Course on Stereochemistry

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Module 4

Lecture No 15

Conformational Analysis of Acyclic Molecules

Okay let us now again come back to the to the very important aspect of stereochemistry that is called conformational analysis okay and to know conformational analysis or to do confirmation analysis the important part is that we have to be very clear about the conformations of molecules, what are conformations and then alongside the other terminologies they are what are confermers of a molecule, okay.

Now conformations arise due to the free rotation around bonds when there is a free rotation around bonds bonds which are which are formed between 2 atoms which are more than which are not monovalent which are either divalent or trivalent or tetravalent or more then what happens, if there is free rotation then you will can arrive at different geometries of the molecule, you can arrive at different geometries of the molecule, like I am standing here I can because my hands are freely rotating so I can have different orientation different geometries of myself but I remain myself but means I remain the same.

If I raise the hand that is one conformation of me if I raise this hand that is another conformation I can raise both hands that is also the conformation. So all these are different conformation of me, so similarly molecules where there is this type of free mase available, then they will also rotate they will also turn around and take different geometries and these are what are called conformations.

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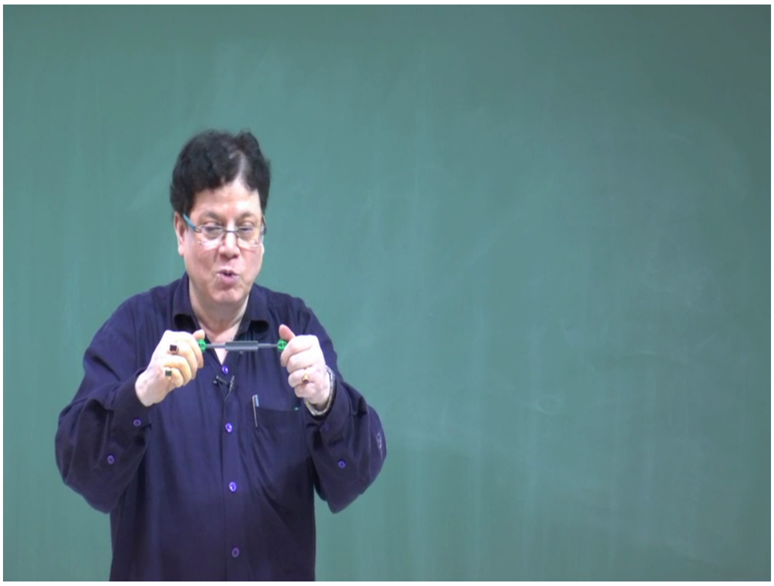

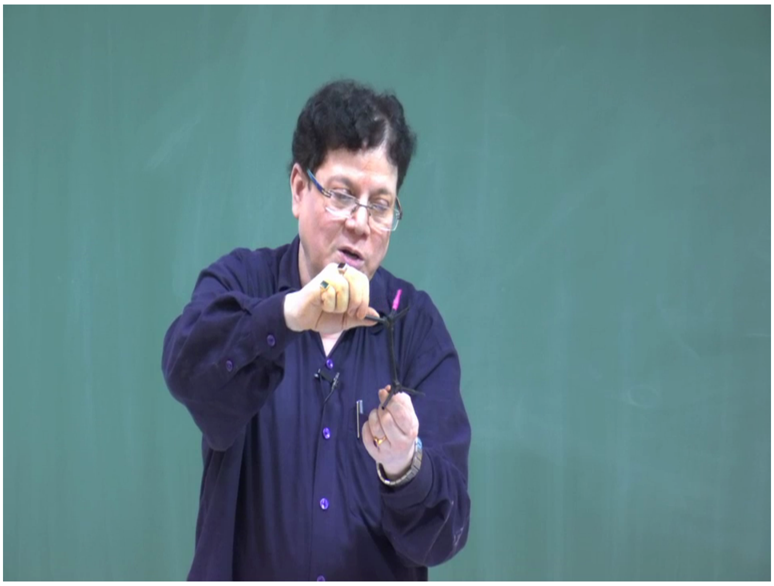

Only thing I wanted to point it out point out is that if you have a diatomic system then even if there is rotation, you do not create any although there is rotation but you do not create a new geometry because it looks the same all the time, but if you have something attached now if you have a tetrahedral carbon which is which is like this the 2 tetrahedral carbons attached to each other then what happens, then there is free rotation about this carbon carbon bond and as they rotate you have different geometries of the same molecule and all these geometries are what are called conformations.

So the definition of conformations is that, the in finite number of or innumerable number of geometrical arrangements that you see in a molecule when you have free rotation about bonds like carbon carbon bonds, okay not in a diatomic molecule, diatomic molecules by rotation you do not have but we are only concentrating mostly on the carbon system so will think of carbon which are tetrahedral in nature and then they are connected by so conformation really starts from ethane not from methane because methane does not have a carbon carbon bond so it really starts with ethane because with methane even if you rotate this this bond it does not it does not create this bond if you rotate it does not create any new geometrical arrangement. So it starts from the ethane, system ethane.

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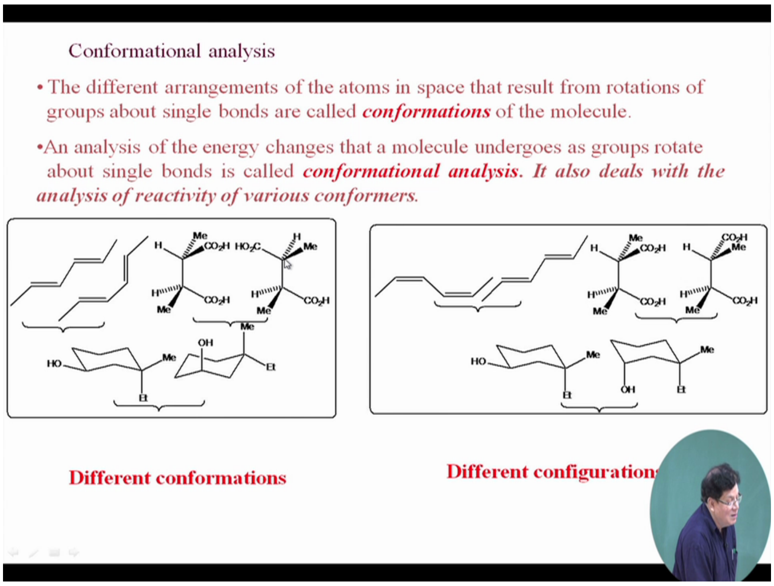

Conformational analysis

- The different arrangements of the atoms in space that result from rotations of groups about single bonds are called ***conformations*** of the molecule.
- An analysis of the energy changes that a molecule undergoes as groups rotate about single bonds is called ***conformational analysis****. It also deals with the analysis of reactivity of various conformers.*

Different conformations

Different configurations

Last time I told you about the conformation of ethane I think I started that concept but again let us just have a repeat the different arrangements of the atoms in space that results from rotations of groups about a single bond about single bonds are called conformations of the molecules. I just added one or a question that this single bonds cannot be between atoms which are monovalent, the singles ones should be between atoms which are at least divalent like hydrogen peroxide, hydrogen peroxide also will have different oxygen is the divalent atom.

It has got different conformations, now out of this conformations some of the conformations maybe more stable than the other. We will discuss that and what are conformation analyses? This is again a sub topic of stereochemistry where we analyse the changes in energy as we do this rotation say around carbon carbon and as we rotate the bond what happens to the energy of the system whether it increases or it decreases or it increases then decreases so lot of possibilities are there, okay. So that analysis of change of energy with change of now rotation has to be measured by angle so it is an angle in case of this type of system it is the dihedral angle or the torsional angle where it is that it is angle between the planes.

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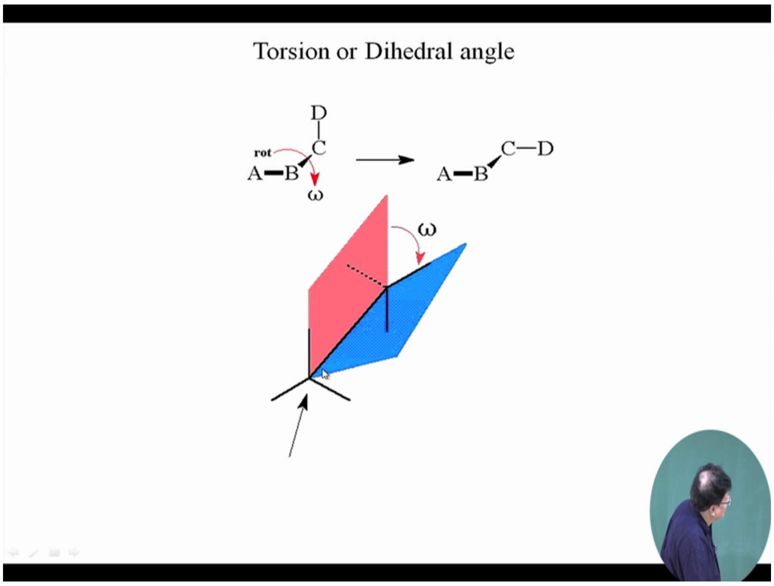

Torsion or Dihedral angle

I will show you in a in a slide that what actually we are talking about? This is this is what we are talking about, that means here we are talking about the angle but this angle is basically see this is the bond and then this is another bond so basically 3 atoms 1, 2, 3 this makes one plane that has that is that is shown by the blue surface and this bond and the same carbon carbon bond and so these 3 atoms they also form a plane and that is this pink surface, okay.

So there are 2 now there are 2 planes one is this blue another is the red and that is the angle between these 2 planes is what is called the dihedral angle or the torsional angle and as you rotate the carbon this is a this is a source representation of all carbon system and as you rotate it then this dihedral angle is going to change, so dihedral angle earlier the dihedral angle was this and now as you rotate the dihedral angle is going to change okay.

So we measure we do the conformation analysis by analysing the change in energy as we change the as you do the rotation and consequently basically what we are doing, we are changing the dihedral angle in the system okay and that is what is called conformation analysis. That has a simple definition now conformation analysis also means that it deals with the analysis of reactivity of various confermers. So conformation analysis not only says about the about the energy variation with dihedral angle but it also deals with the reactivity of various geometries that you get by rotation and the reactivity may also be different okay that is also called conformation analysis.

So it is not only energy it is the function energy as function of dihedral angle and the reactivity as a function of dihedral angle. So all these put together are what are called conformation analysis okay. Here are some examples that what is the difference between conformation and configuration, configuration again I repeat is an arrangement in space but here to change from one configuration to the other is difficult like you see this is what is called a cis double bond the 2 methyl are in the cis direction.

This is not exactly methyl this 2 carbons are in the cis direction and these also these two are also cis. That means this dien is cis cis dien okay now this is the configuration this cis is a configuration of the system and you actually have drawn another one where this is trans because these carbon and this carbon carbon bond are trance, so this is trance trance dien, so now these to the relationship between this 2 are configurational isomers, they have different configuration around the double bond, okay.

On the other hand if you take this this is the trance trance double bonds and do a rotation about this carbon carbon bond, So what you end up is this, this is still trance the configuration still remains trance but the appearance is not look like the same, so this is a conformation of this molecule obtained by rotation around this carbon. Configuration is the arrangement around the double bond, configuration is the arrangement around single bond that is the most important difference.

Of course configuration has another important aspect not only double bond, if you have chiral center then also configuration, configuration can be R or S. If you have a chiral center this this can be R or S and so suppose I have this molecule and where there are 2 chiral centers I rotate this carbon carbon I rotate this carbon around this carbon carbon bond so that the carboxyl comes here carboxyl goes back so I rotate in this fashion I rotate that means carboxyl being to the position of the methyl, methyl goes to the position of the sorry the carboxyl is in the methyl position and the methyl is in the right position, so here there is a change in…so here the relationship between is that you have changed the configuration by rotation you cannot get to this arrangement.

Here is a change in configuration because if you want to if you want to rotate this then the carboxyl should go here, methyl will come here and hydrogen will go there but that is not happening here, what you are doing is basically interchanging the position of the carboxyl in methyl and that changes the configuration, so that means these 2 are configurational isomers, these 2 are configurational isomers, okay. On the other hand the same molecule I have it in here CO2H Me and hydrogen, now what you do you have rotated the carboxyl, carboxyl you have brought here so the then methyl goes there and the hydrogen goes to the position of the methyl, okay. So basically this arrangement is obtained by simple rotation around this carbon carbon bound.

So that means this is a conformer of this, of course the bottom one we have to keep intact do not change that one and that has not been changed. Only the only change is the appearance of the system but the absolute configuration here remains the same, okay. So this is the conformation one of the conformation of this one okay. So likewise you can draw innumerable infinite number of configurations. Now there are certain interesting aspects of conformation versus configuration. Configuration is the absolute arrangement of groups in space around double bond or around a chiral center that is configuration.

Conformation is a (())(12:32) the arrangements that you get by rotation okay. Now in case of going from one conformation to the other conformation, what you do? you just do a rotation but from one configuration going from one configuration to another configuration you have to break the bond and then reform the bond okay so that is that is a big difference and means one configuration cannot easily go to the other configuration because that needs a breakage of bond whereas in conformation you do not need a breakage you only need a rotation.

That is why it is easy to change from one conformer to the other in most of the cases but there are some cases where conformations are really rigid very difficult to change the barrier for this rotation may be restricted. The only case where you change the configuration from one to the another from R to the S is in case of atropisomerism, where without breaking the bond you can just rotate one of the biphenyls I again tell you the concept of atropisomerism, atropisomerism is that isomerism that take place in biphenyls systems okay.

Restricted rotation and it can exist in R and S forms, we have also done the RS configurational (())(13:54) in case of biphenyls and so from changing from R to the S compound what you need, you don’t have to break a bond you just rotate, so that is where conformations are becoming are equated with configuration. That is the only case that you do not need a you do need to break a bond, okay. So these are the certain differences between conformations and configurations.

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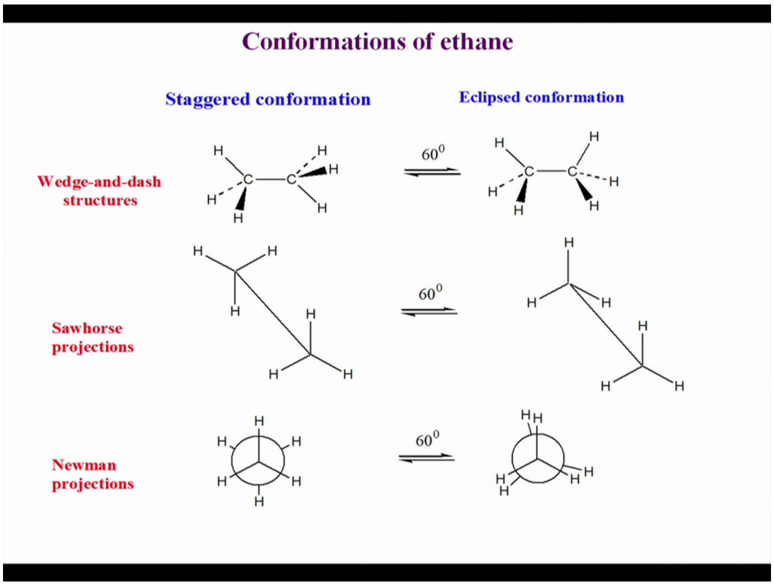

Conformations of ethane

Staggered conformation **Eclipsed conformation**

Wedge-and-dash structures

Sawhorse projections

Newman projections

Now we have done the ethane configuration because I said I conformations, the conformations started with ethane that is a carbon carbon bond because you need a carbon carbon in case of organic compounds to do the conformational analysis. So if you draw the conformation of ethane, see this is the wedge formula, sometimes called wedge and dash structure, okay.

So wedge and wedge formula you see from this you can say that this hydrogen and this hydrogen, they are opposite they are opposite to each other, okay and if you do the sawhorse formula, this is the same hydrogen which is beta and this is the alpha hydrogen this is this one, you see that is what is the that is the sawhorse formula of this this form and if you draw the Newman projection formula of this one, see from looking at this CC bond you can see the Newman projection formula of this, so this hydrogen goes up that means this is the front carbon and the back carbon is the is the this circle that denotes the back carbon, so this is the Newman projection.

Usually we adapt the Newman projection formula while describing the conformational analysis. Now this one is the one which is called last time I also told you that this is what is the staggered conformation, this is the staggered conformation where the dihedral angle between the between the closest neighbours like this hydrogen the closest neighbours this hydrogen the dihedral angle is 60 degree, okay. So the 60 degree dihedral angle between this hydrogen or that hydrogen is a staggered one or better way of representation of staggered is this one where one this is the three bonds, the other 3 bonds are exactly drawn in the opposite sense that means this CH and this CH are anti to each other this CH and that CH is anti to each other and this CH and that CH are anti to each other.

The 60 degree dihedral angle I was telling is about this angle 60 degree angle that means the nearest neighbour either this one or that one considering the mixed carbon not the same carbon, the nearest neighbour in the adjacent carbon that is this one or that one that is got a dihedral angle of 60 degree, okay. So this is the staggered one and this is the… if you rotate it by 60 degree if you go to the Newman projection, so I bring the I take the back carbon and rotate this one in anticlockwise so this hydrogen comes here and they are eclipsing to each other, this hydrogen will go here they are eclipsing to this bond this hydrogen will eclipse the this CH point, so you get the eclipse confirmation, this is for ethane, okay.

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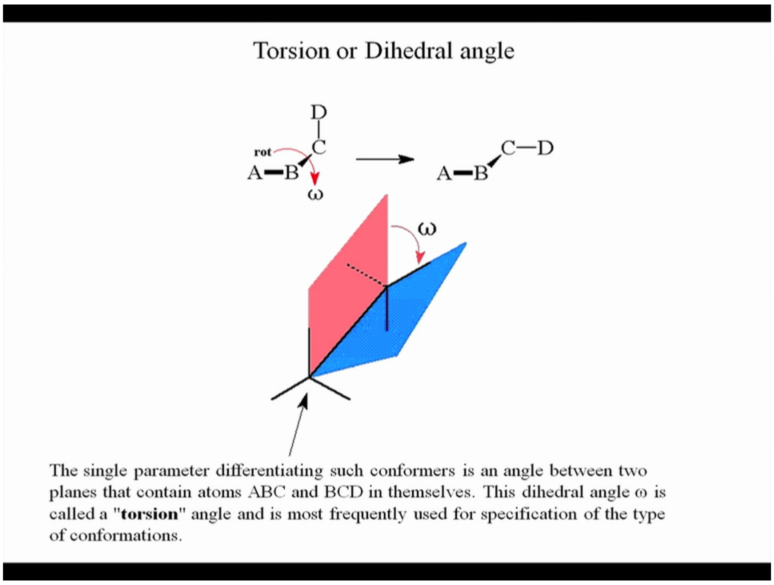
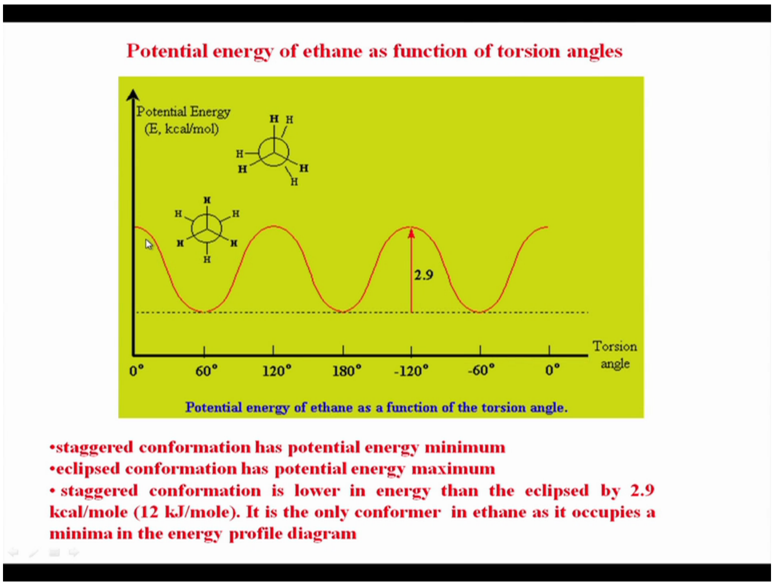


Torsion or Dihedral angle

The single parameter differentiating such conformers is an angle between two planes that contain atoms ABC and BCD in themselves. This dihedral angle ω is called a "**torsion**" angle and is most frequently used for specification of the type of conformations.



Potential energy of ethane as function of torsion angles

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

- staggered conformation has potential energy minimum
- eclipsed conformation has potential energy maximum
- staggered conformation is lower in energy than the eclipsed by 2.9 kcal/mole (12 kJ/mole). It is the only conformer in ethane as it occupies a minima in the energy profile diagram

Now if you draw the if you try to do the conformation analysis, the dihedral angle have already explain that is also called torsional angle that also I told you. So if you now do the energy variation of this system of the various conformation as a function of torsional angle so what you have. Suppose I have started with the eclipsed one, eclipsed one has the highest energy fully eclipsed one that means when there is a fully eclipsed the dihedral angle is 0, okay.

So that is the fully eclipse form that is that is got the highest energy, okay will come back to that what is the reason for this having the highest energy okay that will come later but right now you assume that, that is the highest energy okay and then as you as you rotate starts rotating this suppose the back carbon, so you what you end up will be a staggered form and the staggered form will have lower energy than the eclipse form.

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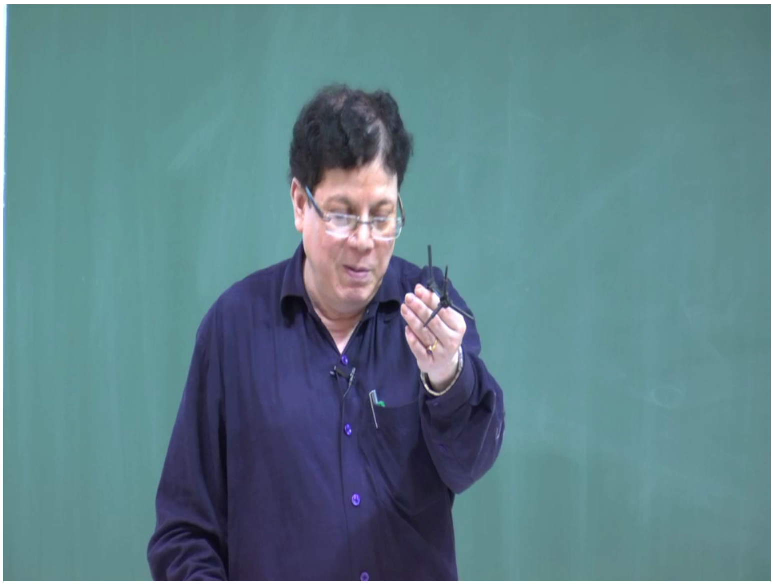

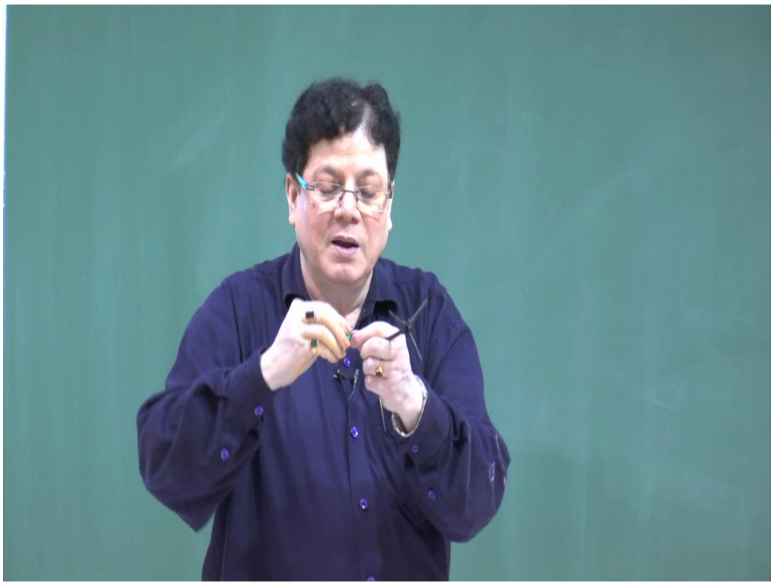

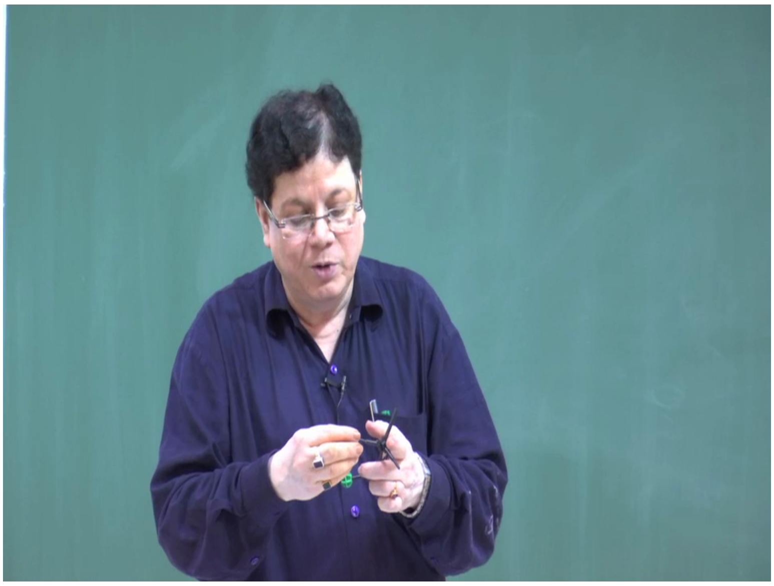

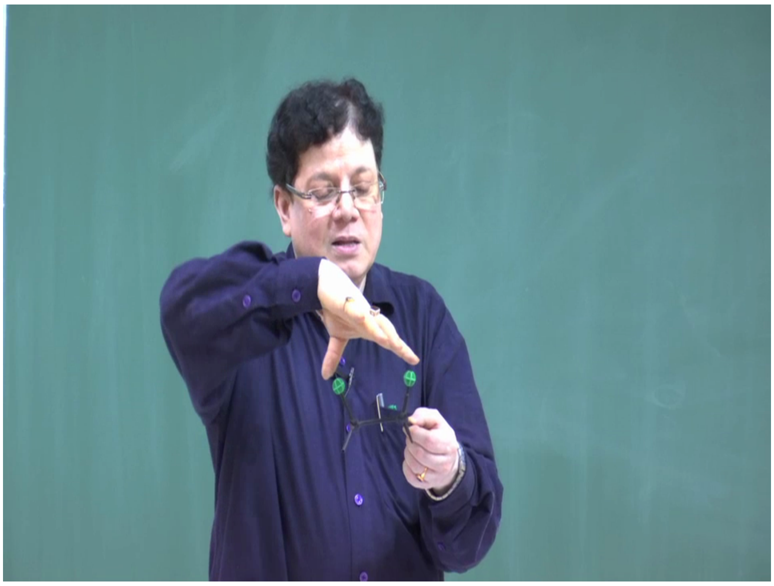

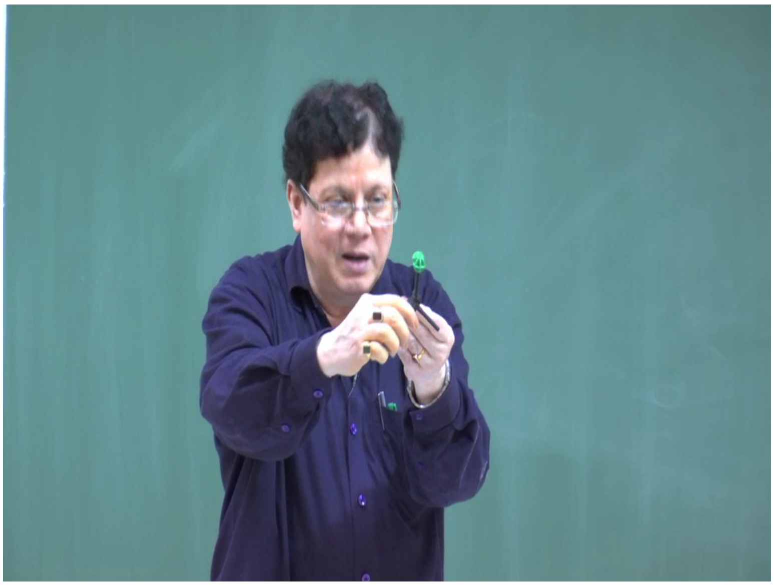

Now let us see why the eclipsed form has higher energy, the reason maybe there are 2 things that can be considered one is there is a hydrogen atom here suppose this is hydrogen this green ball is hydrogen and this green the other green ball is another hydrogen. Now although is shown very small but actually these are much bigger spears, so one thing that can happen is that whether they are heating each other or not okay so that is what is called the steric repulsion or the van der waals repulsion.

So what was actually found that in case of hydrogen this repulsion is not very much because the radius of the hydrogen are such that these repulsion constitutes only 10% of the instability that is associated with an eclipse form, so the van der waals interaction the repulsive interaction is contributing only about 10% so what is the other repulsive forces that is destabilising the eclipsed form, the other is basically this like this is consisting of electrons this bond and this bond is also consisting of electrons, now there will be repulsion between these 2 bonds so they call bond opposition strength is also a repulsive interaction, okay.

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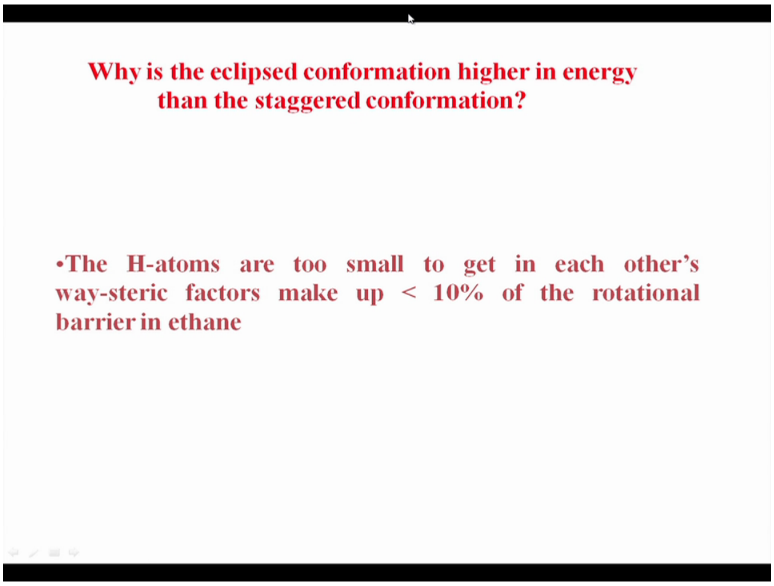

Why is the eclipsed conformation higher in energy than the staggered conformation?

- The H-atoms are too small to get in each other's way-steric factors make up < 10% of the rotational barrier in ethane

So that so what I said the hydrogen atom are too small to get to each other’s way so steric factors make around 10% of the rotational about rotational barrier that means it constitutes it adds about 10% of the energy that the eclipse form has 10% of the excess energy that the eclipse form has over the staggered form, okay. The differences in energies about 3 kcal it is within 2.9. Different books have different values I think you can roughly say that the differences in energies around 3 kcal per mol.

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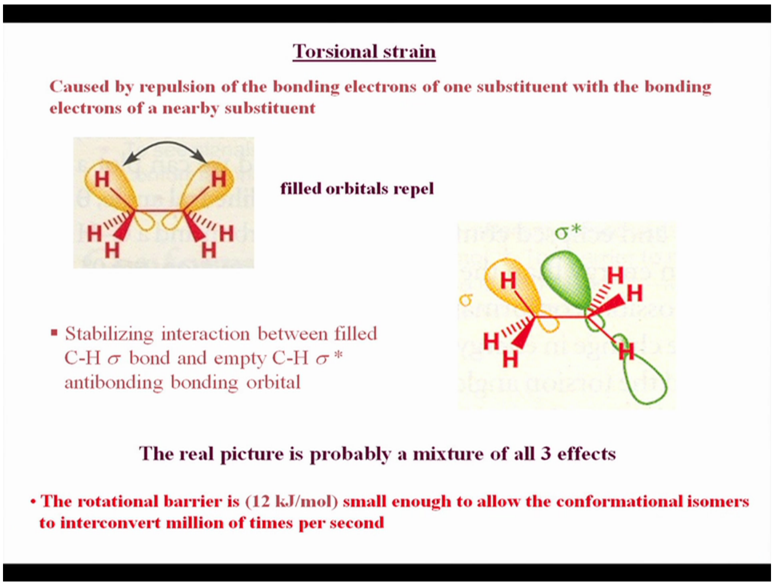


Torsional strain

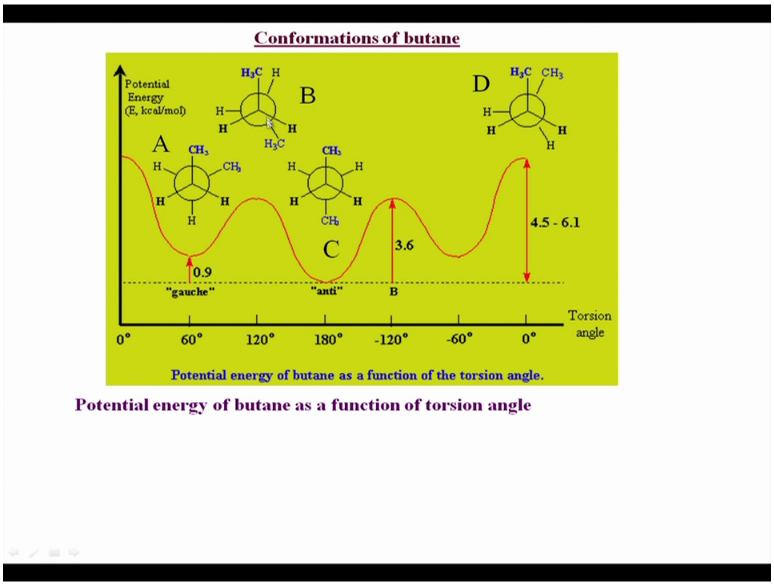
Caused by repulsion of the bonding electrons of one substituent with the bonding electrons of a nearby substituent

filled orbitals repel

- Stabilizing interaction between filled C-H σ bond and empty C-H σ^* antibonding bonding orbital

The real picture is probably a mixture of all 3 effects

- The rotational barrier is (12 kJ/mol) small enough to allow the conformational isomers to interconvert million of times per second



Conformations of butane

Potential energy of butane as a function of torsion angle

So one is the steric factor as I said but that does not contribute much that is only 10% the other is this orbital repel each other means this electrons basically you are saying that this orbitals are made up of electrons so the repel each other, okay. So that is the bond opposition strength or the electron electron repulsion electron pair electron pair repulsion. There is a 3rd concept that is also associated with it and that is that is the that is not considering the eclipsed form that you consider the staggered form so this is the eclipse form and a hydrogen this is beta that is beta that means they are adjacent hydrogens are eclipsing each other, here I have written the staggered form this is the hydrogen and anti-hydrogen is this one okay so that means this is this is the staggered form.

On the side this is beta on this side you have the alpha hydrogen that means this is the staggered form okay so way to, to no way that this is staggered or eclipsed you better take the hydrogen which are in plane I think that is the better concept, you take the 2 hydrogens in the plane and you see they are in the same direction, so that means this is an eclipse form and this is the staggered form because you take the 2 hydrogen which are in the plane and they are anti to each other, so that is the staggered form.

Now interestingly what has been said here that every bond formation when there are orbitals combined with each other to form a bond there is even anti-bonding scenario also an anti-bonding molecular orbital is also formed where the lobe of the orbital is more in the backside okay like here see you see the this is a siege bond and this is the anti-bonding scenario, what is anti-bonding scenario?

When the hydrogen actually this should be written in in this sphere this is not should not be in the because hydrogen does not have… actually it was just spear but because of the opposite phases of the of the side of the p orbital and the S orbital so there will be a kind of a repulsion, kind of a repulsion and you see the lobe the anti-bonding orbital has a bigger lobe on the backside now, if it is bonding than the whole thing will have an electron clouds surrounding this carbon and the hydrogen if it is anti-bonding then there will be a bigger lobe on the backside so this is what is called the Sigma star, we are considering the Sigma star and this Sigma Star will empty because in a carbon hydrogen they are forming a bond you have 2 electrons and both will go to the most stable, the above principle will be applicable.

So both the electrons will occupy the ground that but that means a sigma orbital, the Sigma star orbital which has got bigger lobe on this side so now that is almost that is aligned to the siege Sigma bond on this side, so now what happens these 2 can again interact with each other so electrons can flow from this from this orbital into this empty Sigma star the other way you can say that there is a stabilising interaction between the Sigma CH and the Sigma star of the CH which is in the anti-direction, okay and that stabilises the staggered from.

So what we have learnt that in the eclipse form that is some kind…when little steric interaction when there is hydrogens they are eclipsing each other because hydrogen small but it still contributes our 10% the other factor that contributes to the stabilisation of the eclipse form is the bond opposition strength that means the orbitals or the electrons they are repelling each other because they are basically negative charges they are falling on top of each other and the factor which stabilises the staggered form is this Sigma CH donating to the Sigma star CH of the anti-CH in the adjacent carbon, okay.

So all these 3 probably now it is there is an acceptance of the whole picture is that the real picture is probably a mixture of all 3, so you cannot say that for one reason this is unstable than the other okay. Energy barrier comes from all these 3 effects and that total combined that becomes about 3 kcal per mol. So that is the case of ethane, now in case of butane you have an extra you have 2 extra methyl now so butane, in case of ethane you have, you have only one energy minima and one energy maxima that is in case of ethane.

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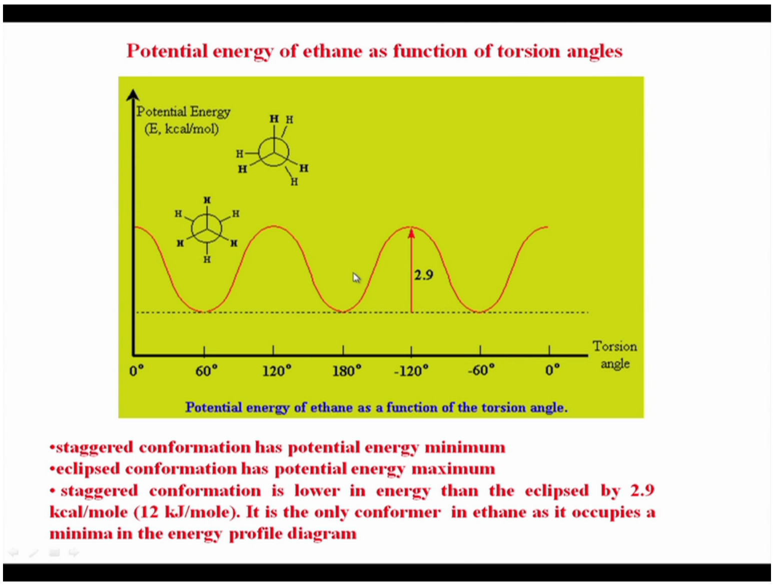

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So at first it is eclipsed and then it goes to the so it goes to the staggered and then again eclipsed then again staggered, so this way it goes so the energy because these bonds these atoms are all same so analogy only the energy minima remains at the same position, we can go back a little bit and then again check the conformation analysis here.

So this this is the eclipsed form, this is the eclipse form, this is the eclipse form they have the same energy because all atoms are same and this is the anti-form the staggered form here it is staggered form, staggered form and the staggered form they have the same energy because the atoms are same this is ethane, okay. When you change the hydrogen, this hydrogen to methyl and another hydrogen to methyl the situation changes, energy profile diagram changes, okay.

And then the you have more you have more number of conformation where you can identify the name, you will see that the staggered form can be of 2 types, okay depending upon the dihedral angle between the methyl the carbon methyl groups okay. Now just one want more concepts which I did not tell you at that time, last lecture I mentioned this that amongst this various conformations some conformations will be there which will occupy the minimum of the energy profile diagram.

So the conformations which occupy the minimum of the energy profile diagram, it is written here staggered conformation is lower in energy that I have said it is the only conformer in ethane, it is the only conformer in ethane as it occupies minima in the energy profile diagram. That means this conformation which has got which lies in the energy minima is what is known as conformer. So confermers are conformations which lie in the energy minima during a conformation analysis that means when you plot the energy versus dihedral angle or torsional angle, only the minima the conformation that is lying in the minima that is called the conformer.

So in ethane there is only one conformer and that is the staggered conformer of ethane, all others are not. One interesting point to note here is that every point is energy profile diagram represents a confirmation of ethane. Suppose I take a point here so this point this point has lower energy than lower energy than the eclipse form definitely, energy profile diagram says that but it is not a conformer so confermers is the only one which occupies the lowest position the minima, this concept is very important.

There is if you want to isolate you want to check by different spectroscopic means at what is the percentage of this staggered conformer in ethane you will see it is more than 99.99%, okay so basically virtually is the only form that is present at a particular time although there is free relation, different eclipse formed different staggered form are generating but there is a difference between these staggered form because all hydrogens, okay. But the situation will change again I will repeat the situation will change when you put 2 methyl and the 2 carbons that means butane and the next half an hour we will consider the butane conformation, okay. Thank you.