Course on Stereochemistry
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Module 4
Lecture No 17
Conformations of Acyclic Molecules Containing Hetero Atoms

Okay welcome back let us consider the confirmations of systems where there are atoms like where there is no possibility of steric strain or maybe much less steric strain. Every atom has a size even hydrogen there is some strain is there as I said 10% of it contributes to the overall energy. However the steric strain is less where there is no possibility of hydrogen bond but where there is possibility of dipole dipole repulsion, okay. So in that case what happens to the gauche form and to the anti-form, so obviously at that point the gauche form will be less stable than the anti-form.

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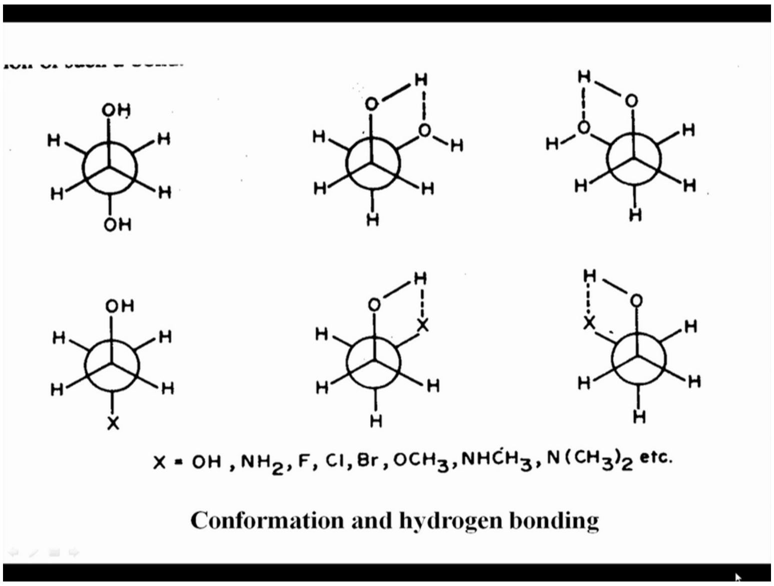
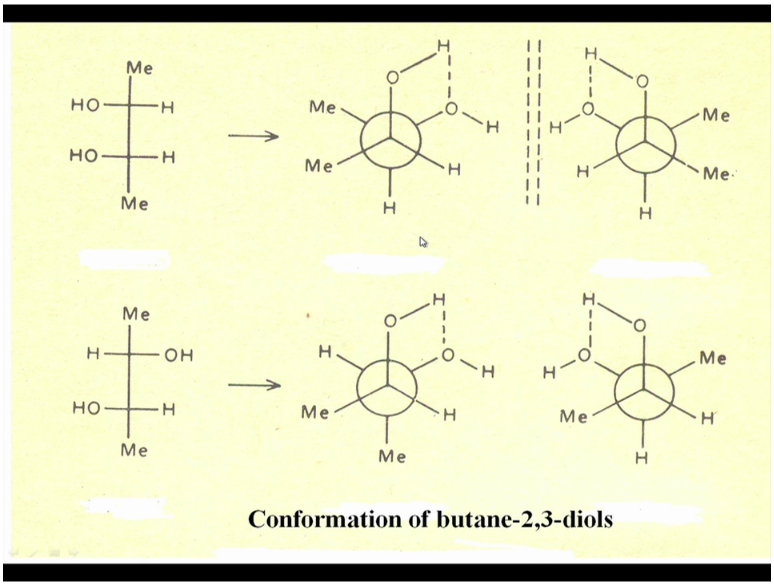


X = OH, NH_2, F, Cl, Br, OCH_3, $NHCH_3$, $N(CH_3)_2$ etc.

Conformation and hydrogen bonding



Conformation of butane-2,3-diols

So this was the hydrogen bond scenario we discussed last time that if you have OH and X in the next atom, next carbon atom then there is a possibility of hydrogen bond which stabilises the system. If you if you have in this case now we have the same system but we have to we have put the methyl groups here also. Earlier it was only ethane and glycol, if you put 2 methyl groups now you know that this molecule can exist in either in a Meso form or it can exist in as a LD pair meso form or a DL pair. If you consider the Meso form what you are seeing is that this is the form where the there is a hydrogen bond formation, okay.

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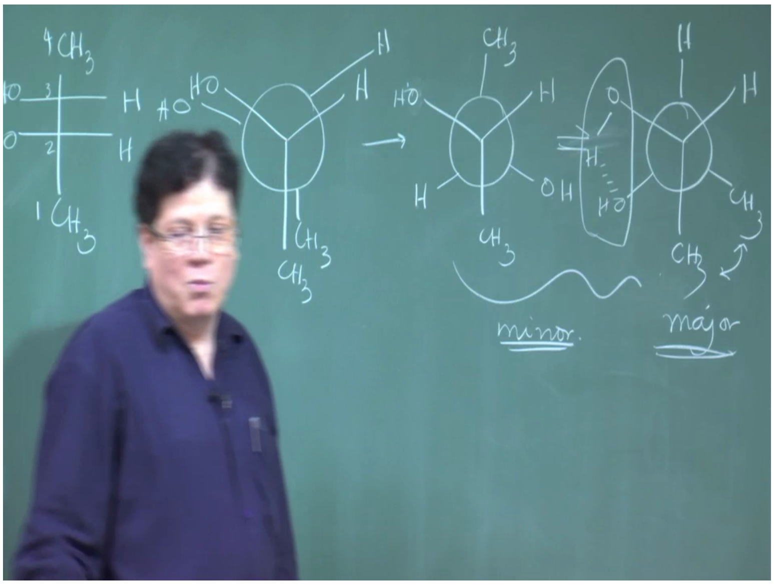

Although while doing so while doing so you are you are bringing the 2 methyl in a gauche in a gauche form, okay. So I can draw it in the board, so what we are seeing I think this was the molecule OH a methyl a methyl, hydrogen, hydrogen so when it is when you draw the

Newman projection of this, I think I told you that is better to look from down so suppose this is 1, this is 2, this is 3, this is 4 so what happens this is the down methyl that means the number 1, this is the number 2 so number 2 the hydrogen goes on the right direction and OH goes to the left and this is the hydrogen and this is the OH and this is the other methyl.

So that is the direct conversion to the Newman projection, however this is the eclipsed fully eclipsed form so it will not exist in this form. So it will try to exist if we follow the the n-butane type of system that scenario where the methyl are opposite to each other anti-to each other so what you do, you keep the front suppose we keep the front carbon same and we rotate the back carbon by 180, so if you do that this methyl will be anti and this is sorry this is OH and this OH will be here and this is the hydrogen. So this should have been the most stable one but the problem is there is no possibility of hydrogen bond formation here.

So if you converted into the gauche form where, so how to converted into the gauche form, so you take the OH here suppose you bring the OH here sorry 1 OH was already there so now you have the hydrogen bond here you have the top carbon remaining the same so do not change the top carbon, the back carbon the OH is rotated and by 120° so the rotation was by 120, so OH comes here hydrogen goes there and the methyl comes here.

It is the same what was actually written there it is in different using a different type of Newman projection, okay but they are same. If you see the… there is methyl methyl interaction gauche butane interaction but there is hydrogen bond formation. So the question is which one is more stable, here the methyl methyl is anti-there is no torsional butane interaction. OH but the OH OH cannot form hydrogen bonds. Here the methyl methyl has gauche butane interaction but the OH OH can have hydrogen bond scenario, okay.

So this is a very interesting case so which one predominates? Actually hydrogen bond predominates over the methyl methyl gauche butane interactions. So if you study the if you can detect the presence of this two we will see that this will be the major form and this will be the minor form because hydrogen bond intra-molecular hydrogen bond is the more stabilising factor over the gauche butane interaction, okay so that is why I brought this case here.

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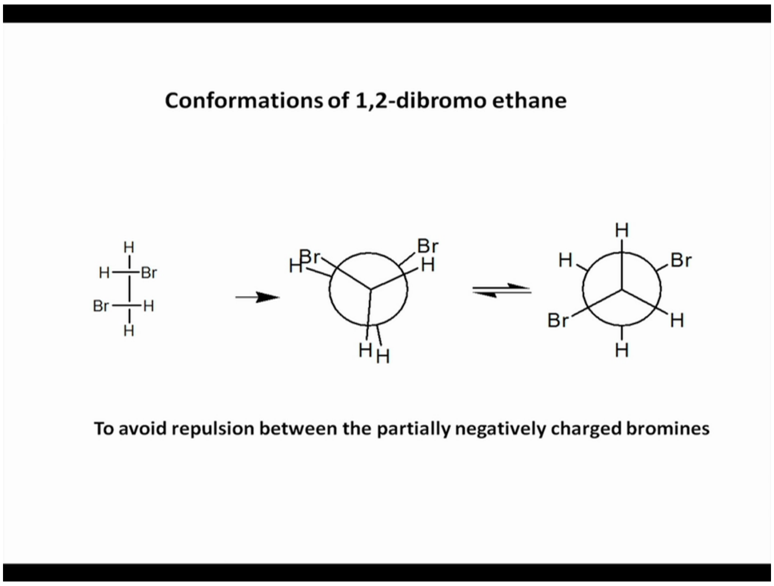

Conformations of 1,2-dibromo ethane

To avoid repulsion between the partially negatively charged bromines

In case of 1, 2 dibromo ethane so what will happen in case of 1, 2 dibromo ethane, I think the it is it is written in a Fischer projections formula but actually does not require because it is a chiral molecule, completely a chiral molecule and this 2 completely a chiral molecule, this is CH2 Br and CH2 Br. But if you write it in a Fischer projection, it may look like this that I can I put the Br on the right side and this Br on the left side but again keep in mind this does not make any there will be no difference if I put the Br here and the hydrogen near it is the same molecule because it is a chiral molecule you can draw it in whatever way you like it, so I will just draw it in this type of Fischer projection okay.

So if this is the Fischer projection of the molecule (())(6:46) ethane so from this I said that always look from the from the from the from the bottom side you do that then this hydrogen will be will be this hydrogen and on the right is this hydrogen and on the left this bromine this is the top carbon, so I am looking from this bottom side looking at this top this carbon and this carbon now becomes the top carbon because this is closer to me and this carbon becomes the back carbon and the back carbon what happens the bromine is to the right this hydrogen is to the left and this hydrogen will Eclipse the this hydrogen so that hydrogen is here.

So this is the conformation okay one of the conformations. Now you try to you rotate it this is this is the one which is anti-form this is the one which is the eclipsed form but this is partial eclipse you can have a fully eclipsed form also where the bromine and bromine well fully eclipse each other okay. So which will be the most stable one? I can actually have a I can do it here I think all the conformations are not drawn in that picture so better draw all the conformation here.

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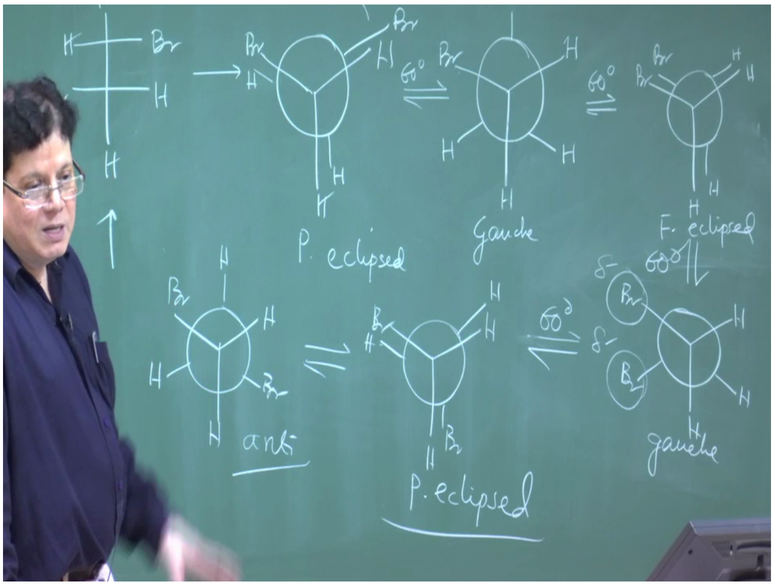

So what we have started with we have started with a bromine so here and a bromine there hydrogen, hydrogen, hydrogen and hydrogen so now we converted into the Newman projection. We are actually seeing it from this side, if you do that than this will be hydrogen that will be a hydrogen this will be the bromine and on the right side there will be the backside of the carbon the back carbon the right-hand side will be bromine and this will be hydrogen and that will be another hydrogen so this is the direct Newman projection formula of this, conversion of this to the Newman projection.

Now you start rotating it, okay so you can have if you start suppose I rotate the back carbon by 60° say anticlockwise, anticlockwise that means this so I rotate it by 60, so if I do that remember the back carbon so the front carbon do not gets disturbed so this is the front carbon hydrogen and hydrogen and this is the back carbon so this is the bromine that is hydrogen this is hydrogen.

Now like here earlier n-butane so this is the gauche gauche form the bromine and bromine as a dihedral angle of 60° so then you further rotate it and further rotate it by 60°, so what will happen? So the bromine and bromines will be eclipsing each other so that is the fully eclipsed form then you further rotate and what you will get is another gauche form the bromine bromine having a dihedral angle of 60 hydrogen, hydrogen okay so likewise you rotate so this is started from here 60 then 60. This is but you remember started from are partially eclipsed one okay partially eclipsed then a gauche form so this is partially eclipsed this is a gauche form. This is fully eclipsed F eclipsed fully eclipsed.

This is another gauche form and then you rotate it and you get the bromine here hydrogen and you have another partially eclipsed form. As bromine hydrogen will be eclipsing each other and there will be an eclipsing interaction here hydrogen bromine, so that is another 60° so 60°, this is 60° and then you have the because I want to come to the anti-form. So ultimately you will come to the remember the top one do not disturb that the top one remains the same so now you come to position which is the anti-form okay so this is the anti-form and this is the partially eclipsed form so likewise you can continue, okay.

So out of this which one is the most stable? Here the gauche form will not be that stable, 1st of all bromine is quite is not is quite big it is not a very small atom it is quite big but the important point is that it has got it is because of CBr the carbon is more electric positive bromine is more electro negative so there will be polarization so that creates dipoles so there will be a dipole dipole repulsion now and that repulsion will make it less stable than the anti-form where it is least because they are anti to each other and they are anti to each other okay. So in this case where you have this halogen at the 1 and 2 positions you see the anti-form more stable and not the gauche form. The reason years there is dipole dipole repulsion under gauche form that is why which makes it less stable okay.

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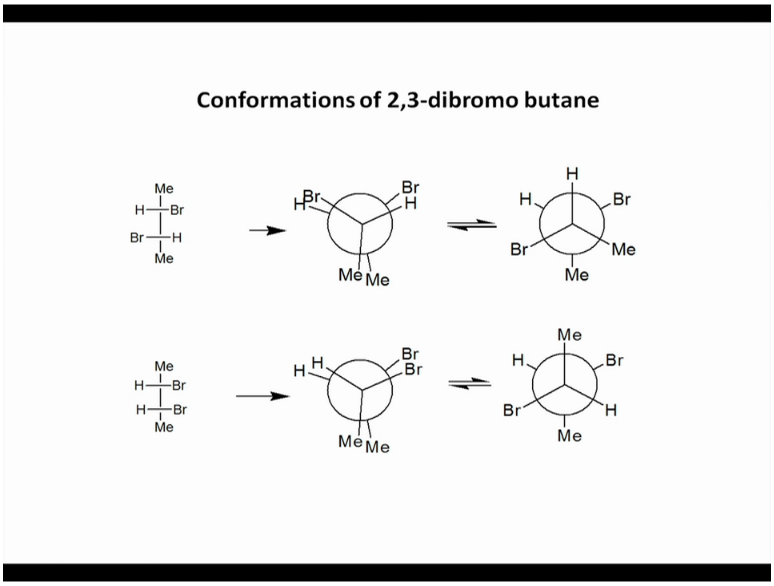
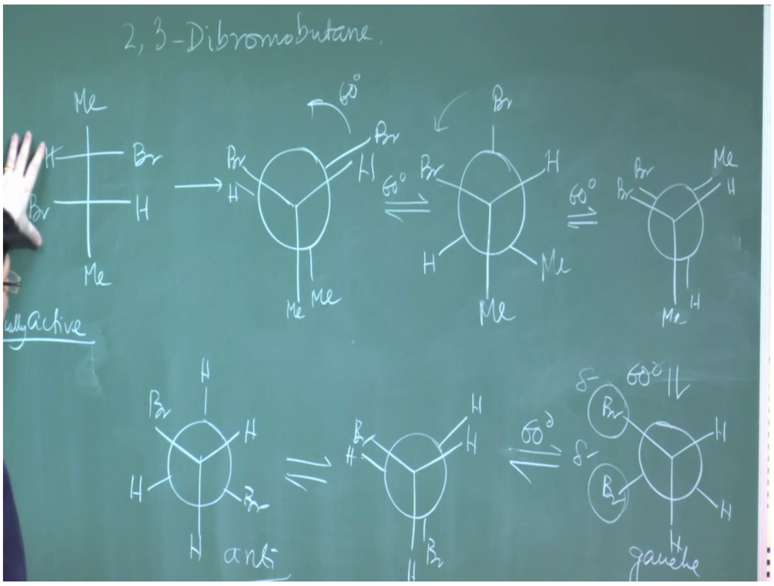


Conformations of 2,3-dibromo butane



If put a methyl now what will be the situation? When you put a methyl what happens? So I just I can start from here so if I put a methyl here, so there will be a methyl now this carbon and I will erase that and I put a methyl, so now I draw the Newman projection so if I draw the Newman projection, what will happen? Is hydrogen this will be replaced by methyl I hope this is clear? Okay. So we are talking about the conformation analysis of now 2 – 3 dibromobutane 2 – 3 dibromobutane okay. So these are the 2 methyl, I replace the hydrogen by methyl, these 2 so that methyl are now methyl are now eclipsed.

Now the question is when I put this 2 methyl here that means I am talking about the active form of the Dibromo the optically active form the optically active from of Dibromo because I can have another form which is the optically inactive form okay we can do that also. So if I get the optically active form, so I just so this is I rotated to by 60° that means the one which I was thinking as hydrogen they can make them as methyl okay.

So this is methyl this is methyl and likewise then again when you rotate by another 60° this side so these 2 so what happens this methyl so this hydrogen, this hydrogen is the methyl and this hydrogen is a methyl so it keeps on it keeps on changing okay so likewise you can, so the names also you cannot see the names also you have to careful. So better erase all these partially eclipsed so we started with this 2-3 dibromo methyl, we converted into the Newman projection formula and then we do a conformation analysis, we started we started rotating the back carbon in an anticlockwise fashion by 60° and you can draw different conformers okay.

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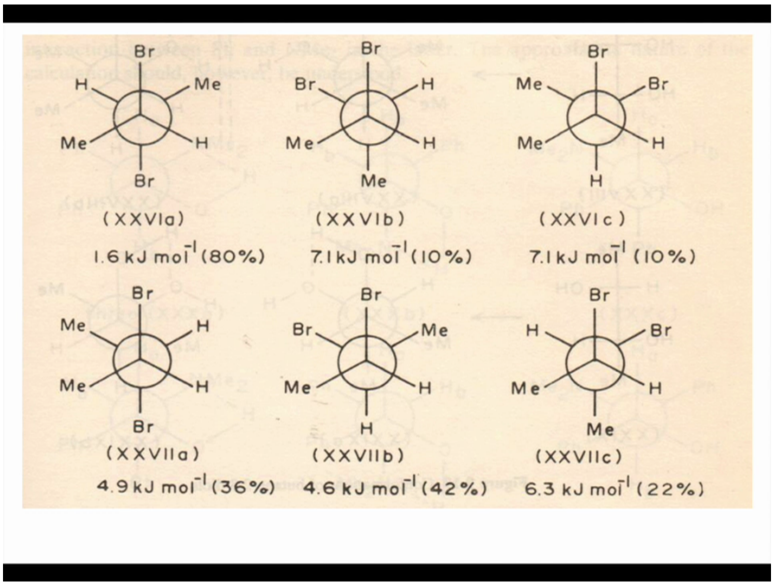

(XXVIa) 1.6 kJ mol^{-1} (80%)

(XXVIb) 7.1 kJ mol^{-1} (10%)

(XXVIc) 7.1 kJ mol^{-1} (10%)

(XXVIIa) 4.9 kJ mol^{-1} (36%)

(XXVIIb) 4.6 kJ mol^{-1} (42%)

(XXVIIc) 6.3 kJ mol^{-1} (22%)

Now let us see the let us see the different conformations of this 2 – 3 dibromo butane which is written in the book, okay. So this is the direct representation from the book. So this is a form this is 2 – 3 dibromo butane, the methyl methyl are anti to each other the bromine bromine are anti to each other, okay. So this molecule now is which dibromo butane.

This will be the Meso dibromo butane because this molecule is no longer optically active what it has is what is called a center of symmetry. There is a point in a middle between the carbon carbon bond when you joined this methyl and extended backwards you get methyl. Similarly that is true for bromine similarly that is true for the hydrogen. So it has got a center of symmetry so this is the Meso dibromo 2 – 3 2-3 dibromo butane the Meso form okay.

So the meso form has this is fully this is the anti-form and then you have a…if you start rotating now so what is this rotation now you bring the bromine so we are drawing different staggered form we are drawing…we are not considering the eclipsed form, we are drawing different staggered form, so this is one staggered form where the groups are really anti to each other. Now I can have this bromine here hydrogen here and methyl here that means I give an anti-clock I could do a clock wise rotation now bromine being here hydrogen here and methyl there and that is exactly the bottom carbon.

So this is the same molecule that given a 120° rotation clockwise and then you do another 120° rotation clockwise, now this bromine will come here hydrogen there and the methyl will go there okay. Now these are what are they? The gauche form according to the nomenclature the bromine bromine are gauche and methyl methyl are also in the gauche in the gauche form okay. So in the in the gauche form we have 2 conformers and this is the anti-conformer okay.

You start with another molecule where the top configuration, do not change the position of the groups of that of that top carbon atom, you change just interchange one of the one of the groups one of the 2 groups that means which interchange the position of methyl and hydrogen that means you bring the methyl here hydrogen there, by doing so you ended up with a with the optically active isomer of 2 – 3 dibromo butane, I hope that is clear so what I am saying that you here there is a I present so this is meso dibromo butane and this is optically active dibromo butane. I got it just by exchanging this methyl and the hydrogen interchanging the position of the methyl and hydrogen. So now that center of symmetry is no longer there, in fact it does not have any symmetry element improper elements of symmetry so it is optically active, okay.

So this optically active form now this is the form where this bromine are anti but the methyl are gauche form so if you now again try to do the same saying that gave a clockwise rotation of 120° at the back carbon so you get the bromine here the methyl there and the hydrogen there. This is another form and he gave another 120° so now this 2 bromine are the bromine is here the methyl is here and the methyl is there so if you now start calculating actually the energy you can actually evaluate the energy of this Systems but to know that you have to know certain values the energy this molecule suffers from what suffers from a bromine methyl interaction gauche interaction, bromine methyl gauche interaction.

Remember what is gauche interaction when the groups are having a dihedral angle of 60°. So this molecule suffers from gauche interaction of bromine and methyl…2 bromine and methyl gauche interaction okay. Gauche interaction of methyl and hydrogen is very little so that does not contribute much, okay so gauche interaction of methyl and bromine to gauche methyl so the question is what is the energy of a gauche methyl bromine interaction. We know the energy of methyl methyl gauche interaction that is .9 and in fact I think this value the methyl and bromine gauche interaction is .8 kilojoules per mole not kilocalories earlier it was kilocalories.

So that was this was the methyl bromine interaction gauche interaction is .8, so this molecule will have energy of 1.6 kilojoules per mole, okay this conformation. If it is in this conformation where the bromine bromine are the gauche in the gauche form, so what will be the energy now? 1st of all you have to see how many interactions are there, so there is a methyl methyl gauche butane interaction, that contributes .9, there will be a methyl bromine that contributes .9 means actually lets us see that contributes .9 methyl there will be a methyl there will be a methyl methyl but remember that .9 was in kilocalories just there is a change, this is in kilojoules so methyl bromine has a methyl bromine gauche interaction has an energy of .8 maybe I can write it here that will make it to remember it better.

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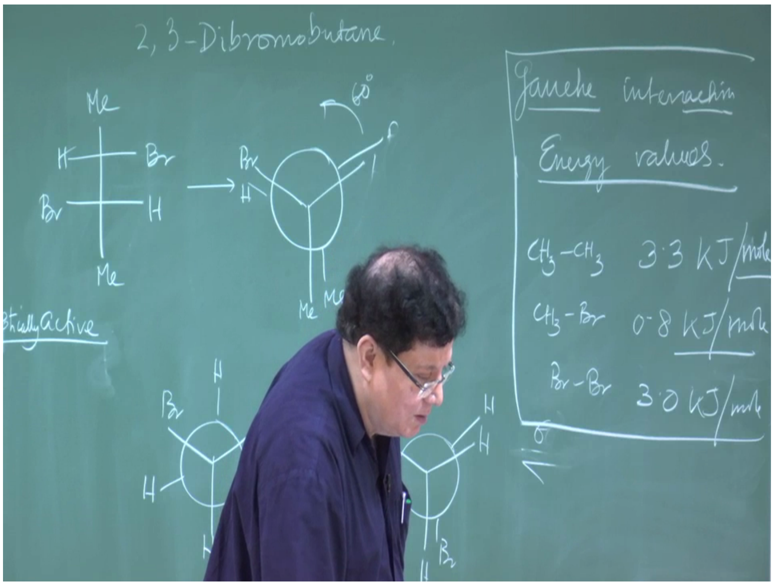

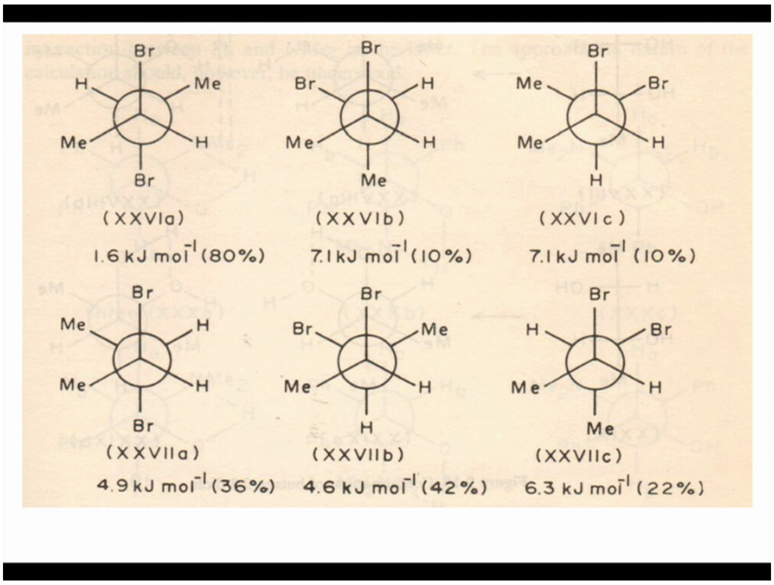

So the energy values are gauche interaction energy values. So if it is methyl methyl so I said .9 kilocalories per mole earlier or if it is in kilojoules it will come around 3.3 so around 3.3 kilojoules per mole per mole okay kilojoules per mole methyl methyl. Methyl bromine is 0.8 kilojoules per mole, okay and bromine bromine is 3.0 kilojoules per mole, okay. So this is the figure that I have, now you can again come back and solve this problem, okay the problem is the question what is the question? Then the question is which one is more stable.

Is it the is it the meso from of dibromo butane or is it the optically active form of dibromo butane, so how to solve this problem? So you have to consider all the confirmations, all the conformers to be to be precise that different conformers you draw possible staggered forms they are conformers so this is the meso form so in this form you have 2 methyl bromine gauche interactions, so that will be 1.6, 2 into .8 and then you have here bromine bromine that contributes 3 and then bromine methyl that contributes .8 and then methyl methyl that contributes 3.3 and if you add up these it will come out to be 7.1 and then if you have the this conformation that will be also 7.1 because this gauche is the mirror image of this gauche form so 7.1 is exactly the same interactions that you have but you have a conformation which is 1.6 kilojoules per mole, so that contributes our 80% of the system okay.

There is a way to calculate also the ratios when you know the delta, delta G if you know the energy difference if you consider that there is no (())(24:40) contribution here then you can just write delta is equal to minus (())(24:44) L and K and from that you can calculate the percentage of each confirmation of his conformer. So this becomes 80% and that is got an energy of 1.6. When you talk about the optically active form you see this is a form where there is a methyl bromine interaction that we already know that methyl bromine contributes .8 there is another methyl bromine that contributes .8 and there is a methyl methyl that contributes 3.3 kilojoules, so the total will be 4.9 and when you have this other conformation where bromine bromine is gauche methyl methyl is anti, there are there are methyl bromine interactions bromine bromine interactions and methyl bromine interaction.

If you add these are it will give 4.6 kilojoules per mole and the there is another one which is this methyl methyl, methyl methyl gauche form that is the 3rd possibility where you bring this methyl here the bromine goes there the bromine goes there and you can calculate the energy here, here the energy will be bromine bromine and then methyl methyl, if you add these up that will be 6.3, 3 plus 3.3 that will be 6.3. So whatever you do you cannot find a conformation which is as low as 1.6, okay so the lowest is 4.6 then 4.9 then 6.3. Here lowest is 1.6, so you can say by this conformation analysis, see so many things are that that can be arrived at so many conclusions.

That what are the preferred conformation, that you can do. Like n-butane what is the preferred conformation we have seen the anti-form. Then we can also by conformation analysis we can tell between an optically active form and the meso form or between 2 optically active form which stereoisomers which one is more stable? Then you can do this conformation analysis and if you know the values of the gauche interactions then you can tell which stereoisomers is more stable so you can say that the meso form of 2 – 3 dibromobutane is more stable than the optically active form okay by this simple conformation analysis of course provided, you have these provided you have the gauche interaction data, okay and those are calculated they are found from various experiments okay.

So that is how that ends up the conformation analysis of acyclic system. So next day what we will do we will do the conformation analysis of cyclic systems because they are cyclic systems are not that flexible because it is a cycle and the shorter the cycle, it needs 3 atoms to form a complete a cycle the 1st cycle is a triangle then it comes a quadrilateral then a pentagon okay then hexagon like that, so the as the size is, if the size is very small then there will be more strain in the doing the rotations so free rotation becomes much more restricted in cyclic systems.

However still you can find different conformations in in cyclic systems where the number of atoms forming the cycle is more than more than 3, only the only the cyclopropane where there are 3 carbon atoms that is extremely rigid you cannot move it up and down or do not you cannot do any rotation but beyond cyclopropane we will see from the next lecture that there is a conformation analysis possible that is different conformations are possible in those systems not in cyclopropane, so that will be in the next day. Thank you.