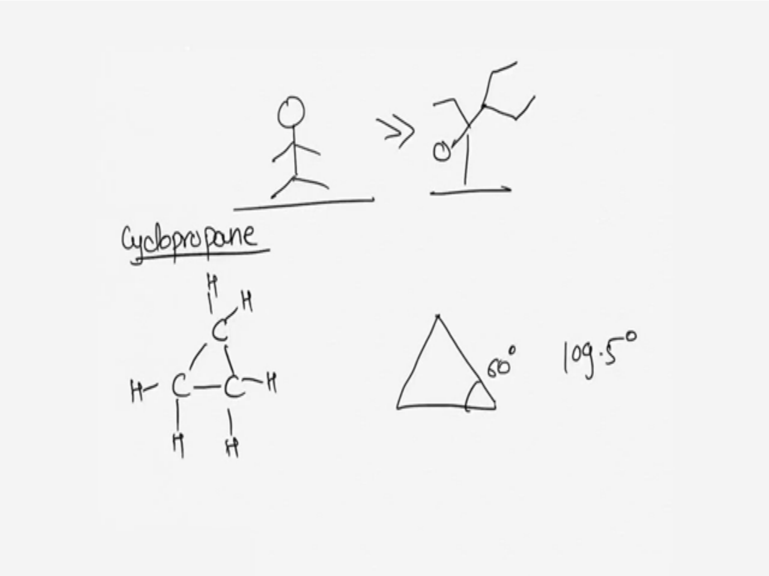

So, the ideal bond angle as we know is 109.5 degrees. So, 60 degrees is a lot of deviation from that ideal bond angle sp3 hybridized carbon bonds and as a result of which there is a lot of angle strain that this molecule experiences. This is also sometimes referred to as small ring strain. So, this is a strain arising because we are trying to place carbon atoms in a small ring which it does not really want to be.

So, this particular cyclopropane molecule is a lot more strained because of the angle strain that is present in the molecule. Remember there is a torsional strain because of these eclipsing C-H interactions and there is an angle strain which is because of the deviation from that 109.5 degrees. So, an addition of these two strains really makes the cyclopropane molecule a lot more strained than any other cycloalkane molecule. The combined result of these two strains is approximately 27 kilo calories per mole.

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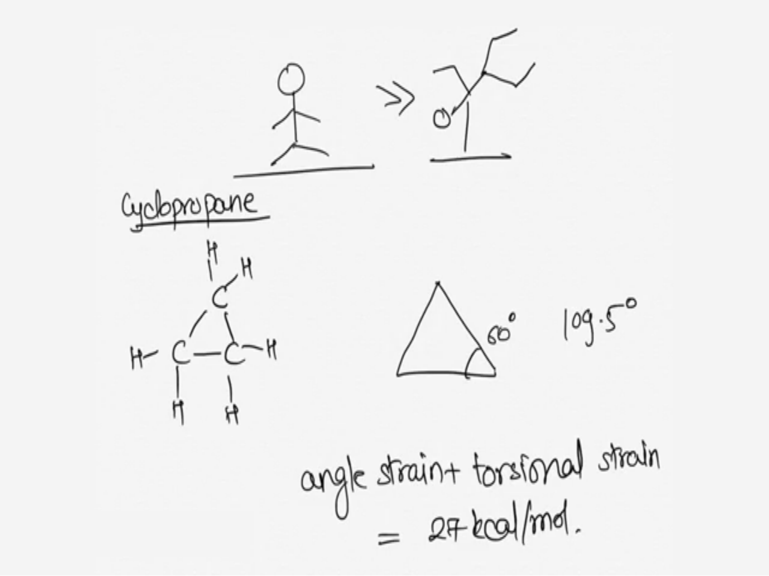

So, I will say angle strain plus torsional strain is approximately 27 kilo calories per mole and because of this the molecule is way more strained. And it is in fact, like that compressed spring wherein the moment you release that compression, the spring is gonna bounce back to its original form. So, you will see that cyclopropane molecules also want to quickly release this strain and open up.

So, most of the reactions of cyclopropane molecules and or for that matter the derivatives of cyclopropanes, you will see that they quickly want to release this angle strain and become a straight chain such that at least you can get rid of some of the torsional strain and most of the angle strain as it does that.

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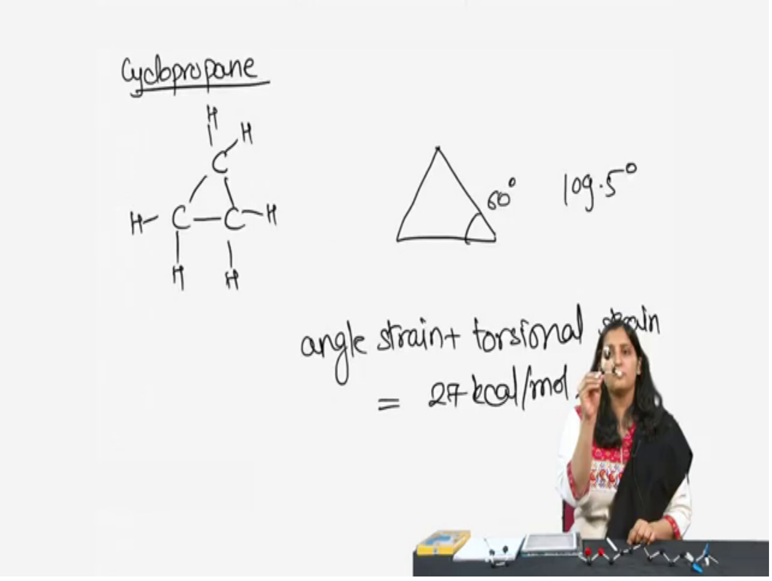

One of the key facts to notice about cyclopropane is as you can see right now, the bonds between the 2 carbons are not straight line and it is kind of puckered or kind of at a curved angle, right.

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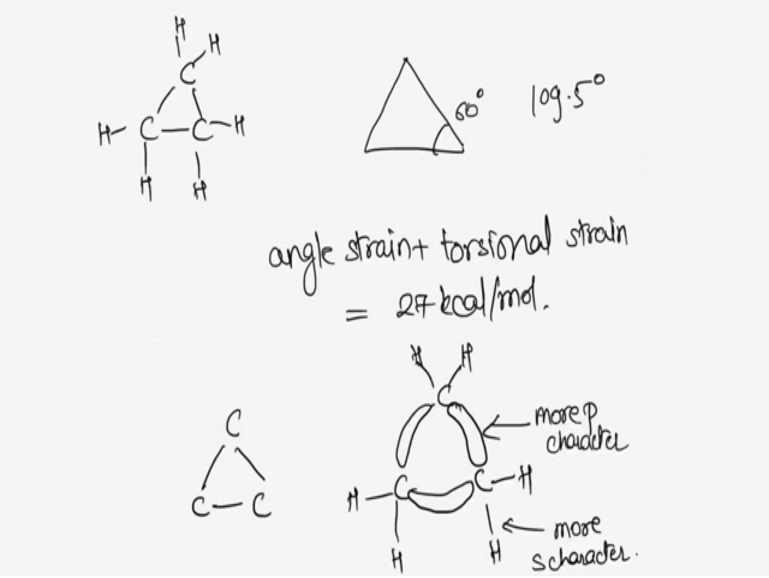

So in fact, instead of it being straight bonds like this what cyclopropane does have, is somewhat called as banana bonds. So, what I have here are banana bonds between the 2 carbon and carbon. So, as you can imagine what does the carbon achieve by having these banana bonds as compared to a straight line bond between 2 carbons.

As you can imagine the overlap is kind of lower in the case of banana bond right because a straight line bond will have a much larger overlap than for example, a curved bond like this, which is a banana bond. But what the carbon really is achieving is it’s trying to deviate from that 60 degrees and trying to make it a little more or little bigger than 60 degrees in order to relieve that angle strain.

In fact, these banana bonds are such that there is more electron density in the C-H bond rather than the C-C bonds. So, you will observe that the curved bond actually has a lesser electron density along the line and what happens is carbon tries to have more s character in the C-H bond and lesser s character in the C-C bond in order to achieve this curved bond to relieve the angle strain.

Yes, I will say the C-C bond has more p character and the C-H bond has more s character. This is evident in the spectroscopic data of cyclopropane wherein we observe that the C-H bonds of cyclopropane are more dense than any other C-H bonds.

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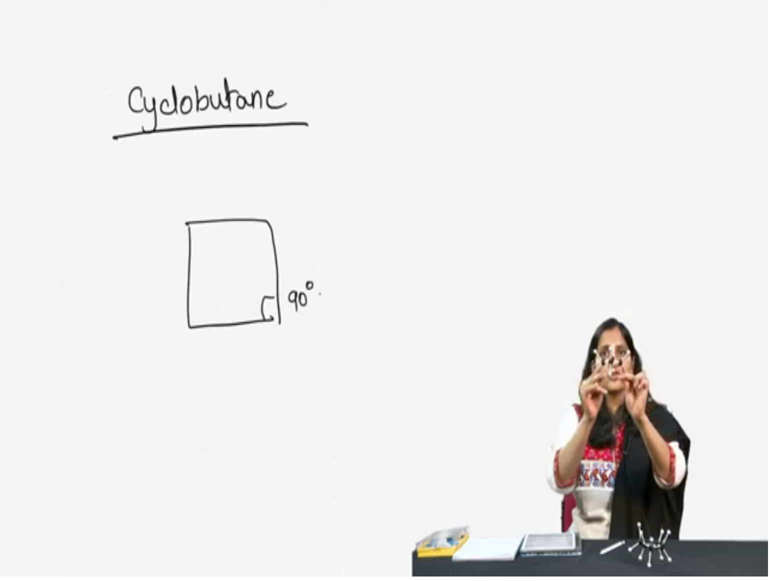

So, now let us talk about cyclobutane; if I want to keep all the 4 carbons in the same plane of cyclobutane, then what happens is I give rise to eight C-H eclipsing interactions because all of these bonds are eclipsing with each other. So, there is, these two are eclipsing, these two are eclipsing so on and so forth. So, I have 8 pairs of C-H eclipsing interactions arising and that puts a lot of torsional strain on this molecule. You can already imagine that the bond angle of a cyclobutane which is that of a square right will be close to 90 degrees.

So, it is not as bad as the cyclopropane which is 60 degrees way deviating from 109. In cyclobutane there is a lesser angle strain because it is close to 90 degrees which is not that deviating from 109 degrees. But now you have given rise to a few extra eclipsing interactions of the C-H bonds. So, now, there is a lot of torsional strain. In order to release the strain what the molecule prefers doing is it kind of puckers like this, okay.

So, this is a straight chain what I am going to do is, I am going to pucker it a little bit such that as you can see once I pucker it, the eclipsing interactions which were there for the C-H bonds kind of get reduced because the C-H bonds are no longer overlapping with each other.

So, as you can see they are not overlapping with each other and this reduces the torsional strain in the molecule.

You can imagine that by making this puckered fashion or it is also called as a butterfly confirmation because it keeps on doing this kind of a motion which is kind of flying of a butterfly; so, something like this, right.

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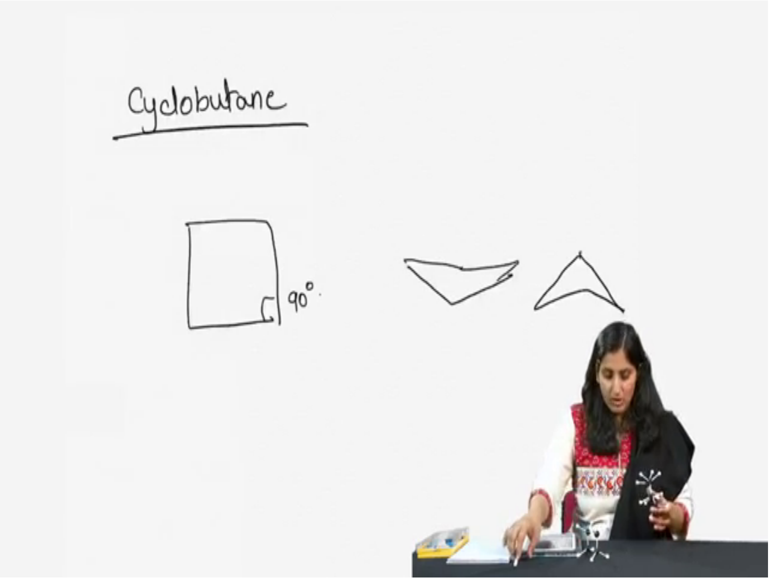

So, it will keep on going up and down like this; the cyclobutane molecule and really try to avoid any kind of torsional strain in the molecule.

By doing this you are not really reducing the angle strain. In fact, in the puckered fashion or the butterfly conformation, the angle strain is actually little more. So, the bond angle in the case of the puckered state is 88 degrees which is even lower than 90 degrees. But as you can see by going from this planar structure to this puckered structure, we have gotten rid of most of the torsional strain in the molecule. So, what we have done is we have increased the angle strain a little bit, but we have reduced the torsional strain considerably more such that the molecule prefers to be in this puckered fashion.

So, the cyclobutane molecule will keep on kind of going in this butterfly conformation such that it keeps moving in order to reduce the torsional strain in the molecule.

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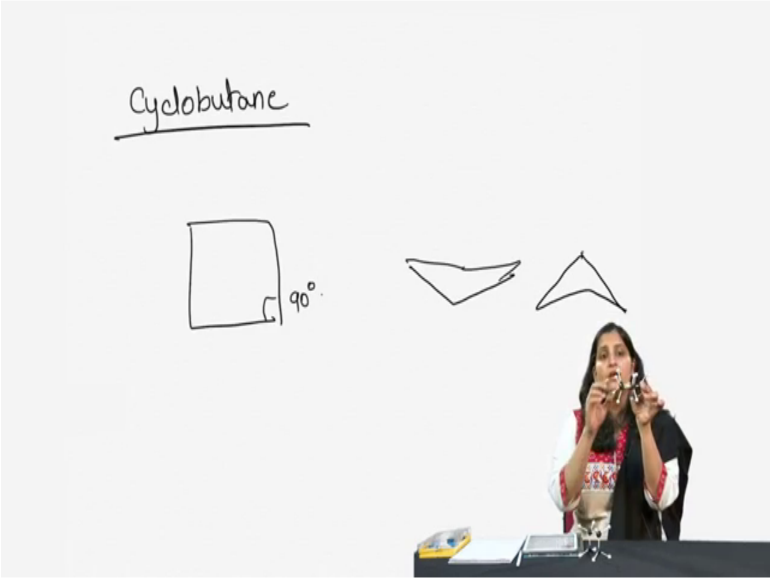

Now, if I look at cyclopentane molecule, I get closer to the bond angle of 109.5 degrees. The bond angle in the case of planar cyclopentane molecule is close to 108 degrees. We are very close to that 109.5 degrees, but as you can imagine; we have given rise to ten pairs of this C-H eclipsing interaction which puts a lot of torsional strain on the molecule.

So, there is very little angle strain, but a lot of torsional strain on the molecule. So, what this cyclopentane molecule does instead is it goes in something called as an envelope fashion or the envelope conformation. So, in the envelope conformation what happens is, these four molecules of carbon any 4 of the molecules of carbon are in the same plane, but one of the carbon is out of the plane.

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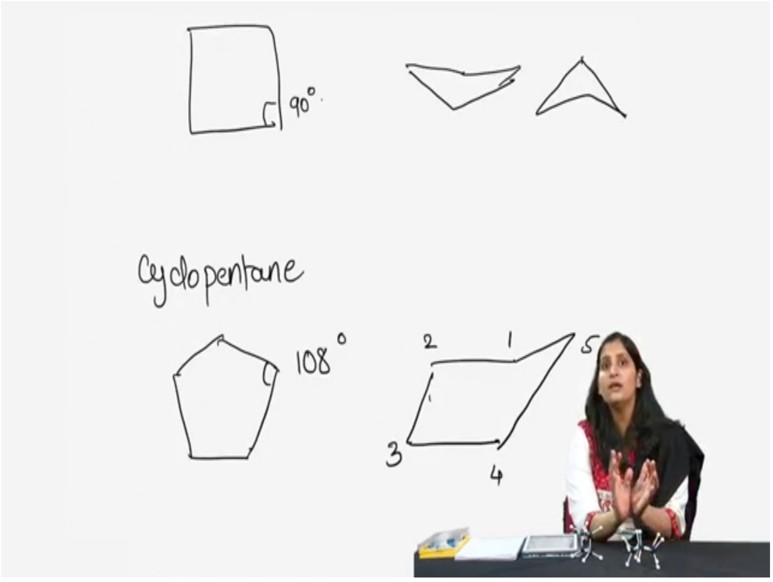

So, this is very similar to an envelope wherein the 4 corners of the envelope are on the same plane and the leaf of the envelope keeps on going back and forth.

So, in the case of cyclopentane; in the straight or the planar fashion, we have a bond angle of 108 degrees, but there is a lot of torsional strain. So, we give rise to this envelope conformation wherein let’s say carbon number 1, 2, 3 and 4 are in the same plane, but the fifth carbon is not. So, what this carbon does is in order to leave that around 10 kilo calories per mole of strain, it’s going to keep on going back and forth such that it no longer remains in the same plane as that of the 4 other carbon atoms.

Now, remember that this carbon is not always fixed such that it will always be out of the plane. In fact, each of the carbon atoms will take turn and will be going out of the plane such that the other 4 are in the same plane, but as a result of which the cyclopentane molecule keeps on moving back and forth kind of in the envelope fashion. So, that each carbon is out of the plane at least once, or alternating such that each carbon is alternating in order to be out of plane.

When the molecule goes in the envelope conformation, the bond angle is actually reduced from 108 degrees and it goes to close to 105 degrees. So, in this case as well as the conformation changes, the bond angle reduces putting more angle strain on the molecule. But we are getting rid of the torsional strain which is way more in this case around 10 kilo calories. So, we get rid of that torsional strain and we can make the molecule much more stable.

So, as you can see as we go from cyclopropane to cyclobutane to cyclopentane, the angle goes on increasing from 60 to 90 to around 105 which makes the angle strain decrease and you can also say that the torsional strain goes on decreasing, really making the ring more and more stable. So, as we go to cyclohexane, we will get to see one of the most stable conformations of cyclohexane molecules in which we have much stable ring as compared to the cyclopropane or cyclobutane. And as a result cyclopropane is way more reactive as compared to any of these cycloalkanes in its reactivity.

So, in the next class we are going to go over the conformational analysis of cyclohexanes and we will look at that conformational analysis in way more detail because it will help us to look at a molecule and its conformations and its reactivity as well.