Course on Stereochemistry
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Module 4
Lecture No 16
Conformational Analysis of Acyclic Molecules (Contd.)

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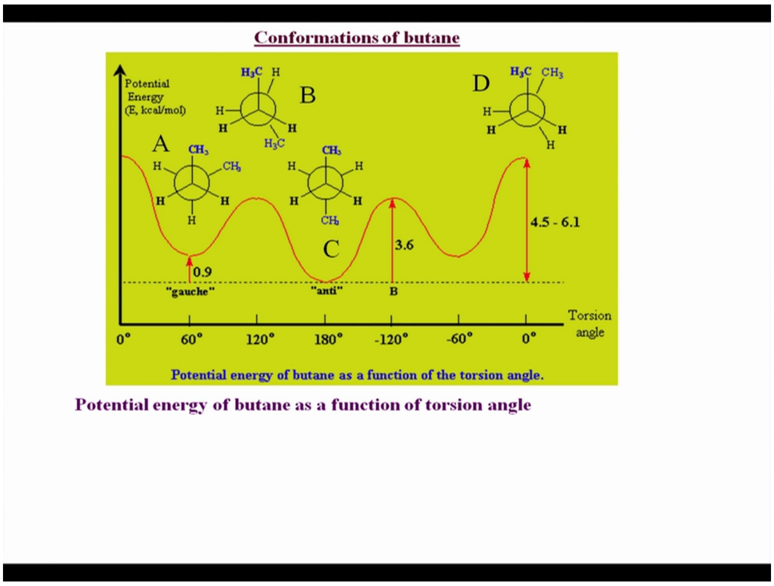
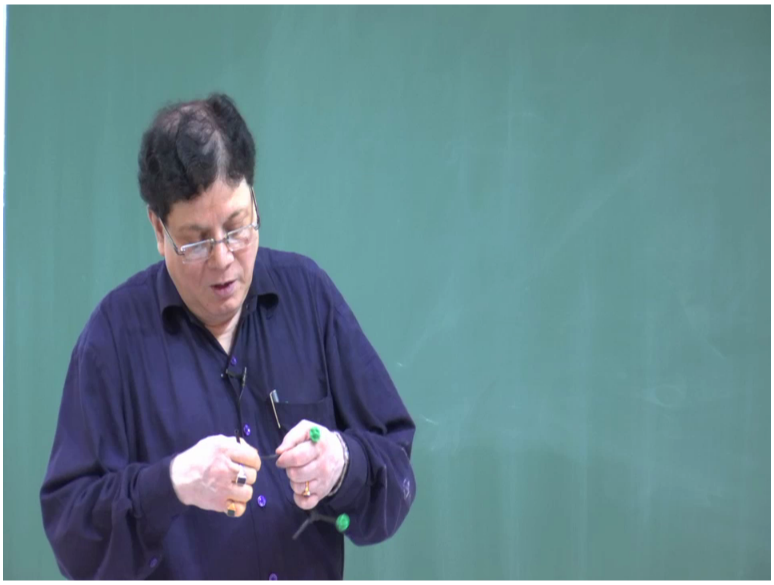
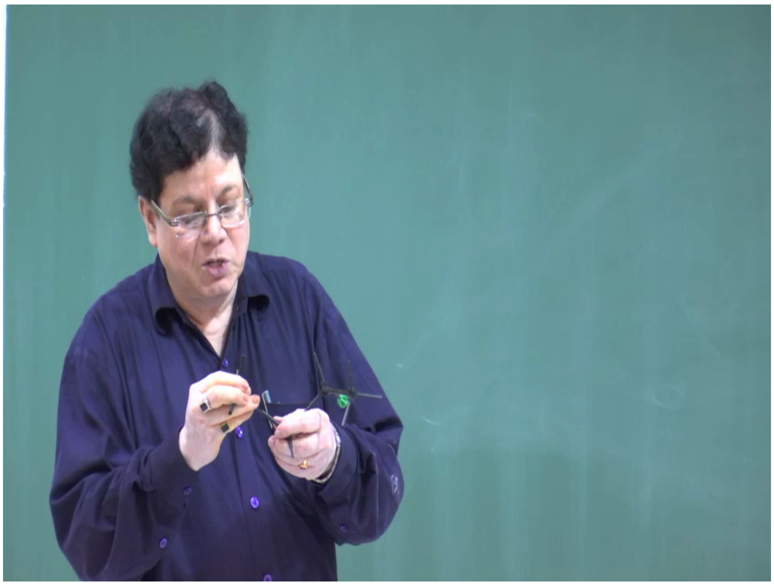
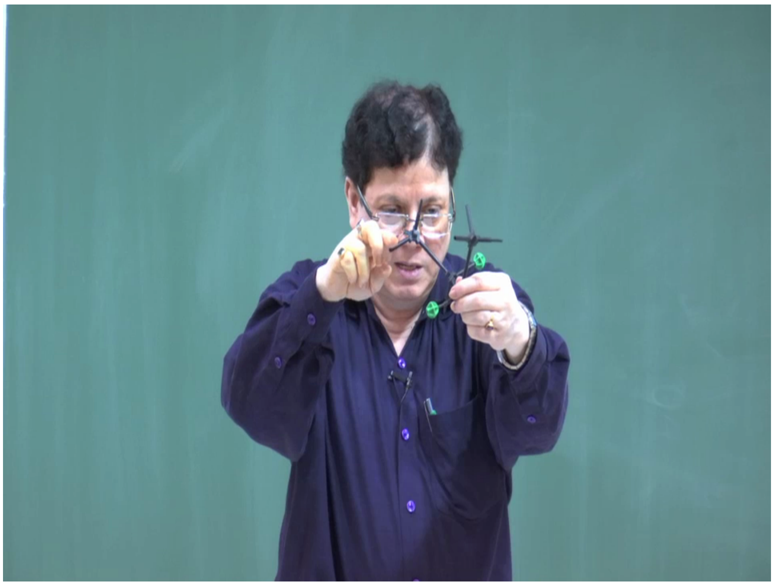


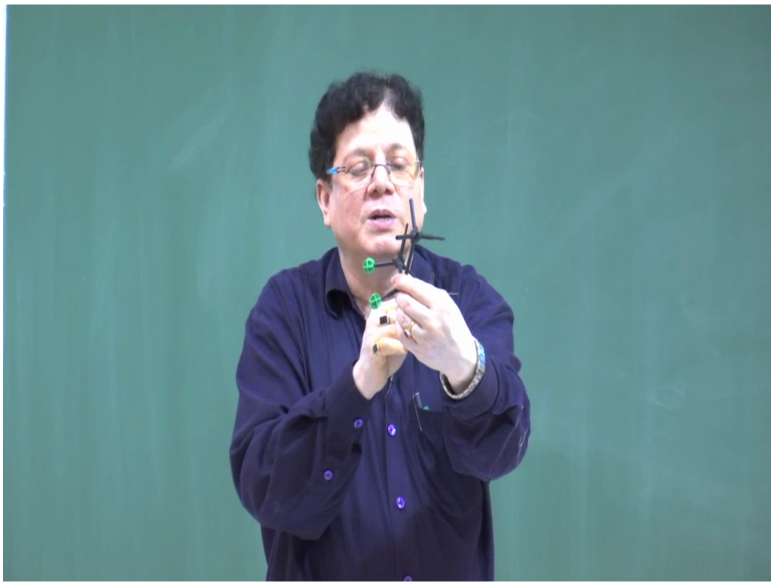
Conformations of butane

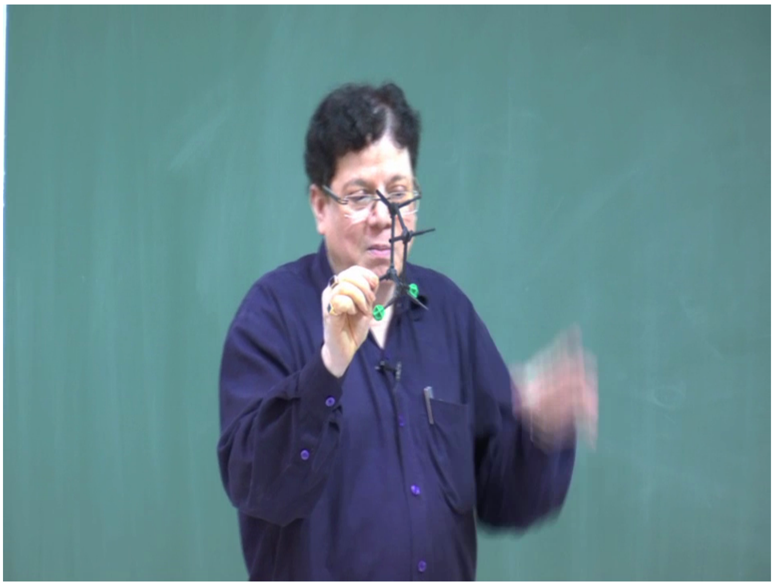
Potential energy of butane as a function of torsion angle











Okay so welcome back so let us now consider the confirmations of, we have finished the conformation analysis of ethane now we will start and discuss the conformation analysis of butane. So what happens in butane? This was we have already so on butane, conformation analysis in butane, okay. So in in butane you have one extra carbon on the 2 carbons okay so this is the suppose the extra carbons, so now you have this is the in butane and you see there is again the free rotation, these are the hydrogens these are the hydrogens and this is the methyl, okay.

Now you have you have this is eclipse conformation because we bonds are eclipsing each other and as you start rotating see this is the staggered conformation where the bonds are anti-to each other but this this is a staggered conformation. Just remember these things now the 2 methyl are really not that away from each other they are quite away from each other but not really anti-to each other, so if you start moving this carbon carbon bond you come to a again an eclipse conformation.

Now where this methyl is now eclipsing a hydrogen, earlier the methyl was eclipsing a methyl, now the methyl is eclipsing a hydrogen, you rooted it further now you really come to situation and staggered form of this to methyl are anti-to each other, okay. Then you further rotate so if now you see that you have come back to an eclipse conformation, where methyl is eclipsing a hydrogen, and you rotate other another 60 degree and you see now the 2 methyl are again in an angle of 60 degree but in the opposite since like the earlier situation and but this is a staggered conformation and then finally you come back to your original position. So this is how the molecules will the molecules that arrangement will look like when you rotate the carbon carbon bond, okay.

So let us come back to this analysis now, 1st of all we have to identify you cannot just say that that one is in staggered form and one is in the eclipse form because I have shown you that eclipse has different two different types where the methyl methyl can eclipse each other or the methyl hydrogen and eclipse each other okay. So one is called partially eclipsed another is called fully eclipsed, okay. Fully eclipse means the methyl methyl are eclipsing each other so you have 2 different…

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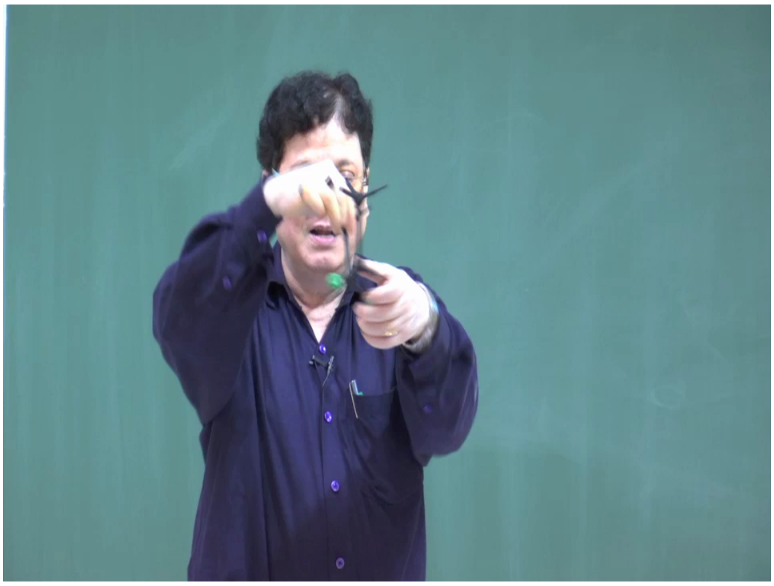

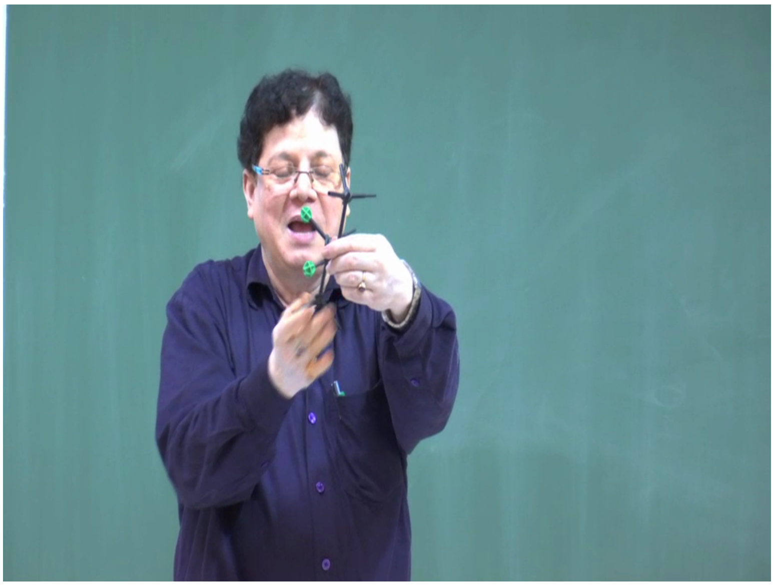

Now eclipse conformations one is fully eclipsed another is partially eclipsed and similarly you have 2 different staggered conformations, one is where the methyl methyl are totally anti-to each other and that is called anti-conformation, so this is a staggered conformation but this will be called anti.

That means here is the methyl groups have dihedral angle of 180 degree. On the other hand you can have a staggered conformation where the when I say methyl has a dihedral angle which think of that that (())(3:48) dihedral angle cannot be between only groups, this carbon that carbon this carbon that constitutes a plane and this carbon methyl carbon this this carbon and that carbon, that constitutes a plane. But for simplicity and saying the angle between the methyl that means the dihedral angle between the lanes containing the methyl groups, so that is 60 degree that is another staggered conformation but this is now called a Gauche conformation. G A U C H E a Gauche conformation, okay.

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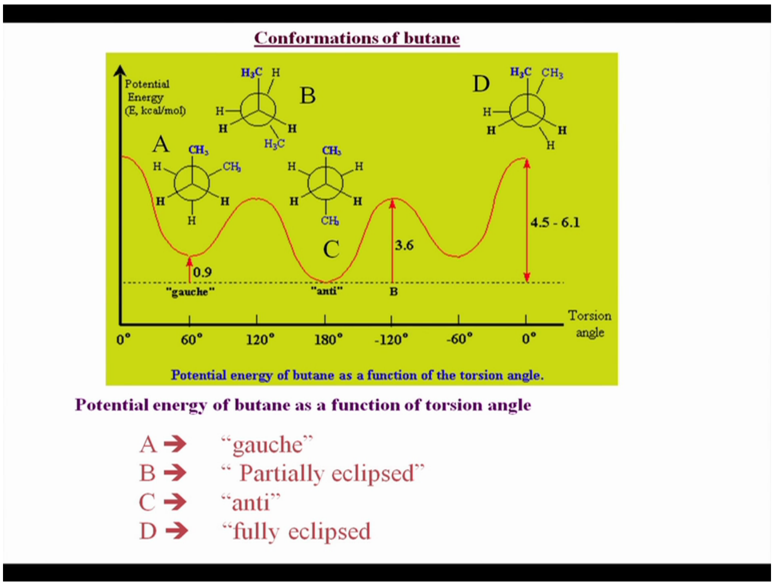

Conformations of butane

Potential energy of butane as a function of the torsion angle.

Potential energy of butane as a function of torsion angle

A ➔ "gauche"
B ➔ " Partially eclipsed"
C ➔ "anti"
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Now how the energy varies… we have identified 4 different conformations here specifically, okay. We have identified 4 but again remember do not forget that this molecule as in innumerable number of conformations we are just identifying based on the dihedral angle we have given some names the forms. This is what is the, this A form is what is A form is what is called the where the dihedral angle between the 2 methyl are 60 degree and that is what is called the Gauche form, okay. The B form, where the methyl and the hydrogen, although it is written slightly inclined fashion has just to show it otherwise perfectly eclipse form you cannot show because one will cover the other so it is very shown slightly in the in this direction.

So here you just consider it that this is eclipsing this CH bond, that is called partially eclipsed, so be will be partially eclipsed. C where the methyl methyl dihedral angle is or torsional angle is 180 degree, so that is what is called anti and then you have a fully eclipsed form where the methyl methyl is eclipsing each other okay on top of each other that is the fully eclipsed. Now suppose we start with an eclipse form, fully eclipsed form will have the highest energy and that is quite easy to understand because now what you have is that 2 methyl I eclipsing each other so there will be there will be van der waals repulsive force now acting on each other because this is not hydrogen unlike ethane.

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So now this contributes enormously to the energy of the system okay the so this is the highest energy. So apart from bond opposition strength that is there but now this methyl methyl interaction steric interaction, the van der waals repulse force that contributes a major portion of the energy to this eclipse system, okay. So fully eclipse has the highest energy, then as you rotate start rotating that means they you are now decreasing the distance between the 2 methyl and as you come to the staggered form now what happens to the staggered form, this is 1st of all this is called a Gauche form the angle between the methyl are 60 degree 60 degree, so that is called Gauche form and this Gauche form is certainly has lower energy than a fully acreage warm because the 2 methyl are now apart from each other and the bond opposition strength is gone.

However although they are part from each other but they are not that far apart that it will completely vanish reduce the steric interaction that was happening earlier to 0. So there is still some steric repulsion that is between this 2 methyl okay 2 methyl, the other way the another stream actually I should have told you that the which is called this torsional strain is another kind of strain that we also consider, torsional strain is not there in case of staggered form. Now what is torsional strain?

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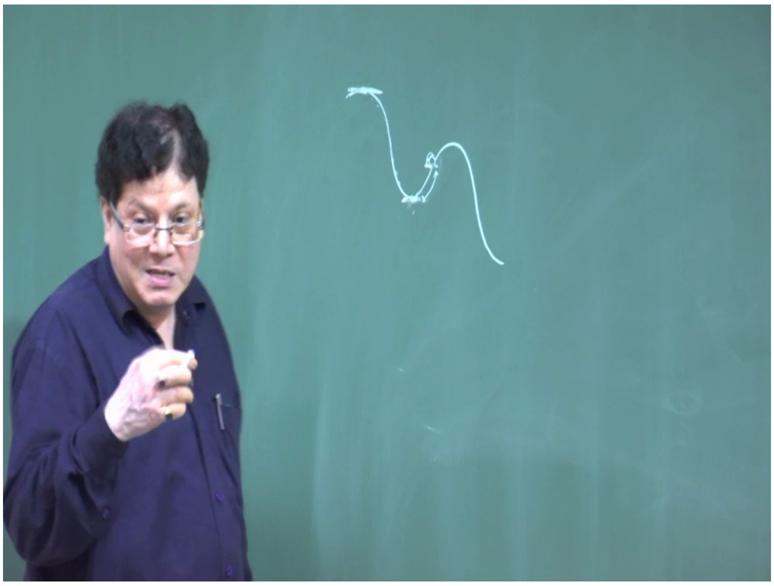

Torsional strain is that suppose there is a form in the board I can explain it, suppose I have a… when I do the conformation analysis, I have suppose this type of energy diagram, now if when I am I am here there is there must be this is higher energy, there must be some there must be some strain here associated press form because it has got higher energy okay or the highest point here.

Now and I slowly reduce the when I do the change in the torsional angle, I the energy gets reduced and energy gets reduced and that comes to a minima, okay. Now from the minima if I go further suppose now I am increasingly angle, torsional angle, so as I increase the torsional angle, I am now going moving away from the minima, going to a I am I am raising the energy, so the molecule will have what the molecule have a tendency because you are now taking the molecule away from a stable state which is a minima to an unstable state, so there will be some strain that will now will be there in the molecule to come back to the original state. It is like if I if I take a spring which is lying in the ground steady, if I have hold one of the point and then try to twist the string, so what happens?

They will be a string that will now come in to the string to go back to the original position, so if I release it now to go back to the original ground state. So this twisting, when you twist the string so that will be called a that is what is a torsional string but that means your rotating you are rotating the system and what you are trying you are deviating the system from a stable system or bringing the system from a stable to an unstable system and if you do that they will be always a tendency of the molecule to go back to the original form and that is what is called torsional strain because here the because what you are varying is the torsional angle.

So if by doing this torsional angle change if you see that you are crossing and energy minima, then and it is bringing to an energy maxima, then there will be a torsional strength that will be associated in the molecule, okay. So when I am here means when the molecule is here will suffer from a torsional strength because there is a minima here.

If I put a drop of water here the water will not remain at this point, the water will slowly go down and come here that is because the waters sees that it is much more stable if it comes back here that means as a kind of strain happening in the water droplet, so due to that strain it comes here. So similarly when you bring the molecule here there will be a tendency of the molecule to go back, this so this tendency that string that is happening in the molecule that is what is called torsional strength because it is depending on the torsional angle so that is called torsional strength.

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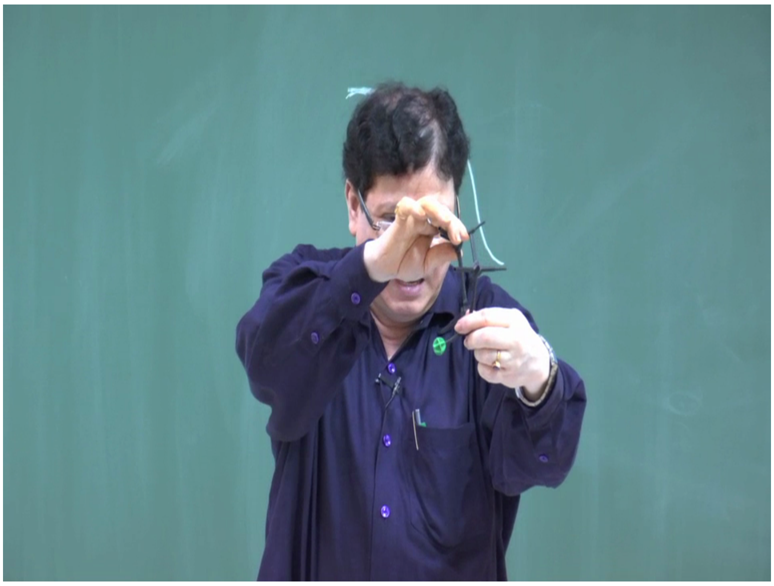

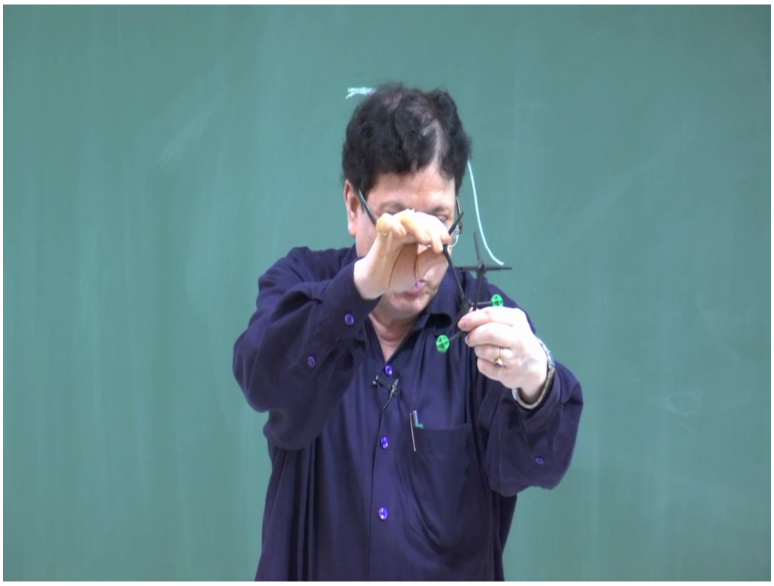

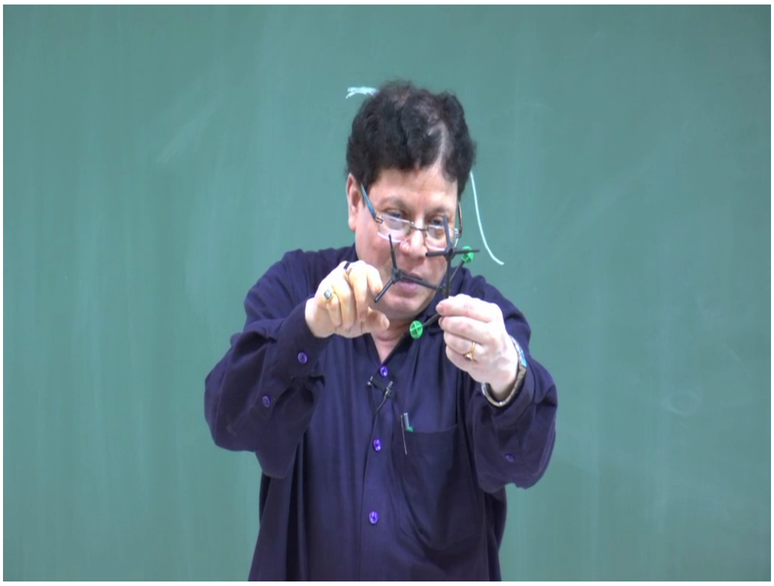

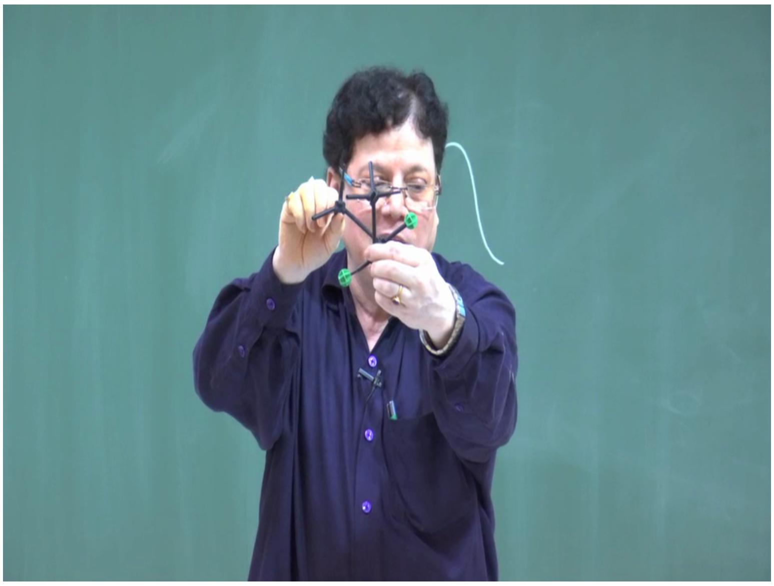

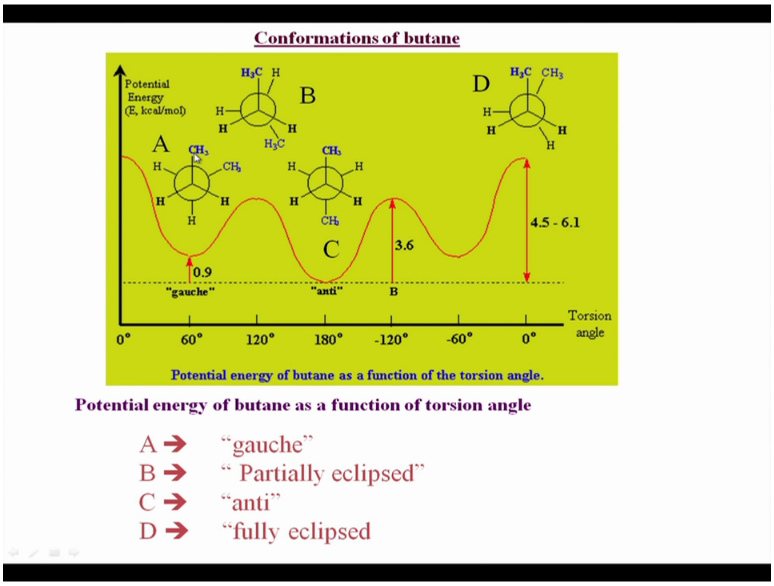

Conformations of butane

Potential energy of butane as a function of the torsion angle.

Potential energy of butane as a function of torsion angle

A ➔ "gauche"
B ➔ " Partially eclipsed"
C ➔ "anti"
D ➔ "fully eclipsed

So again coming back to this in this Gauche form there is no torsional strength because you have attained because of the reason that the energy goes down down down and attains a minimum value at 60 degree, if you cross the 60 degree then what you are increasing your bringing a methyl hydrogen torsional methyl hydrogen steric strength and you are bringing back the bond opposition strength that electron electron repulsion.

So basically the energy goes to a minima and then again it rises goes to the maxima, so the torsional there is no torsional strength here and the angle and 60 degree but there will be torsional strength here because it wants to go back to the staggered to the staggered form which is Gauche form. As you go again further down that will increase about 60 degree, it again wants to go back so there is a torsional strength which is present when you deviate from 60 degree okay when you deviate from the staggered form, so torsional strength is not there. So I hope the torsional strength concept is clear, okay.

So there is a torsional strength in the Gauche form but what strain is present, the strain that is present is this methyl methyl, still they are not far away so that the van der waals repulsive force is 0 so there is some van der waals repulsion is still there between this methyl and that methyl. However this has got lower energy than the fixed form and that is exactly what is shown here, okay so you have this fully eclipsed as you increase the angle to 60 degree, now you are torsional string is (())(12:53) but the van der waals repulsion is less as compared to here but it is still there, so energy goes down and it reaches a kind of a minima when the dihedral angle is 60 degree or torsional angle is 60.

As you increase the angle further now bringing an interaction between methyl and hydrogen and your bringing that bond opposition strength that that repulsive force between the electrons. So that energy will start again going up and it actually goes up and reaches the maxima when you have this partially eclipse form, okay. So this is the partially eclipse form that reaches the maxima.

So what happens after you reach the partially eclipse form, you further rotate the methyl so you are rotating the methyl, now you are reducing so 1st you are reducing the methyl methyl interaction when you go to the Gauche form and then after the beyond Gauche form you are increasing the methyl hydrogen interaction and the bond opposition strength so you come to the eclipse form that has got a maximum energy maximum point and then not the maximum energy eclipse has the maximum energy but what I am saying that comes to a maxima and then again as you cross the partial eclipse it goes the energy again starts going down okay because you are now removing the methyl hydrogen interaction and also your reducing the bond opposition strength and it becomes the minimum when the methyl are anti-to each other.

Now there is no steric repulsion here okay so that is what is called anti and this if you assume that this is the 0 line, that this is got… suppose the anti-form assumed to be 0, then it is not actually 0 it has got an energy but if you say this is 0 point energy then this is the Gauche form which is got which is calculated to be about .9 kilocalories per mole extra energy that the Gauche form has. What is the reason for this .9 kcal extra energy? That is basically the repulsion between the of the steric repulsion between the methyl and ethyl because they are at a dihedral angle of 60 degree they are still quite close enough to give a repulsive force, okay so it has got .9 kcal per mole extra energy and this is this interaction.

Now we have a we have we call this as a Gauche butane interaction, so each Gauche butane interaction has an extra energy of .9 kcal per mole, so if in a molecule you see there is there are 2 Gauche butane interactions, then that molecule will have an extra energy of 2 into .9 that means 1.8 kcal per mole extra energy over the molecule which you are comparing where there is no such Gauche butane interaction, okay.

This is so now you have this anti, after the anti as you further rotate you come to the partially eclipse form that will have the same energy like here, so this is 120 here it is in minus you can actually write in plus form also, this will be 240 degree and this will be 300 degree and this will be 360 degree, here it is actually they have divided it into plus and minus rotation but you can do 180 and this is 240 60 degree so that means 240 rotation you come back to partially eclipse form them 300 degree rotation you come to the again the Gauche form and then they fully eclipse form so you complete the over 360 degree rotation, you come back to the original okay. So here now how many maxima we are seeing, here there is one maxima, there is another maxima, there is another maxima and there is this maxima.

These 2 maxima will be same because they represent the fully eclipsed and these 2 maximum will be will be same because they are partially eclipse they will have less energy than the fully eclipse one. How many minima we are seeing now, we are seeing a minima here that is for the Gauche form, we are seeing a minima here that is called the anti-form and here we are seeing minima for again the Gauche form okay. So this is the conformational analysis of n-butane.

Now the question is, how many confermers this molecule has? This molecule has 3 confermers to Gauche confermers because they are occupying…What are confermers? The conformations lying at the energy minima in the energy profile diagram, so this is a conformer, that is a conformer and that represents a conformer, okay. So these are the 3 confermers of n-butane. What is the relationship between this Gauche form that Gauche form? That is quite interesting if you work it up you will see that this Gauche form will be the mirror image of the other Gauche form and interestingly to complicate the to complicate the situation further these 2 Gauche forms are not superimposable to each other.

So basically if this Gauche form his plus rotation that Gauche form will have minus rotation because Gauche form do not have any center any the improper elements of symmetry that means the I or the Sigma or Square, so that is why they are optically active. But here n-butane is totally optical inactive okay, so although some of the confermers are optically active and they are mirror images to each other, so if you try to isolate n-butane you have… see majority will be anti because that is the energy minima that has got the minimum energy.

Then some we will say about 70% anti and 30% Gauche form. Out of this 30%, 15% will be plus Gauche form and other 15% will be minus Gauche form. Interestingly is that you cannot isolate like the nitrogen scenario, you cannot isolate these Gauche forms because they are inter-compatible by rotation. Earlier it was inter-compatible by inversion now they are inter-compatible by rotation, so you cannot really isolate these things, so n-butane so these are the 3 confermers.

Now one can ask one very valid question is that, you are saying that 70% is about anti and 30% is about Gauche I just roughly say that 70 – 30, suppose 70 – 30, now one can ask that a point here suppose I take a point here which is lower than the point which is represented by the Gauche form so this point represents a confirmation no doubt but it does not represent or conformer, although it has got less energy than the Gauche form, so if student can ask that you are considering this as a conformer but you are not considering a form which is got lower energy than the Gauche form as a conformer because by definition confermers are the one which are lying at the energy minima, so even if something has energy minima energy lower energy than the gauche form that is not a conformer, okay.

So these thing has to be clear and the best way to understand this is that why these are the only the confermers and why these are the only ones which are present in the system and not the other one in spite of having lower energy than the gauche form is by saying that suppose these are nothing but hills and you have clouds here suppose they are dark clouds and if there is rain then where will rain drops collect, the raindrops will collect only at here minima, here and there. The raindrops will never collect here because it will slip down and go to the anti. So that is actually the scenario, basically the molecules it is true for molecules that is true for human beings also.

If I am tired and if I see there is a chair and bed, I will definitely go to the bed and not I will sit on the chair because I am tired, similarly if the molecules is here the molecules see that there is a better situation where it can sit comfortably so it will go to the immediately to the energy minima. So if you molecule is here which is lower in gauche form in energy terms but still it sees that there is a better position for me to go there so it immediately goes to the minimum position so that is my only the minimums are considered when we consider the confermers.

So confermers again I repeat are the forms which lie at the energy minima in the energy profile diagram, okay. Remember again this gauche what is gauche butane interaction, when the 2 methyl are at an angle of 60 degree that is the dihedral angle or torsional angle of 60 degree that is called gauche butane interactions and that energy you should remember that it is about .9 kcal per mole, okay.

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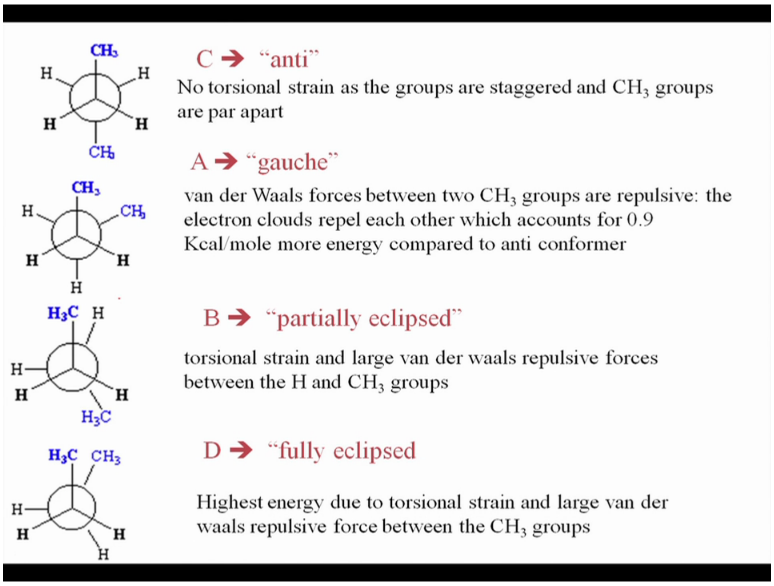


C → “anti”

No torsional strain as the groups are staggered and CH_3 groups are par apart

A → “gauche”

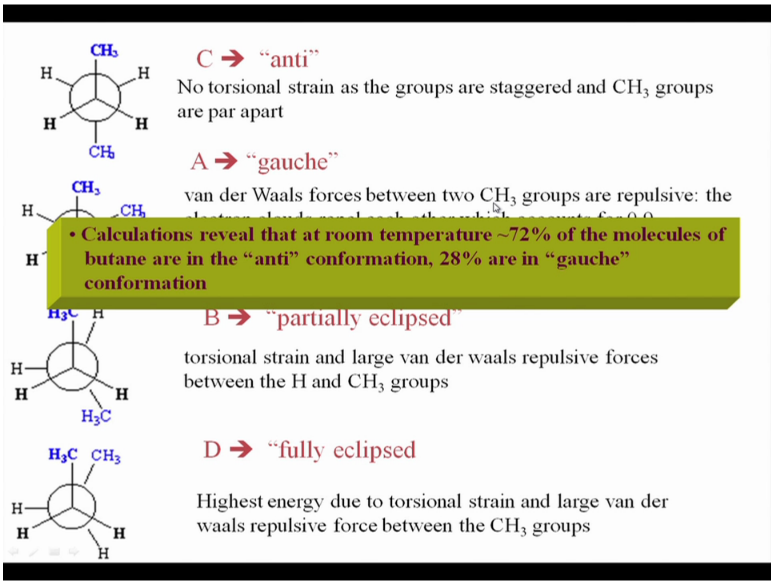
van der Waals forces between two CH_3 groups are repulsive: the electron clouds repel each other which accounts for 0.9 Kcal/mole more energy compared to anti conformer

B → “partially eclipsed”

torsional strain and large van der waals repulsive forces between the H and CH_3 groups

D → “fully eclipsed

Highest energy due to torsional strain and large van der waals repulsive force between the CH_3 groups



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No torsional strain as the groups are staggered and CH_3 groups are par apart

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- **Calculations reveal that at room temperature ~72% of the molecules of butane are in the “anti” conformation, 28% are in “gauche” conformation**

B → “partially eclipsed”

torsional strain and large van der waals repulsive forces between the H and CH_3 groups

D → “fully eclipsed

Highest energy due to torsional strain and large van der waals repulsive force between the CH_3 groups

I think here…these are the…everything is written here the anti-form, no torsional strain as the groups are staggered and CH3 groups are this should be far not p there should be f they are far apart. Gauche form, only van der waals forces between the methyl groups, these are repulsive: the electron clouds repel each other which accounts electron clouds in a gauche form van der waals forces between the 2 methyl are repulsive, right as I said the methyl groups are still not far each other so that accounts for about .9 kilocalories per mole more energy as compared to anti-conformer.

The partially eclipsed form that there is optional strain because it is lying in the maxima, so there is torsional strain and there is quite large van der waals repulsive force between hydrogen and ethyl and in case of fully eclipsed the highest energy because due to torsional strain as well as large larger van der waals repulsive force between the methyl groups methyl methyl groups okay, so that is the scenario.

I said about 70 – 30 but calculation actually said it has been now it is known by spectroscopic means or calculations, you can do computations, he says that about 72 %of the molecules are in the anti and 28% are in the gauche conformation, okay.

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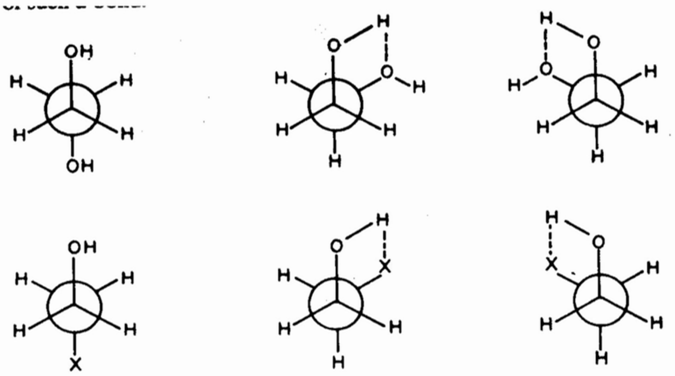

X = OH , NH_2, F, Cl, Br, OCH_3, $NHCH_3$, $N(CH_3)_2$ etc.

Conformation and hydrogen bonding

Now if you come these are n-butane now let us take systems, see n-butane we see we have seen that anti is the most stable form and that contributes to the maximum form when you try to isolate when you try to analyse but it is not always true that always the anti-form will be the most stable because sometimes the gauche form becomes stable due to other reasons like if you take ethane and glycol, if you take a system this is the ethylene glycol CH2 OH CH2 OH.

Ethylene glycol this is the anti-form, this is the this is the gauche form because they OH OH like the methyl methyl, so this is the OH OH and this is the other gauche form so what happens here, this because of intra molecular hydrogen bonding now possible between the between the OH which is acting as a hydrogen donor and this OH oxygen acting as an acceptor as an acceptor, that forms this intra molecule hydrogen bond and that stabilises that as a stabilising effect. When there were methyl there were destabilizing effect due to van der waals repulsive force, but now when you have OH and OH, now you have the hydrogen bonding scenario that stabilizes the gauche form okay.

So when there are (())(26:00) we have to be careful if there is a possibility of hydrogen bond then is then the gauche form becomes more stable than the anti-form. It is not only in (()) (26:13). If you have one OH and another X which can form a hydrogen bond then that will applicable, so X could be any of the hetra item containing systems like OH and H2 fluorine, chlorine, bromine, methoxy then aminomethyl and dimethylaminos groups etcetera, okay.

So which confirms hydrogen, so it is not always true that the gauche form is the less stable than the anti. When there is formation of hydrogen bond possible and that is only possible in the gauche form anti-form only intra-molecule hydrogen bond is possible but we know intra-molecular hydrogen bond is much more stable so that is stabilises the gauche form and gauche form becomes the more stable one in that case, okay.

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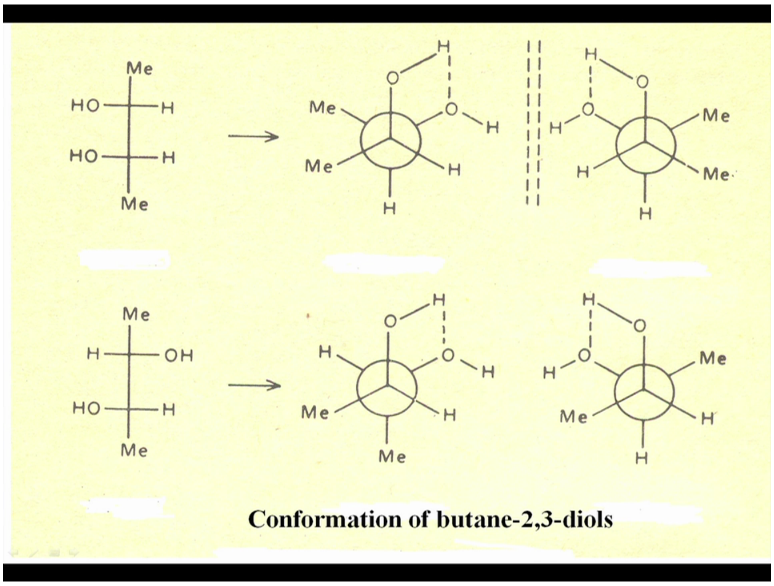
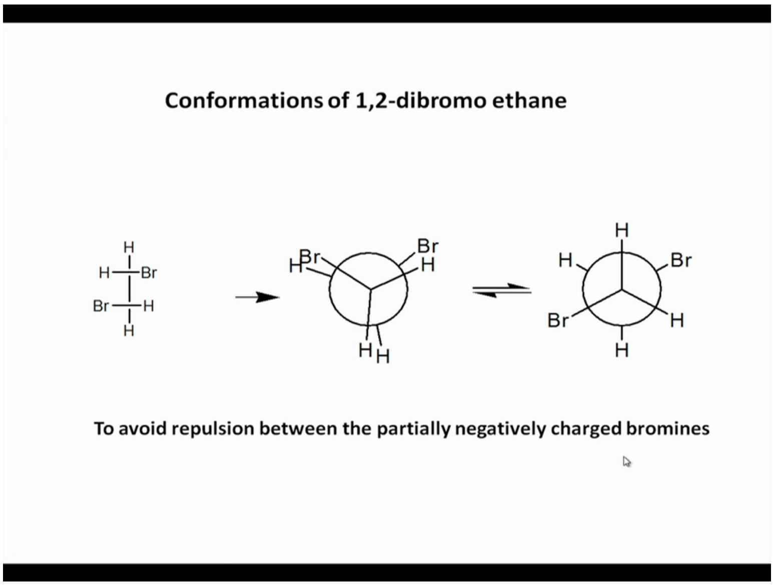


Conformation of butane-2,3-diols



Conformations of 1,2-dibromo ethane

To avoid repulsion between the partially negatively charged bromines

I think that is the what we had to say about this tetra atom and we have seen the conformation analysis of in butane. Next we will go to the other systems where dipole dipole repulsion take place. See there are many scenarios when there are groups which are sterically bigger they have bigger size bigger in size, there is a question of charge separation or anything then steric strain will make the gauche form stable than the anti-form.

When there is formation of hydrogen bond possibility of formation of hydrogen bond then goes (())(27:43) becomes more stable than the anti. Another case that can come that the repulsive force can come due to dipole dipole question that means this has the negative charge and this has got partially negative charge and then they repel each other, so all these things can happen and we will discuss in the next lecture we will discuss the cases where dipole dipole repulsion takes place. Thank you.