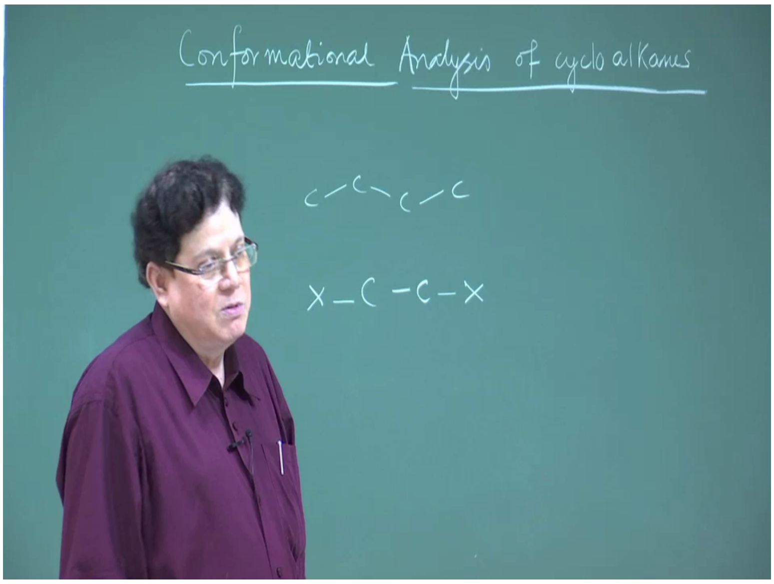
Course on Stereochemistry
Prof. Amit Basak
Department of Chemistry
Indian Institute of Technology Kharagpur
Mod05 Lecture 18
Conformations of Cyclic systems

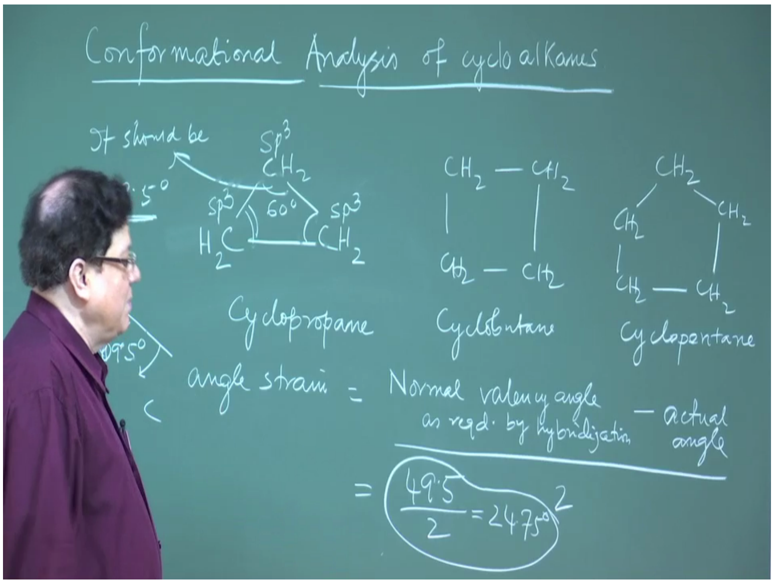
(Refer Slide Time: 0:42)



Okay, welcome back to this course on stereochemistry, during my last lecture what we have discussed is the conformational analysis of acyclic systems that means compounds, which are not cyclic which has got only, carbon chain like this in a linear fashion and then we have done the conformational analysis of n-butane, then we have done the conformational analysis of systems, which I have got also, this type of a two carbon system with different hetero atoms attached to the vicinal carbons and we have done the conformational analysis.

So today we will start the cyclic system the conformational analysis of cyclic system. Now there is a the first difference between the cyclic and the acyclic system is that, cyclic systems do not have that much flexibility like the acyclic systems. In acyclic systems, the flexibility that means the (())(1:34) rotation is having a very free (())(1:39) and it is occurring much faster than in a cyclic system. Cyclic systems are much more rigid than the acyclic systems.

(Refer Slide Time: 2:00)



Now the cyclic system starts with, it a 3 carbon obviously you need 3 atoms to form a cycle. So it is starts with a 3 carbon system called cyclopropene. So if you have all these hydrogens then, so this becomes cyclopropene that is the first member of the cycloalkane series. Then the second member is the cyclobutane and so like that the third member will be cyclopenten and so on. So you can increase the size of the cycle by adding more carbon atoms in the ring, okay. So cyclopropene, this is cyclobutane, this is cyclopenten. So we try to focus on our attention first to these 3 systems, okay.

Now initially what was what was thought about the cyclic systems that they are planar molecules? They are flat molecules, they are planar and if it is planar then what happens? There is a question of what if the what is the angle them between the this carbon-carbon bonds between the 3 carbons what are the bond angles there if it is cycle, it is flat, it is planar, okay.

Now we know that different kinds of strain are there that can be present in a molecule like, the torsional strain, the steric strain, okay the bond of positions strain. Those type of strains we have already we have been introduced. Now this now today we are going to introduce another kind of strain, which is called the angle strain, okay. The angle strain is that whenever the bond angle cannot maintain, the angle which is required for the kind of hybridization that the atom is having and that demands an angle according to the type of hybridization. So if the angle, deviates from the angle that is demanded as per hybridization then the molecule suffers from what is called an angle strain, I repeat again the angle strain arises, when the angle, which is required as per the hybridization of the ring atom we cannot be maintained then the molecule will suffer from what is called an angle strain, okay.

Now let us take this example, cyclopropene. Now cyclopropene obviously is as it is a 3 carbon system, so it has to be planar, because 3 carbon system cannot be a non-planar molecule. So the assumption that the people who are having people means scientist in those days, it is I am talking about let 19 th century, when there was a scientist his name was Bayer, there was (())(5:32) you know something about Bayer strain Bayer's Bayers rule those are there.

So Bayer he was the one who proposed that this molecules cyclic molecules are all planar and while adapting this planar conformation, they suffer from what is called this angle strain. So addition to the other kinds of strain, which is the torsional train, or steric strain, it also suffers from another strain a new concept which is the angle strain, again I repeat angle strain is the strain that is imposed, because the proper valency angle as per hybridization cannot be maintained in the system, okay.

Cyclopropene it is 3 carbon system. It has to be planar, so Bayer said must be correct that it has to be a planar, it is planar you cannot get a non-planar system out of a non-planar cycle out of a 3 carbon system or a 3 points that means the triangle has to be planar, okay. Now if it has to be a planar molecule then what happens? The angle becomes 60 degree if we think that this is a for a rigid system like this. It is a mechanical system that only this is the tied up by bonds, okay.

Now the angle is 60, now what is the hybridization states of these carbons? They are sp3, so the sp3 hybridization of carbon renamed (())(7:05) that the angle should be, it should be 109 degree around 109.5 degrees, but it cannot maintain that, because while making the cycle, it is not possible. So the angle is now 60 degree, again I repeat considering that this is a very mechanical system that these are just connected by straight lines which are acting as bonds, okay. So now this molecule will suffer from angle strain, because the normal valency angle cannot be maintained. So what is the angle strain? Now the definition of angle strain is that what is the normal valency angle what is the normal valency angle or you can say what is a normal valency angle as required by hybridization minus the actual angle**.**

Now this interesting, this has to be divided by 2, so what is the angle that is required as per hybridization that is the normal balance angle that is 109 degree 109.5 degrees, but the angle is 60 degree as per this geometry of cyclopropene. So the valency the difference comes out to be 49.5, okay. So the angle strain has is 49.5, but that is not the correct representation of angle strain. It has to be divided by 2. Why divide by 2, because if you have the normal valency angle like this 109 degree to in 109.5 degrees. So in order to make cyclopropene what we have to do? We have to bring this bond towards this carbon and you have to bring this bond towards this carbon.

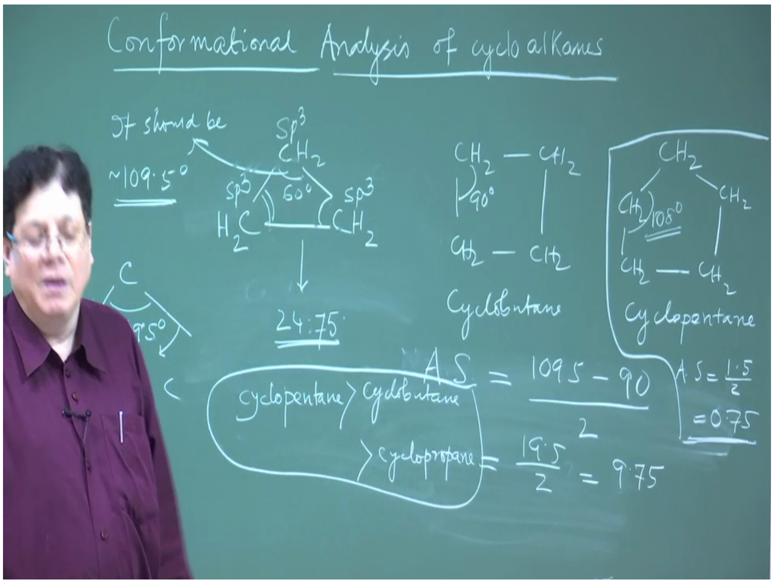
So ultimately, this 49%5 degree deviation is evenly distributed between the between both the bonds, okay. So each bond is suffering an angle strain of half of this 49.5, because this you have to bring about what 24.75 degrees and you bring this to 24.75 degrees then you can combine these carbons with this carbon. This carbon you can connect with this carbon by lowering the bond angle by moving this by 24.75 degrees, okay. So basically the angle strain, because it is sheared between both the hands of carbon both the bonds of the carbon, so we have to divide it by 2. So that is the angle strain in case of cyclopropene. It is an enormous strain and if you try to build up the model of cyclopropene.

So let us see cyclopropene can be this is the this is what is propene, okay. This is what is propene. Now in order to the end the propene is only one, so it is propene. So if you want to make cyclopropene out of the propene then what we have to do? We have to combine these two bonds, but you see there is lot of strain and bending that is associated with this. So what happens to these bonds look at the bonds very carefully if I place it here, let me see whether it comes in the in the camera, but it is not coming, so better again lift it up.

So you see that the strain that is now involved in the molecule. The molecules are no longer linear. So it has to be bend we have to force these bonds to connect with each other and then make the cyclopropene. So these bonds are suffering from this angle strain and as I said, because you have to move both the bonds, so it is equally sheared by the by both the bonds that is why attached to the carbon that is why we have to divide the angle strain. The deviation from the normal angle divided by 2, the magnitude of deviation divided by 2.

So this is how the story started, okay. People started Bayer started calculating the angle stain and he said that as the angle strain is more in cyclopropene. So it is highly unstable compound and if you make the cyclobutane now if you consider cyclobutane, so this is cyclobutane you see you compare these two, you can say this the amount of bending of the bonds is less in cyclobutane the amount of bending in both the bonds. So a this is cyclopropene, so you see the, I have forced almost the molecule is breaking apart, but in cyclobutane you see, in cyclobutane that type of strain is not present, it is still it is little bit bend, but it is less than the cyclopropene why is that? You can calculate the angle strain and then this is the angle strain in cyclopropene, so what happens.

(Refer Slide Time: 13:34)

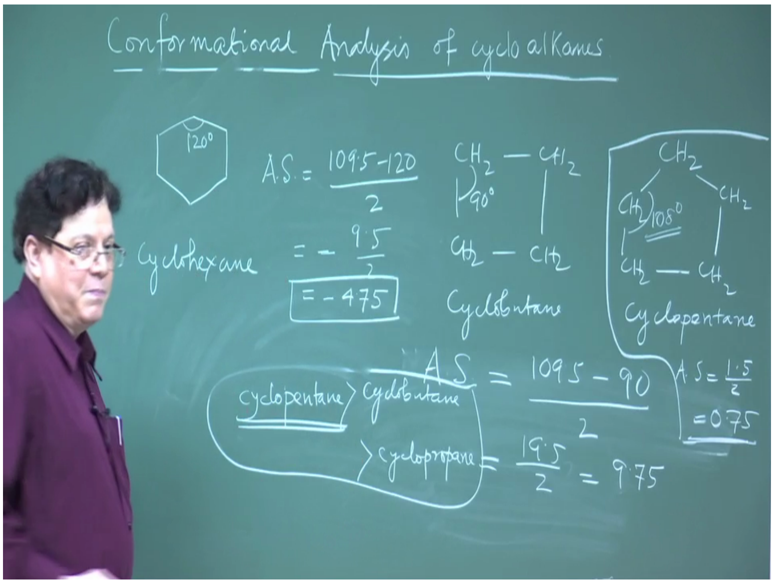


The angle strain in in cyclobutane will be the angle strain, so if I say AS is equal to 109.5 minus 90, now it is cyclobutane. So these angles are 90 considering, these are regular the square okay, considering it as a square so that angles are 90 degree. The regular polygon, so 109.5 minus 90 divided by 2, so that comes out to be 19.5 by 2 and finally you see, it will be 8. , sorry it will be 9.75. So 9.75 is the angle strain. So earlier it was 24 inside the pentene the angle strain was 24.75, okay.

So the angle strain is more in cyclopropene than in cyclobutane. So this is more unstable then this and this instability is due to what is call the angle strain, sometimes it is actually referred to as Bayers strain also, Bayers strain means Bayers angle strain, okay. So Bayer strain is more in this system. So this is less stable then cyclobutane, okay.

So after this point was very find then if you take cyclopenten, you can calculate the angle strain again and what will be the angle strain here, if it is regular pentagon then the angle will be 108 degree and you see, it is so close, it is very close to the angle that is required as per hybridization of the carbon that is 109.5. So the angle stain here is very little you can calculate that is angle strain will be only 15 divided by 2. So 0.75, so according to Bayer strain theory, the stability order will be cyclopenten should be more stable than cyclobutane which in turn should be more stable than cyclopropene, okay. This was find after this point was find, but the problem started when you increase the size of the ring beyond five, okay.

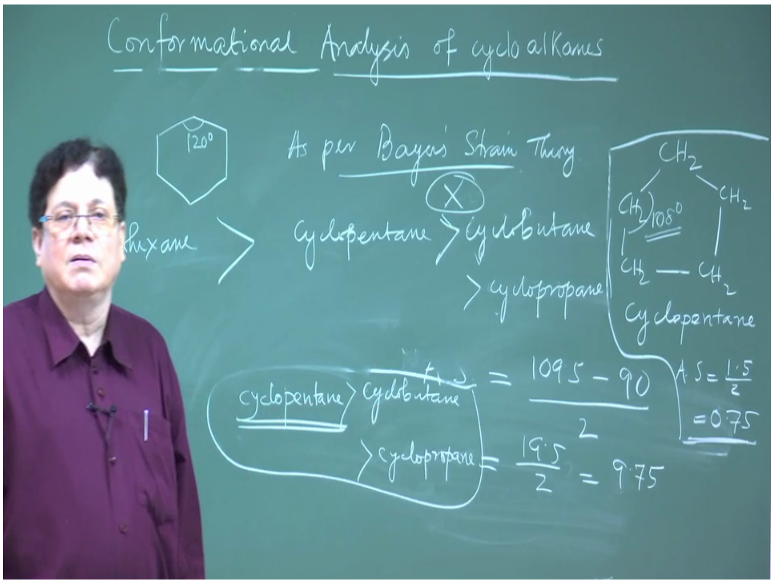
(Refer Slide Time: 16:26)



So what is the next homologue of cyclopenten is the cyclohexane. So you now write cyclohexane I remove the carbons just the normal way otherwise it will take more time if I write CH2s. So this is your cyclohexane. Now if cyclohexane is a flat molecule is a planar molecule. It is a regular hexagon then the angle becomes 120. So the angle strain will be, now the angle strain will be 109.5 minus 120 divide by 2. So it becomes a negative quantity now, because you are now increasing the angle beyond whatever is required as per valency (()) (17:08). So this will be now 9.5 divided by 2, but there will be a minus sign with a minus and so that will be minus 4.75. So the angle strain the magnitude of angle strain whether it is positive or negative that is not the important issue that important issue it how much you have deviated from the normal valency angle, okay.

So you have deviated 4.75 here the angle strain. In case of cyclopenten, it is only 0.75. So according to Bayers train theory, cyclopenten should be more then cyclobutane that is correct that will be more than cyclopropene in terms of stability, but what about cyclohexane. So as per Bayer strain theory, cyclohexane should be less stable than cyclopenten.

(Refer Slide Time: 18:19)



So again I write, so these are the calculations I write this is the, so now the, so we can, so as per Bayers strain theory, strain means the angles cyclopenten should be more stable than cyclohexane and if you continue to increase the number of carbon atoms then cyclohexane should be more stable than cycloheptane, okay. So if you try to draw a graph above a stability of these systems, so if cyclopropene is here, then cyclobutane, then cyclopenten, then cyclohexane, then cycloheptane, then cyclooctane, so again it rises than history (())(19:12), but in actual case, that does not happened. So after this 3 to 5 whatever Bayer stain theory is telling, this is followed that means cyclopropene, cyclopenten is more stable than cyclobutane, cyclobutane is more stable than cyclopropene that was followed and that can be explained in terms of the angle strain, which was introduced by Bayers, but then the theory falls apart if you increase the, when you increase the number of carbon atoms and in fact ultimately, it was found that amongst all the cyclic system, the most stable system is cyclohexane.

So the actual is, this is wrong what is correct is the reverse, cyclohexane is more stable than cyclopenten then comes the cyclobutane and cyclobutane is more stable than cyclopropene. So here we have a problem now, so there must be something wrong with Bayers strain theory, okay that. So it is not dictated by angle strain. When the number of carbon atoms increase gets increased in a cyclic system, okay.

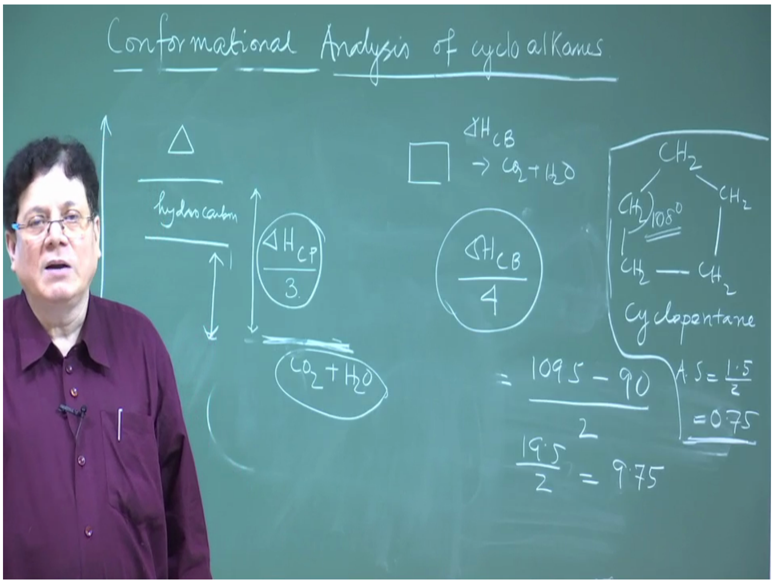
So we will come back to Bayers stain theory, but before that one might be ask a question that how do you measure the stability of a compound? How are you measuring the stability of this systems the cyclopropene verses cyclobutane all these are. So the very good way to measure the stability that is a very valid question, how do you know which one is more stable which one is less stable.

Now here again a very important concept that sometimes students get confused that sometimes students feel that a less stable system is more reactive than a more stable system that may not be true always, because reactivity depends is a kinetic factor, is a kinetic issue, so there may be compound, which is more stable then another compound, but is more reactive, okay so that may happen, because reactivity depends on the activation barrier of process.

So if I say that cyclopropene is very unstable and it reacts with so many reagents like cyclopropene reacts with hydrogen you can get back (())(22:02) the linear propene if you add bromine, it adds bromine like a double bond is present so you will get 1,3-dibromo propene, but that does not really tell you that it is less stable than cyclobutane. Stability is a thermodynamic quantity and reactivity is a kinetic quantity, okay.

So you must be very careful if somebody ask that show that cyclopropene is less stable than cyclobutane and if you say that cyclopropene reacts with so many reagents whereas cyclobutane does not that does not that is not the correct answer, because that is a reactivity thing. Reactivity depends on the activation barrier, okay. So stability is a thermodynamic stability, the how do you determine the order of stability of this cyclic systems.

(Refer Slide Time: 23:10)



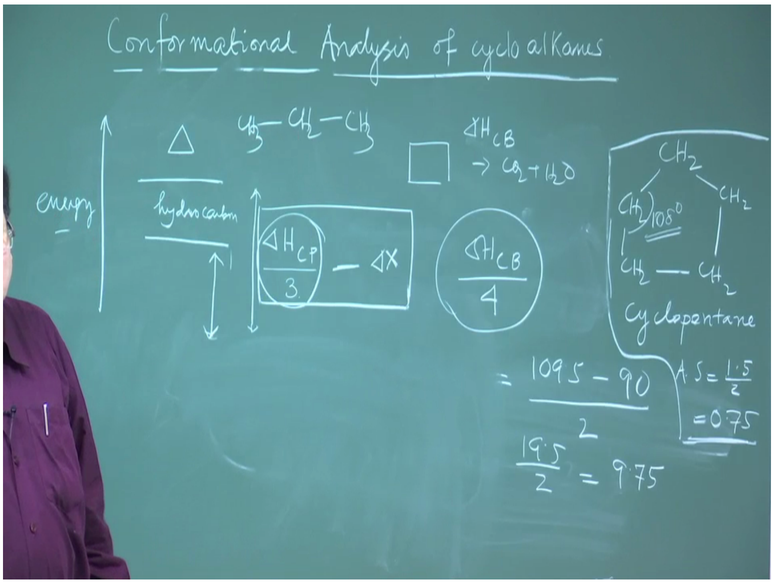
The best way is that if you burn these if you burn any hydrocarbon, the product that you get carbon dioxide and water. So the end product is same, so if your hydrocarbon lies at this energy level suppose this axis is energy, so if this is the energy level and if this is your hydrocarbon, so when you burn this hydrocarbon, so what you get is the end product carbon dioxide and water, suppose the combined energy lies here, okay. So that is this as more stable, so it is always an exothermic process, okay. So some heat is liberated from the hydrocarbon, okay.

So if you take suppose cyclopropene you burn it, so you will get carbon dioxide and water, okay and suppose, this is delta H for cyclopropene CP. Now there are three carbon atoms here, so in order to normalize these values in comparison with cyclobutane and cyclopenten what we do we calculate the heat of combustion that is they are divided by 3, because there are 3 carbon atoms 3 methylenes are there in cyclopropene, okay. So you divide it by 3 and see what is the value and you do the same thing with cyclobutane, so if you burn cyclobutane you will again get carbon dioxide and water and if the this is cyclo, this is the H the delta H of cyclobutane.

So when you want to compare, this verses that in terms of stability, so you compared delta H for cyclopropene divided by three and for cyclobutane delta H cyclobutane divide 4, because there are 4 carbon atoms. So obviously more energy will be liberated, but for a particular methylene per methylene how much energy is liberated for that you have to divide it by 4 you have to see number of methylenes here and you have to divide this by 3, okay.

So that is now you can compare, because both are given to the same product, so this level is, these are the same, this energy level is at the same position irrespective of cyclobutane or cyclopropene, only think that if cyclopropene is here and cyclobutane is here, then there will be less energy that will be liberated when you burn cyclobutane, again I repeat cyclo, this is I am comparing the energy that is liberated for each methylene in cyclobutane. So if you compare this heat of combustion per methylene of cyclopropene verses cyclobutane verses cyclopenten verses cyclohexane. So that will be a very good way to compare the stability of these systems, okay.

(Refer Slide Time: 26:23)



So another some books write it this way, they compare the heat of combustion per methylene and you can divide you can subtract it from the if you take the linear compound a linear hydrocarbon compound suppose n propene and then you burn it, so this is a linear compound and you see how much it is liberated per methylene in a linear compound, suppose that value is say delta x, okay, so that is a constant value. So you can actually see that what is the extra energy that a cyclopropene has a cyclopropene methylene has over a methylene in a linear system that difference also tells you about the instability of cyclopropene relative to a linear system.

So some books actually gave the values of these cyclic systems by not only saying the heat of combustion but they do this difference that means you get the heat of combustion per methylene for the cyclic system minus the heat of combustion for the methylene in an acyclic system and then these values are compared for different cycloalkanes, okay.

(Refer Slide Time: 27:51)(29:57) (30:39)2 slides

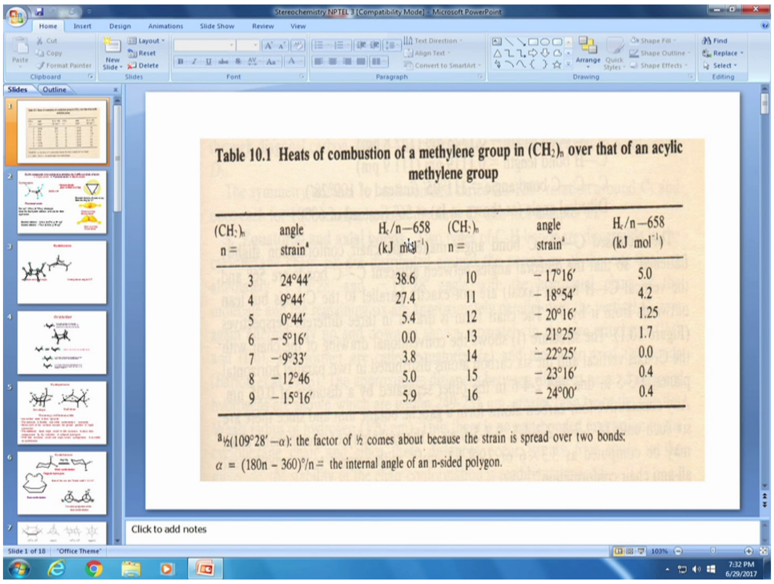
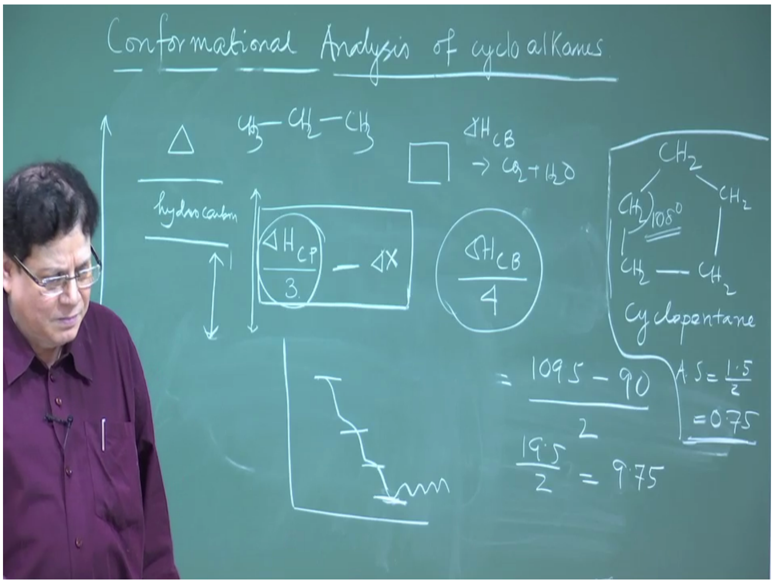


Table 10.1 Heats of combustion of a methylene group in $(CH_2)_n$ over that of an acylic methylene group

$(CH_2)_n$ 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] ½(109°28′ − α): the factor of ½ comes about because the strain is spread over two bonds; α = (180n − 360)°/n = the internal angle of an n-sided polygon.



So I will show you one slide that is there which tells you about these values that what are the values of the different for different cyclic systems, see this is a I said 24.75, I think they get they took the correctness I approximated 10.5 degrees, so it is very close to 24.75, so do not worry about the values here, they are very close, so about I can say 25 degree is the angle strain, in case of cyclopropene and you see what is that value that difference what I said that the heat of combustion per methylene in an cyclic systems minus the heat of combustion for a methylene in an acyclic system (())(28:39) subtract those values and you see ,the values coming as for cyclopropene, it is 38.6 then 27.4 then 5.4, so it is decreasing that means this is the least stable compared to the linear system. This is at least more stable than the cyclopropene and this is here the value is the angle stain is only about 0.5 and then the heat of combustion that difference is 5.4.

In case of cyclohexane, this is interesting the difference is zero that means the amount of heat that is liberated per methylene in a cyclohexane is exactly the same if you take the normal hexane. So the that that difference is only zero, so that immediately tells that this is the most stable system then as we increase the carbon chain you see the carbon in a carbon number of carbons is a cyclic system then again it starts going up, it is starts going apart, it never reaches these values, it remains more or less (())(29:49) very close to between 5, 5.9 then it is again 5, 4.2, so it is really fluctuated.

So the graph will be something like this. The stability graph of cyclopropene is here then comes cyclobutane then comes cyclopenten then comes cyclohexane and then it just fluctuates like this, but this should be the actually the to the bottom line, the minimum point. So this is cyclohexane, this is your cyclopropene, cyclopenten, this is your cyclobutane and this is the cyclopropene, okay.

So this is the first thing that we have learn that the stain theory whole is good for cyclopropene that is a and then cyclobutane, it also as per the Bayer strain theory, this is this is also unstable, but this is more stable than cyclopropene and then cyclopenten. Cyclopenten is a five member ring where there is you see the bonds are almost linear there is no bending of te bonds, so that is not suffering from angle strain and is very minimal angle strain. So it is more stable than that.

So Bayer stain theory, these 3 are this following the lines, but Bayer said, but then after this the whole theory falls apart. Cyclohexane is more stable then all these systems we have thank you. So in the one we will discuss the modern day concept of the cyclic systems conformation of cyclic systems, okay.