Symmetry, Stereochemistry and Applications
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Module No # 3
Lecture No # 11
Conformational Analysis-Part I

Welcome back to the course entitled symmetry, stereochemistry and applications.

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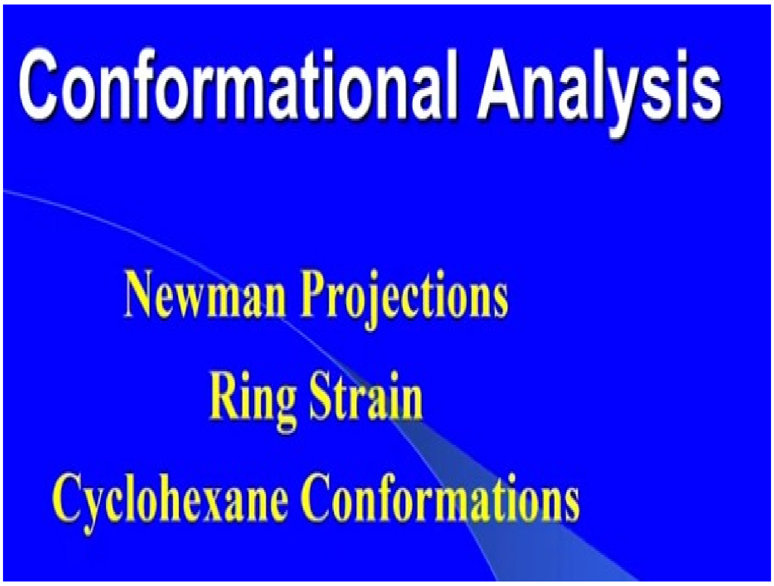

Conformational Analysis

Newman Projections

Ring Strain

Cyclohexane Conformations

So in the previous lecture we were trying to discuss about the Newman projections, rings strain and cyclohexane conformation. So we will continue our discussion in that direction.

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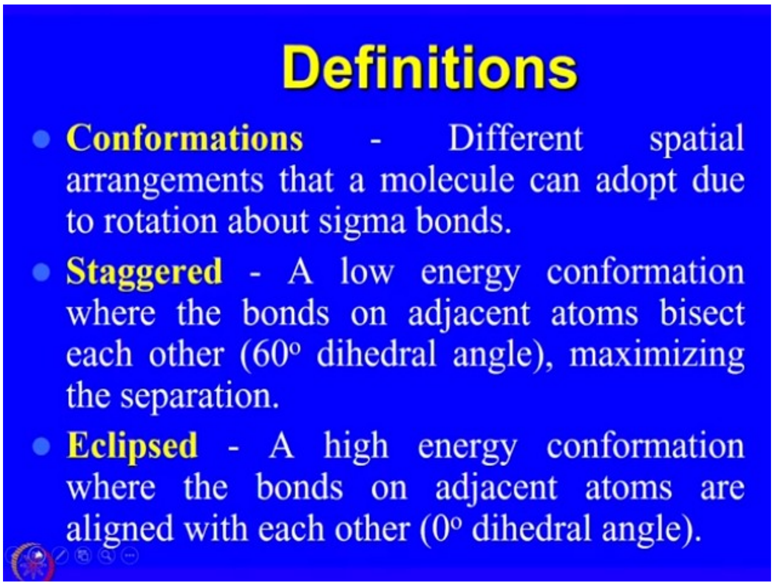

Definitions

- **Conformations** - Different spatial arrangements that a molecule can adopt due to rotation about sigma bonds.
- **Staggered** - A low energy conformation where the bonds on adjacent atoms bisect each other (60° dihedral angle), maximizing the separation.
- **Eclipsed** - A high energy conformation where the bonds on adjacent atoms are aligned with each other (0° dihedral angle).

So in the last class we were talking about various conformations like staggered and eclipsed conformers. So when we have understood that a staggered conformer is a low energy conformation and the eclipsed conformation is one of the high energy conformations. We will try to understand the same using some energy values.

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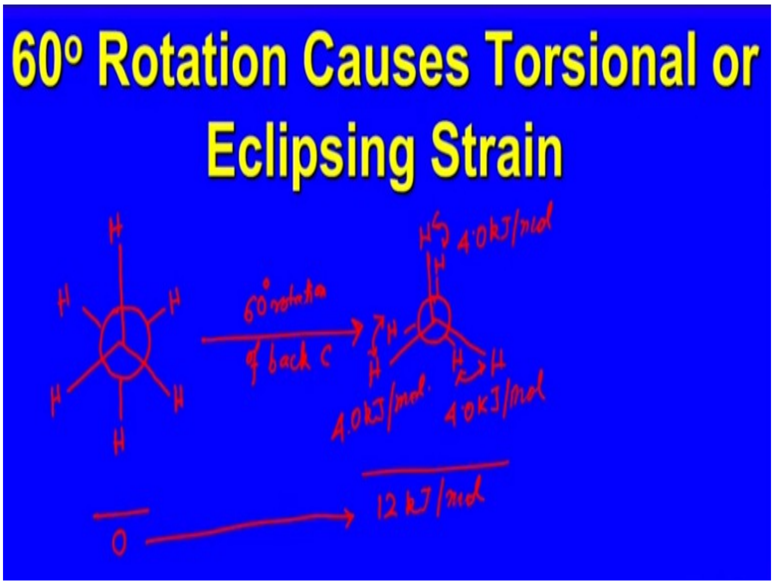

60° Rotation Causes Torsional or Eclipsing Strain

So when you have drawn a Newman projection of ethane molecule in the staggered conformation like that like the way I am drawing here. This is the most stable conformation of ethane. So now if you rotate the back carbon by 60 degree what we get is the eclipsed conformation where the front carbon atoms, hydrogens from the front carbon are exactly behind; when the hydrogens on the back carbon are exactly behind the front carbon atom.

So as a result what we end up getting is a conformation like this from the staggered conformation which was like that. So from this staggered conformation we have come to the eclipse conformation when these atoms are eclipsing one another. So the strain that is generated due to this eclipsing of hydrogen 3 times, as you have 3 pairs of hydrogens, each of those is 4 kilo joules per mole.

Which essentially means that this eclipsed conformation; is 12 kilo joules per mole in energy higher than this one. So if we assume this to be having the 0 energy or the lowest energy, the other one has the energy 12 kilos joules per mole higher.

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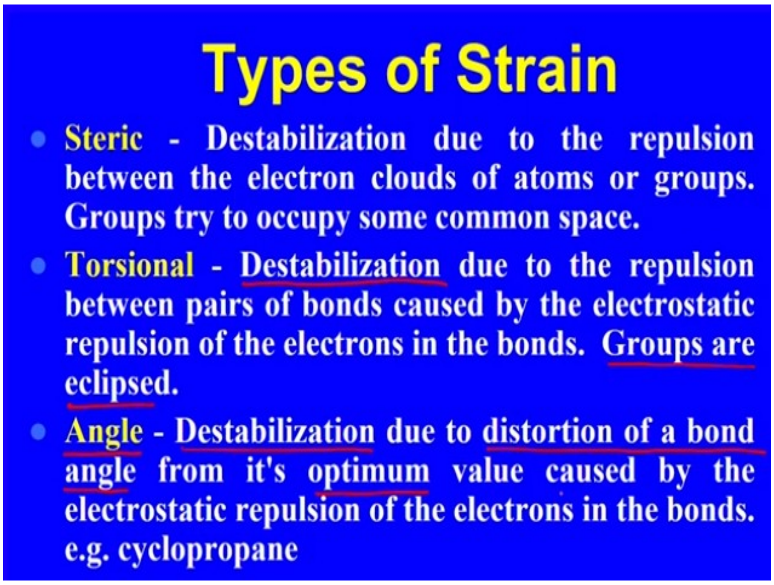

Types of Strain

- **Steric** - Destabilization due to the repulsion between the electron clouds of atoms or groups. Groups try to occupy some common space.
- **Torsional** - Destabilization due to the repulsion between pairs of bonds caused by the electrostatic repulsion of the electrons in the bonds. Groups are eclipsed.
- **Angle** - Destabilization due to distortion of a bond angle from it's optimum value caused by the electrostatic repulsion of the electrons in the bonds. e.g. cyclopropane

So when we talk about this strain that is generated due to various orientations of the molecule, what we learn are there are different types of strains, the one first type of strain this steric strain that is the destabilization due to the repulsion between the electron clouds of atoms or groups of atoms. They try to occupy the same common space. So suppose for example if I had 2 bromine atoms connected to the 2 carbon atoms on ethane as I tried to show in your previous lecture.

When these 2 bromine atoms are in the eclipsed conformation there is a steric strain because these 2 bromines are large enough to repel each other the electron densities are very large on bromine atoms and that create a steric repulsion and that gives, you a steric destabilization due to repulsion. The next type of strain or destabilization is due to the repulsion between the pairs of bonds caused by the electrostatic repulsion of the electrons in the bond.

So this again happens when the bonds are in eclipse conformation or groups are in eclipse conformation. So in this particular case we have 2 types of strains one is the steric strain because of those 2 bulky groups being eclipsed and the bonds, every bond is behind another bond CBr bond behind CBr bond this CH bond is behind another CH bond this CH bond is this CH bond is behind another CH bond.

So every bond is behind another bond and that the bond strain that is called the torsional strain is present in eclipsed conformation. The third type of strain is the angle strain or destabilization due to distortion of a bond angle from its optimum value. So for example in case of cyclopropane or cyclobutane the carbon atoms are sp3 hybridized. So by default we know that the carbon bond angles at the carbon should be 109 degree.

But in case of cyclopropane or cyclobutane that angle is no longer 109 degree but it is distorted from that 109 degree.

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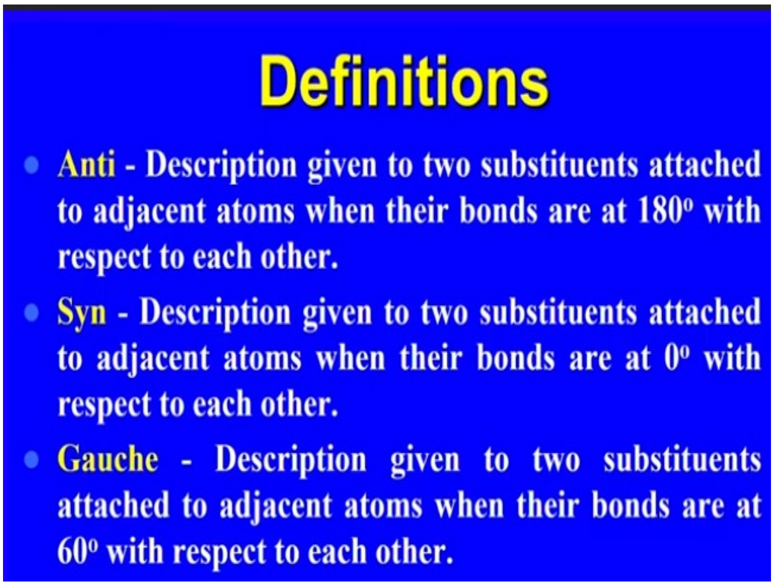

Definitions

- **Anti** - Description given to two substituents attached to adjacent atoms when their bonds are at 180° with respect to each other.
- **Syn** - Description given to two substituents attached to adjacent atoms when their bonds are at 0° with respect to each other.
- **Gauche** - Description given to two substituents attached to adjacent atoms when their bonds are at 60° with respect to each other.

So when we have different possibilities of molecular conformation we should then try to identify them with appropriate nomenclature. So when we try to draw the molecule in different ways we see different conformations and we try to name them as Anti, Syn and Gauche conformation. An anti-conformation is a description given to 2 substituents attached to adjacent atoms when their bonds are at 180 degree with respect to each other.

So that means if I am considering this 1, 2 dibromo ethane if the CBr bonds are opposite, So this CBr bond is up and that CBr bond is down so this conformation of this molecule is called the anti-conformation. Syn is the description given to 2 substituents attached to adjacent atoms when their bonds are at 0 degree with respect to each other. That means when they are eclipsed either this is eclipsed or this eclipsed, are different syn conformations.

And the last type or third type is Gauche conformation is given, this description is given to 2 substituents attached to adjacent atoms, when their bonds are at 60 degree with; respect to each other that means when it is like that. So let us try to draw these different conformations in the next slide.

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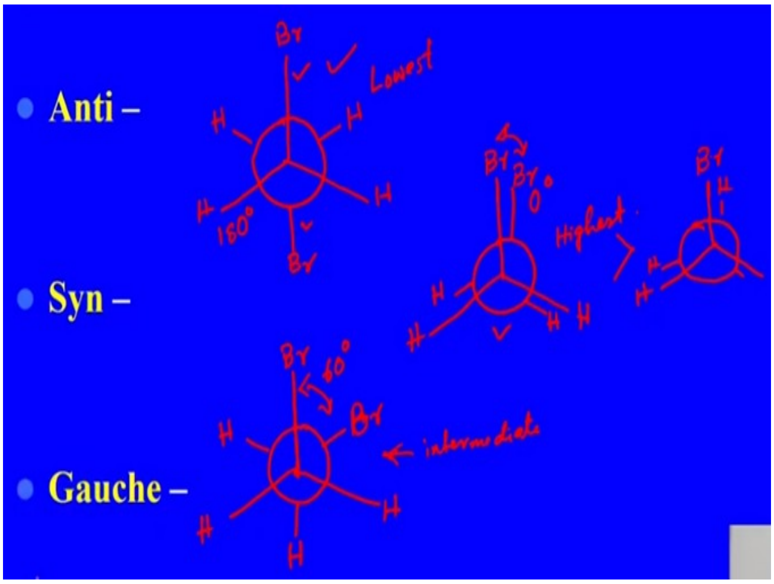

- Anti –
- Syn –
- Gauche –

The anti-conformation should be drawn like this. The syn conformation should be drawn like that, and the Gauche conformation should be drawn like this. So here the 2 bonds in anti are at 180 degree, here the 2 bonds of CBr is at 0 degree and here the 2 bonds about bromine are at 60 degree.

So now if I ask you to tell me which conformer has the highest energy which has lowest energy and which has intermediate energy, you should be able to quick say that the anti-conformation has the maximum separation of bromine atoms, the maximum separation of bonds. So this must be the lowest energy. The syn conformation has the minimum separation of bromines and bonds are eclipsed.

So this should be the highest energy and this one should be having the intermediate energy. There is another different syn conformation that is possible, is, this particular case of dibromo ethane where the bromine and hydrogens are eclipsed instead of 2 bromines being eclipsed.

So this syn has slightly lower energy compared to this syn conformation because here the bromine.. I am sorry this incorrect drawing this bromine and that should be separate. So here in this particular case the bromine are far apart so there is no steric strain, it has only the torsional strain present. So this slightly lower energy compared to the other syn conformation.

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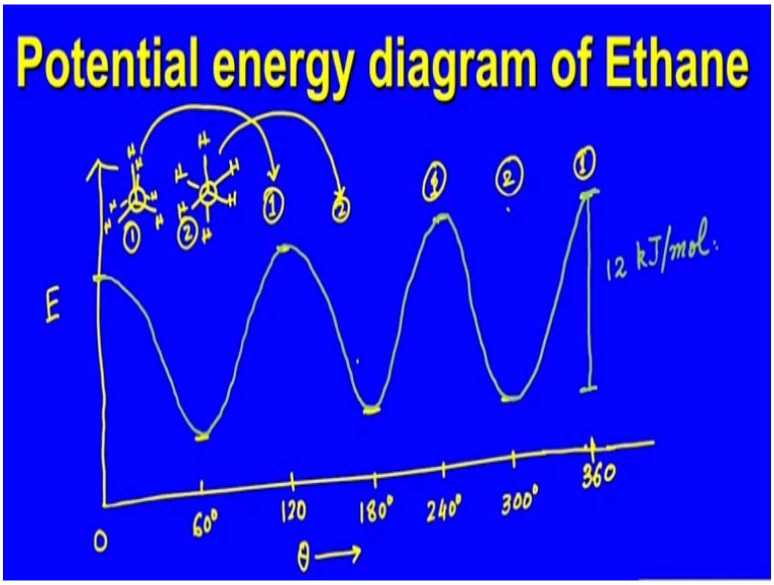

Potential energy diagram of Ethane

So then when we have various different conformers that can be there for simple molecule like ethane. So what we try to draw is a potential energy diagram for different conformers of ethane. So in this diagram we draw energy on Y axis and the torsional angle in X axis or the theta in X axis. So when the torsion angle is 0 which means what we have is a fully eclipsed conformation.

So it has altogether 12 kilo calories per mole energy higher than the Gauche conformation which is suppose at 60 degree appears here. So the Gauche conformation would look like this. So the energy would be somewhere here if you rotate the molecule by another 60 degree and go to 120 degree what we would get is something very similar to one. So the energy will be somewhere here if you rotate the molecule, if you rotate the back carbon by another 60 degree and go to 180 degree.

What we would get is very similar to number 2 and the corresponding energy will be same as number 2. And then if you rotate the back carbon by another 60 degree and reach 240 degree you will get the conformation 1 which is 12 kilo joules per mole higher in energy. And rotate the back carbon once again by another 60 degree you reach 300 degree here.

So at 300 degree of rotation the energy of the molecule will be same as 2 so here it is again 1 there it is 2. And then again if you rotate molecule by another 60 degree and reach 360 degree we reach the molecule 1, the conformation 1 once again. So these are the energy values for the 1 conformation 1 those are the energy values of conformation 2. So if I want to join these energies by a smooth curve what I would get is like that.

So the potential energy of different conformers of ethane varies along this curve and the difference between the highest and lowest energy conformer is 12 kilo joules per mole. So this is called potential energy diagram of ethane and hope you are able to understand why this is like this sinusoidal curve.

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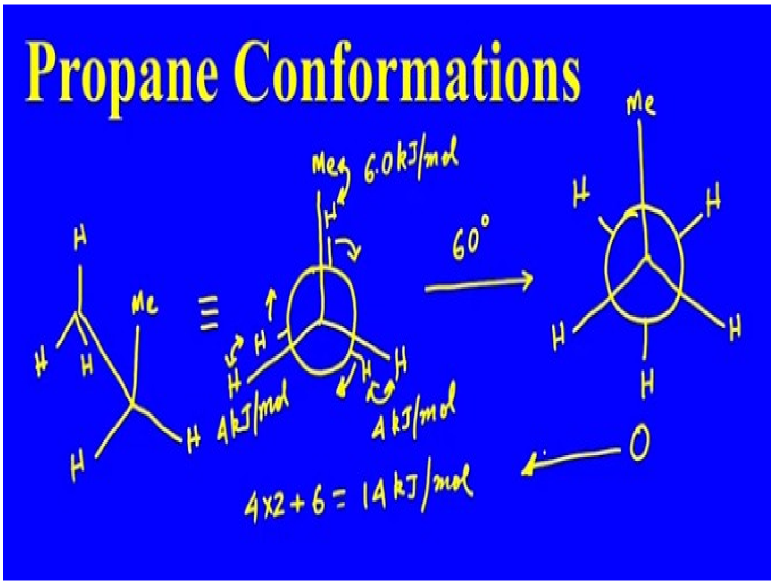

Propane Conformations

So let us now see the different conformations of propane and we will see here that the interaction energies or the torsion strains are different because of the presence of 1 methyl group. So when we try to draw propane using the sawhorse representation we write this and have a methyl group at the top position and these 2 are hydrogens when on the other side you have 3 hydrogen atoms.

So the corresponding Newman projection that one should draw is the following. The front carbon contains the methyl group and there are 2 hydrogen atoms. The back carbon has 3 hydrogen atoms which makes it propane. So in this particular conformation what we see is there is a torsional strain that appears because of the methyl and hydrogen being eclipsed. And that torsional strain results into 6 kilo joules per mole of destabilization energy.

While as usual it was like in case of ethane these, 2 hydrogens the torsional strain are 4 kilo joules per mole for each of them. So overall the total torsional energy that is associated with this conformation of propane is nothing but 4 into 2 + 6 = 14 kilo joules per mole. If I rotate the back carbon that means this hydrogen is rotated by 60 degree. We get the corresponding Gauche conformation which would look like this.

And we can now then avoid these 3 different torsional strains. And this molecule is supposed to be the lowest energy or 0 energy conformation or the lowest energy conformation. So when you try to draw the potential energy diagram like that for ethane we have drawn in the previous slide the energy difference here will be 14 kilo joules per mole.

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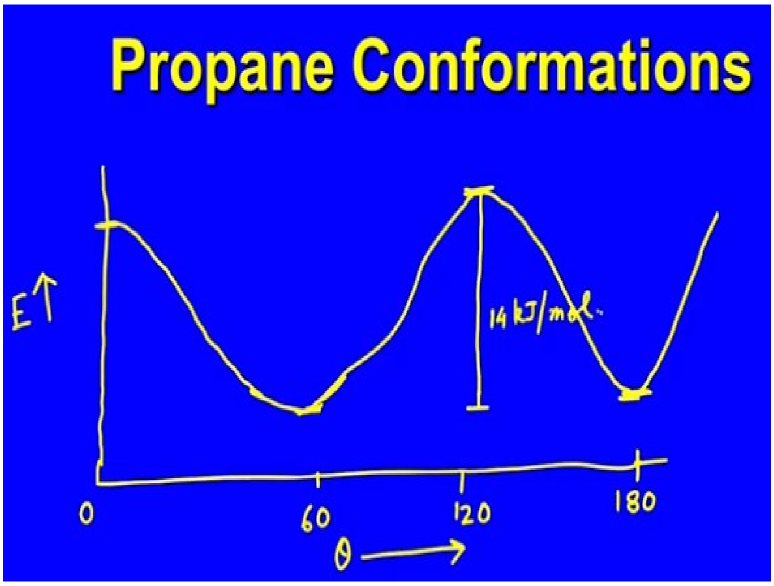

Propane Conformations

So if we try to draw the potential energy diagram I will not draw for all the possible conformers I will just draw 3 of them energies plotted in Y axis as usual and the dihydral angle theta is plotted in X axis. And we will draw the positions with 0, 60, 120 and so on. So when it is 0 as we have seen in the previous slide the energy is higher when it is at 60 degree the energy is lower.

And then again at 120 degree the energy should be higher because again we get the eclipse conformation and in case of 180 degree it will be again the same as the conformation at 60 degree. So if you join these points with a curve you pass through minimum at 60, 180 etc., and maxima at 0, 120 and so on. And the difference here is going to be 14 kilo joules per mole.

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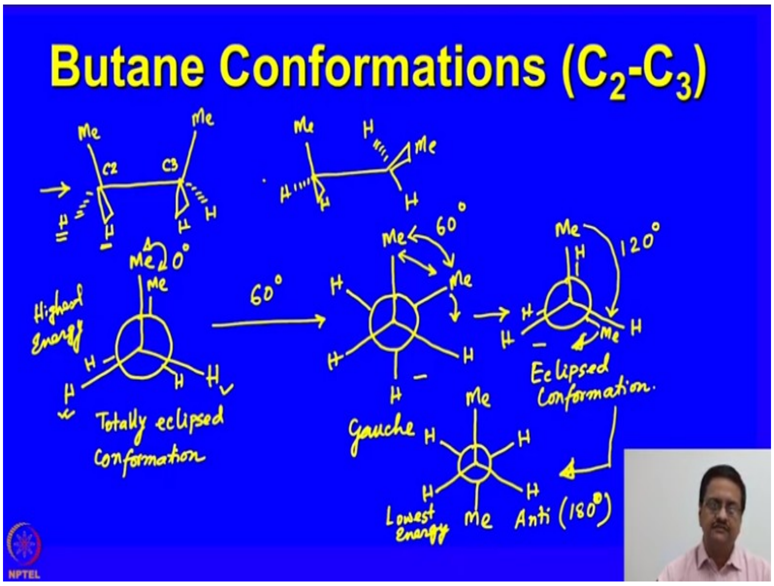

Butane Conformations (C_2-C_3)

So now let us move to the next higher alkane which is butane. So in case of butane let us first try to draw butane using the Wedge and dash formula. The way I have drawn this is a C2, C3 bond is used as the middle point of the molecule and then if I try to look at this molecule from this side taking that C2 atom is in the front. So what we can draw is. This is my front carbon.

So there you have a methyl group and then we have 2 hydrogen atoms in the front carbon which are this and that, you see when I am drawing from this side this hydrogen comes here and that hydrogen comes there that is on the right and left. Similarly for the back carbon I am drawing the methyl group the other 2 hydrogens which are back together. So this is called the fully eclipsed conformation or totally eclipsed confirmation.

So what we see here is the dihedral angle between the 2 methyl groups is 0 degree and then slowly if we start rotating the back carbon by 60 degree, the corresponding diagram for this molecule would be like this and the Newman projection look like this. This is called the Gauche conformation where this torsional angle between the 2 methyl groups is 60 degree. The next possible conformation that we can think of is by rotation of this back carbon by another 60 degree. So in that case what we would get is this conformation.

So what we see here is that the methyl and hydrogen are eclipsed and here the hydrogens are eclipsed unlike the first one which was totally eclipsed conformation this is partially eclipsed conformation or we can call it as a simple eclipsed conformation. So here the angle between the 2 methyl groups in now 120 degree. The fourth one that one can think of is by rotating this methyl group by another 60 degree and you can draw the conformation like this.

This particular conformation is called the anti-conformer where the angle between the 2 methyl groups is 180 degree. If ask you now to identify the most stable and least stable conformer, it will not be very easy to identify that without the values of the torsional strain and other strains that may be present in this particular molecule. But it can be guessed that in case of totally eclipsed the torsional strain will be the maximum so this will be the highest energy.

And here we do not have any torsional strain we do not have any steric strain. So this anti will be the lowest energy conformer. But to find out which one among these 2 is having a lower energy than the other we need to know the values of these energies. So in the following lecture we will continue from here and discuss about that Gauche interaction which is present here.

And this particular we talk about this interaction we will talk about the energies that are associated with this kind of interactions and we will try to then draw the potential energy diagram for n-butane various conformations.