Module No # 04
Lecture No # 20
Absolute Configuration in Biphenyls and D/L Systems

Welcome back to course entitled symmetry, stereochemistry and applications. In the previous lecture we were discussing about the isomerism arising out of biphenyl system.

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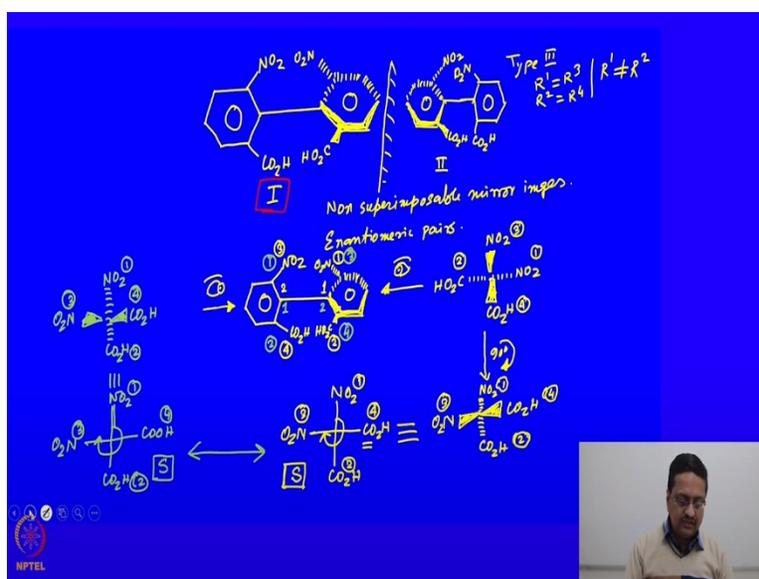
So then we were talking about how to identify the R and S notations for biphenyl systems. So here I had taken one example where one compound had 2 different substitution as R1 and R2 being different and we tried to identify their name by looking at those 2 molecules from 2 different sides. So in the previous class we had discussed about the how to find out the absolute configuration of molecule 1.

So in this current lecture we will see what happens, how do we identify in the same way for the molecule 2 which is the enantiomeric pair of one. So if we draw this second molecule in the next slide and then do the same as we had been doing in the previous class.

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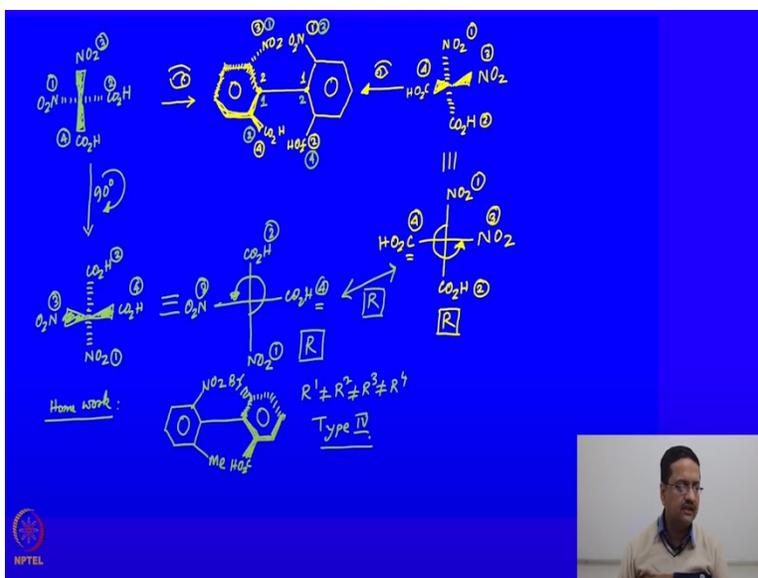
We will see how we can identify those, absolute configuration of this molecule. What we had is the mirror image where the left hand side group was above and below the plane, carboxylic acid was above the plane and the NO2 group was below the plane. So we should draw the same here. So remember that this bond which is drawn in as a dashed line is below the plane. So now if you look at this molecule from the right hand side what we see is this carbon should be numbered as one and the other carbon should be numbered as 2.

So, on the front carbon I think this should be corrected. This is not above the plane this is actually on the plane of this projection. So if we look at that front carbon which looks like this NO2 is up and CO2H is down, and those two are target pointing below the plane of this carbon atom to which it is bonded. So what we should draw there as the dashed lines for NO2. And the dashed lines for the CO2H group.

And then for the second carbon which is pointing towards me but the left side is CO2H and the right side is NO2. So that NO2 is above the plane of that carbon number 2 and CO2H is also above the plane of that carbon number 2. And then when we try to identify the priorities it is again based on the carbon number 1. So 1 and 2, 3 and 4 so, this is 1, 2, 3 and 4 and now if we see this Wedge projection which is very similar to the Fischer projection methodology that these groups which are in the vertical line are below the plane of projection.

So in that case we can straight away convert this into a Fischer projection as I am drawing here. So this is 1, 2, 3 and 4. So now if I try to identify the correct designation for this chiral compound we should go from 1 to 2 to 3 is in the opposite direction that is the anticlockwise direction. So this should be S but the fourth group is in the horizontal line. So the designation of this compound should be R. If we just quickly go back to the previous slide we can see that the enantiomer 1 was found to be S.

And in the next slide we find that enantiomer 2 is having absolute configuration R. Therefore the mirror image is an enantiomerically pure compound. So if I do this from the right hand side as usual what we do is then change our reference this first carbon become carbon number 1 and that gets carbon number 2. The priority order also changes because the priorities are given based on the front carbon so this is 1, this is 2, 3 and 4.

So now when we are looking at this molecule from the left hand side what we are seeing is the molecular plane which is in the front is horizontal plane and on the left I have NO2 group. And on the right I have CO2H group and both are pointing downwards. Similarly for the second carbon, 2 groups are pointing towards me above the plane of carbon number 2 and the above one is the nitro and the lower one is CO2H. So the nitro is here and CO2H is there.

Now if I right down quickly the priority this is 1 because this is on the front carbon, this is 2 and this is 3 and this one is 4. If you look at this projection you see that the horizontal line has bonds which are below the plane, the vertical line has bond which are above the plane of projection. So therefore to convert it into Fischer projection we should rotate the molecule by 90 degree and draw the Wedge projection once again.

I think this should be 4. So now we can draw the Fischer projection of this molecule just like before, NO2, CO2H with 1 and 2, O2N and CO2H here as 3 and 4. So if we do it 1 to 2 to 3 is anticlockwise. So this look like S but the fourth group is in the horizontal line so this is the configuration R. So, these two gives you the same configuration R. So no matter from which side we look at these molecules we end up getting the same absolute configuration.

So here I would like to give you homework as this one. Draw the mirror image of this compound and identify the corresponding absolute configurations of these two, configuration of the

corresponding enantiomers. So you see that here the 4 groups R1 is not equal to R2 is not equal to R3 is not equal to R4 this is a type 4 molecule in this series and you should try to found out what the absolute configuration comes out for this particular molecule.

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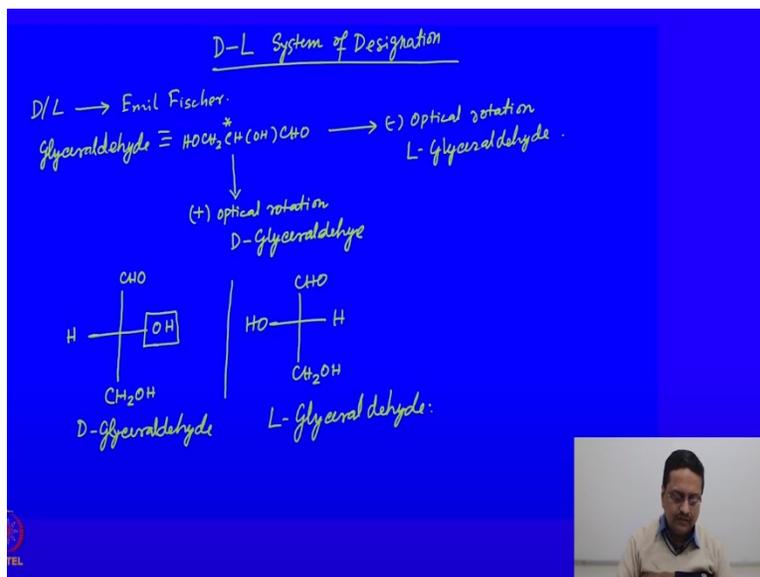
Now let us move to the next part of this course where we will introduce you to a different ways of notation of this chiral centers which are formally called the D and L system of designation. This D-L system of designation was first introduced by Emil Fischer. He actually identified isomers of glyceraldehyde which has the chemical formula CH2OH, CHOH, CHO with one chiral center in the molecule.

So when he was working on this particular molecule, the chiral compound which was found to rotate the plane of polarized light to positive direction. So which showed positive optical rotation he labeled that molecule as D-glyceraldehyde. And the one which gives the negative optical rotation he designated that compound as L-glyceraldehyde. And then also he identified this molecule using his unique projection formula the Fischer projection formula that you have already learnt and identified the 2 molecules like this.

When the OH group is on the right hand side of Fischer projection he identified the molecule as D glyceraldehyde and the other one which is essentially the mirror image he identified that as L glyceraldehyde. So this concept of designation D and L was then continued for few years and similar compound having 1 chiral center where designated using this D and L notations.
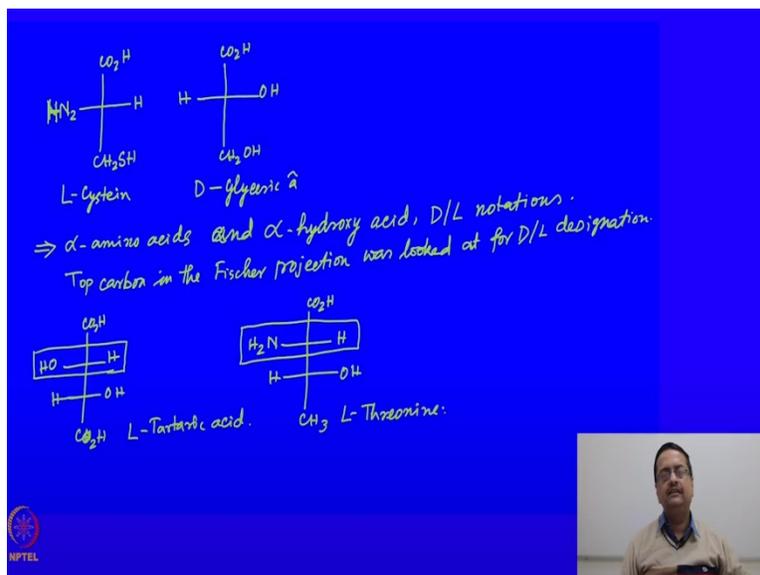
So the compound which is having NH2 group in place of OH and CO2H and CH2SH this is called cysteine. This isomer was termed as L cysteine. Similarly this compound which is oxidized version of glyceraldehyde was named as D glyceric acid and the corresponding L isomer had a OH group on the other side. This was then extended to the class of compound called alpha amino acids. So in case of alpha amino acids and alpha hydroxy acid, this D-L notations were also used.

So in that case the top carbon in the Fischer projection was looked at for D or L designation. So the compound which I am drawing here is one of the versions of tartaric acid which has CO2H at the top and bottom. And you have hydrogen and OH here and OH and hydrogen there. This isomer of tartaric acid was designated based on the orientation of OH in the top carbon as L tartaric acid.

Similarly this compound which is an alpha amino acid had NH2 group on the left hand side and OH group here on the right hand side with the methyl at the bottom based on the orientation of the NH2 group this was identified as L threonine. So this is how the alpha amino acids and alpha hydroxy acids were initially designated by D and L notations. And then this concept was also extended to the carbohydrate chemistry as well.
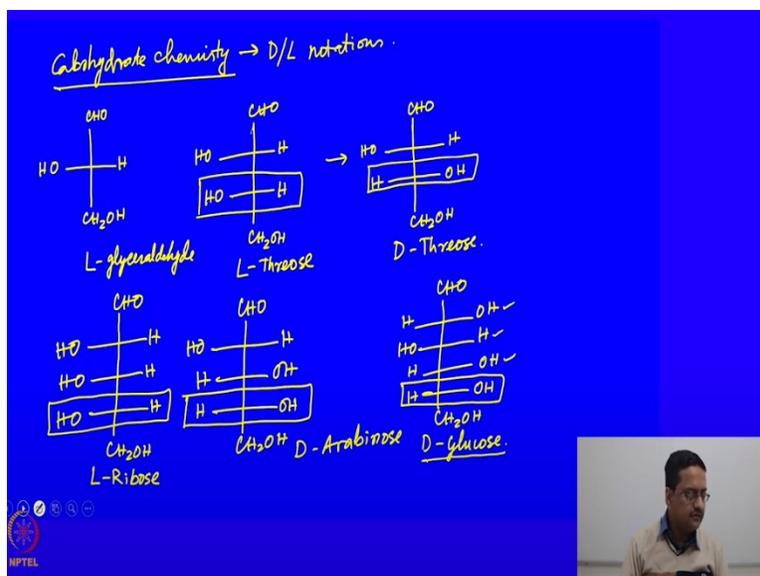
So in case of carbohydrates the last chiral carbon of the carbohydrates in a chain was used to identify the D and L notation for those carbohydrate molecules. So for simplest carbohydrate, the glyceraldehyde, which it was started when you have the OH group on the left hand side hydrogen and on the right hand side you name it as L glyceraldehyde. If we have 2 carbon atoms 2 chiral carbons with aldehyde at the top and the CH2OH at the bottom OH and H here and this also as OH and H.

Looking at the last carbon atom in the Fischer projection the bottom most carbon atom, this is also designated as L threose. And the other isomer of L threose with a different orientation of OH group on the last carbon was identified as the D threose. Similarly if you try to identify L ribose it would be this one. And the other isomer of this compound is D arabinose which is this one.

And the well-known glucose which is this one was also designated using the D and L notations in the carbohydrate chemistry. So once again by looking at the bottom most carbon, this designation of D and L was given. So we can see that by looking at one chiral center the designation for the absolute configuration of a molecule was identified. So certainly I am sure it is coming to your mind that this method has lot of shortcomings, yes of course this has lot of shortcomings.

It only signifies the chirality of only one carbon atom in a compound where you have multiple chiral centers and if you have different orientation of this OH or this H or that H keeping the same OH on the right hand side it will still be called D glucose which is not correct. So now if we see that if this D glucose is oxidized to glutaric acid or altaric acid same product have 2 different names.

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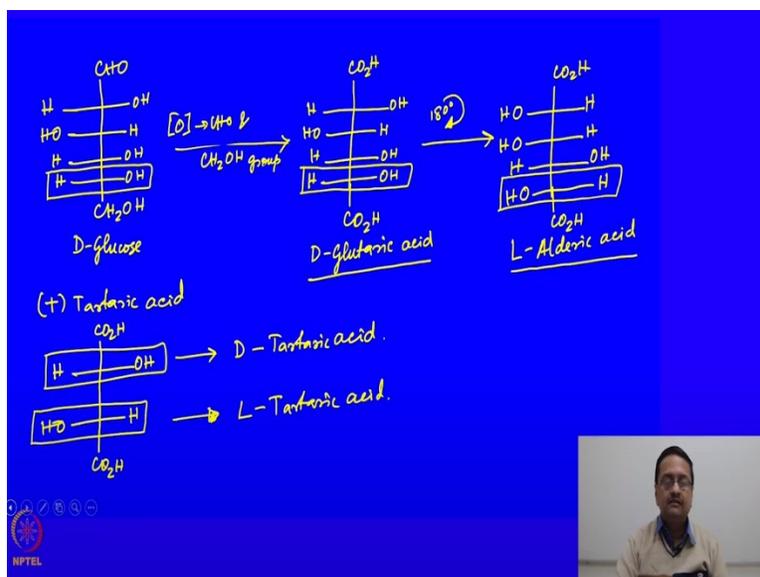
So if we have CHO which is the starting point of this reaction CH2OH. And we have OH, OH, H and OH and here H, OH, H and H what we are trying to do is, we are trying to oxidize the CHO and CH2OH groups simultaneously. So if you do that, what you will end up is CO2H at the bottom also CO2H. And we have 4 chiral centers where OH, OH, H and OH on the other side hydrogen OH, H and H.

Looking at this molecule considering this chiral center we started with D glucose based on that chiral center, the name of this should be D glutaric acid. But then if I rotate the molecule in plane by 180 degree. What we get is this molecule. By rotating 180 degree, these 2 OH groups will go to the left hand side at the top carbon. Then the third hydrogen which is here will come here with OH there and this will be OH, H.

So now in this case by looking at this group following the same convention gives me L Aldric acid. So this D and L nomenclature gives me 2 different notations for a given compound. So, there is a short coming related to this notation system. Now if I look at a simple molecule like the

plus tartaric acid. What is plus tartaric acid? The plus tartaric acid is CO2H here CO2H down OH and H.

If we consider that this is alpha hydroxy acid then we should give priority to this group which is at the top position of this Fischer projection. So this would be termed as D tartaric acid. If we assume that this was formed from a compound like glyceric acid so we should consider this in as we do it in carbohydrate chemistry. This compound then will get named as L tartaric acid. Therefore we get ambiguity in identifying the correct compounds.

So in that following slide we will see what happens is when we do a sequence of reaction on a given compound. Suppose we take a compound which is D glyceraldehyde.

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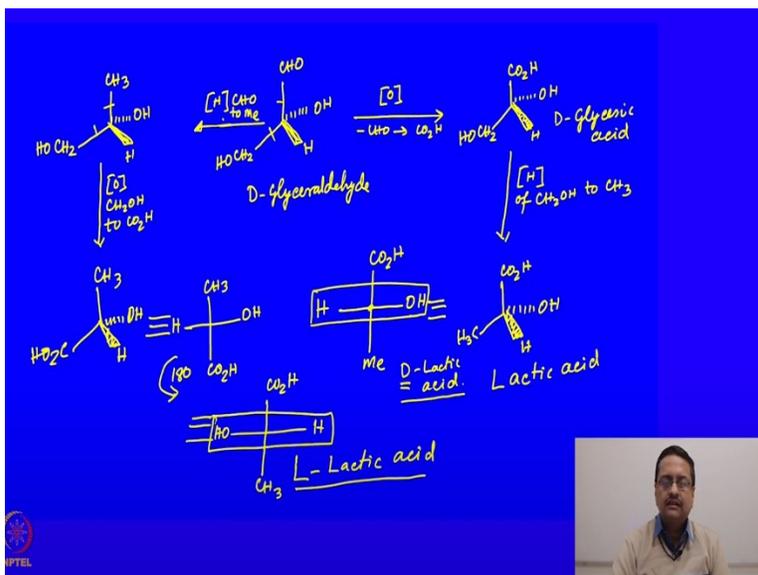
I am drawing it in the Wedge dash representation. This is D glyceraldehyde. So if we oxidize this molecule to convert the CHO group to CO2H group what we would get is this one. So this is D glyceric acid. And then we do a reduction of CH2OH to methyl. So what we get is this compound. So this compound is called lactic acid. If we draw the Fischer projection of this compound this would turn out to be this one.

Therefore if you look at this molecule then it should be termed based on the orientation as D lactic acid. But if we do a different sequence of reactions, we first reduce the CHO to methyl. What we get is this compound. And then if we oxidize CH2OH to CO2H we get this compound.

So therefore if we then convert it into the corresponding Fischer projection what we get is this one. And then if we just do in plane 180 degree rotation we get the Fischer projection like this.

So we have got the same compound lactic acid but now the configuration is L. So what we have achieved is by breaking or making any C-C bond we have been able to change the absolute configuration of a chiral center from D to L lactic acid. Therefore this method of designating the chiral centers using D and L is inappropriate for many different systems. So these short comings led us to always stick to the R and S notations for the chiral centers. So from here we will continue in our next lecture. Thank you.