Symmetry, Stereochemistry and Applications
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Module No # 05
Lecture No # 21
Asymmtery and Dissymmetry Molecules

Welcome back to the course entitle symmetry stereochemistry and applications. In the previous class we were discussing about the optical activity and isomerism.

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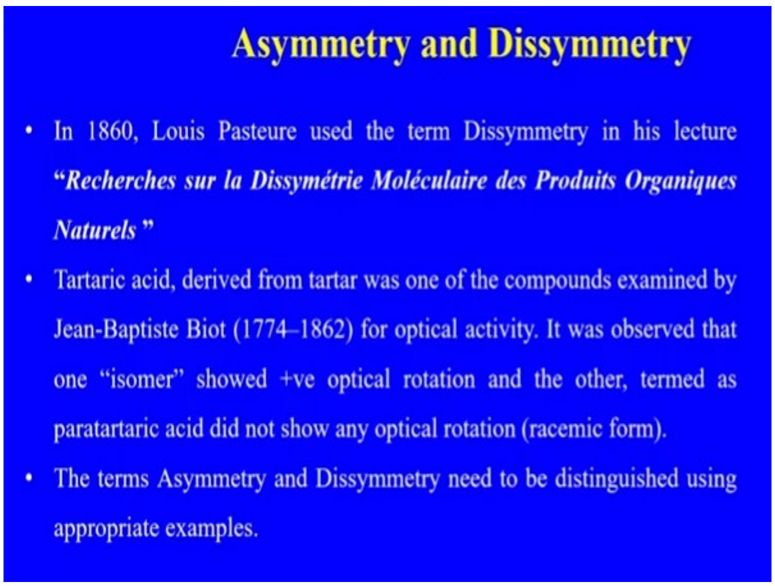

So in this context we would like to start talking about the terms asymmetry and dissymmetry. So there is a need to define these 2 terms and identify the difference between asymmetry and dissymmetry. See as early as in 1860 Louis Pasteure used the term dissymmetry in his lecture "recherches Sur la Dissymetrie Moleculaire Des Produits Organiques Naturels". Which essentially means that the essential organic materials can have dissymmetry molecules.

So before Pasteure identification of dissymmetry molecules tartaric acid derived from tartar was one of the compound examine by Biot in his early days for optical activity. It was observed that one isomer showed positive optical rotation and the other isomer termed as paratartaric acid did not show any optical rotation which means that was racemic mixture. So the terms asymmetry and dissymmetry need to be distinguish using appropriate examples.

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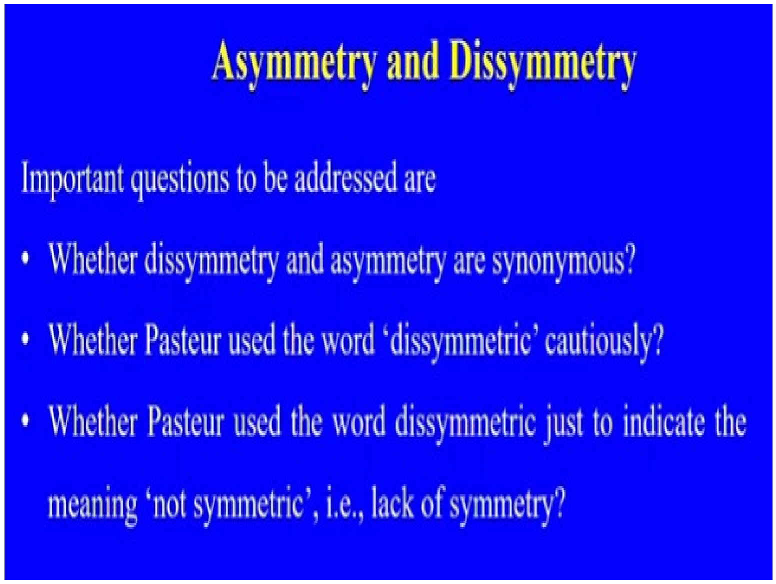

So in this lecture in this class today we will discuss about asymmetry and dissymmetry and we will try to address these 3 important questions. The first question is whether the dissymmetry and asymmetry are synonyms? Whether Pasteur used the word dissymmetric cautiously? Whether Pasteur use the word dissymmetric just to indicate the meaning not symmetric that is the lack of symmetry.

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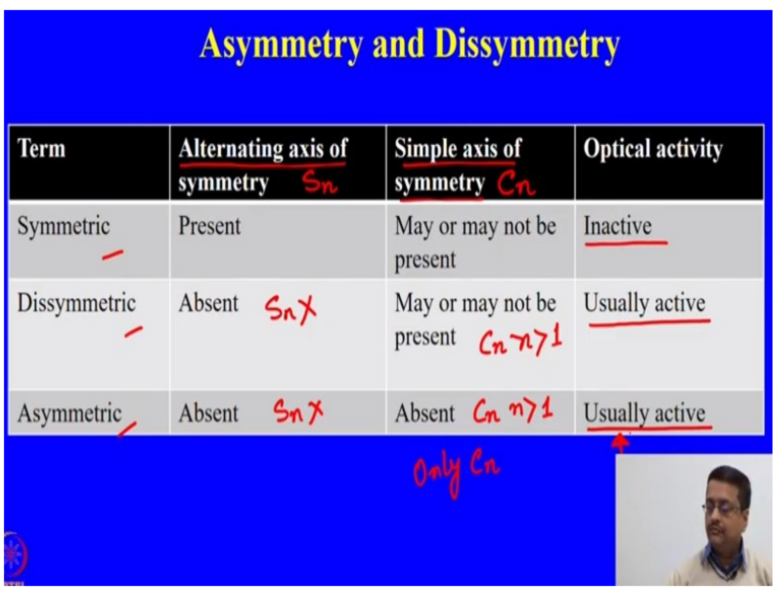

So to start the discussion today I would like to draw your attention to this very simple table which will be very useful in understanding this topic of asymmetric and dissymmetric. As you can understand from here that we were trying to understand the difference between a symmetric molecule a dissymmetric molecule and asymmetric molecule. So when we try to identify molecule whether it is symmetric dissymmetric or asymmetric we look for the presence of alternating axis of symmetry.

That means we look for the presence of some kind of Sn so if we see in a molecule there is one of those Sn is present. Then we look for whether the molecule has any simple axis of symmetry that is Cn. And then we infer that if these 2 are present or Cn may or may not be present then the symmetric molecule will be optically inactive. That means it will not rotate the plane of plane polarized light.

But when we look at a dissymmetry molecule the first thing that we find is that the absence of Sn. But a dissymmetric molecule may have Cn where n is greater than 1 and in general usually this molecules are optically active. In case of asymmetric compound asymmetric molecule it does not have Sn it does not have Cn with n greater than 1 which essentially means this has only Cn.

And these molecules are also usually active you see the term that we are using usually because we will see towards the end of this lecture that an asymmetric molecule also may not be optically active.

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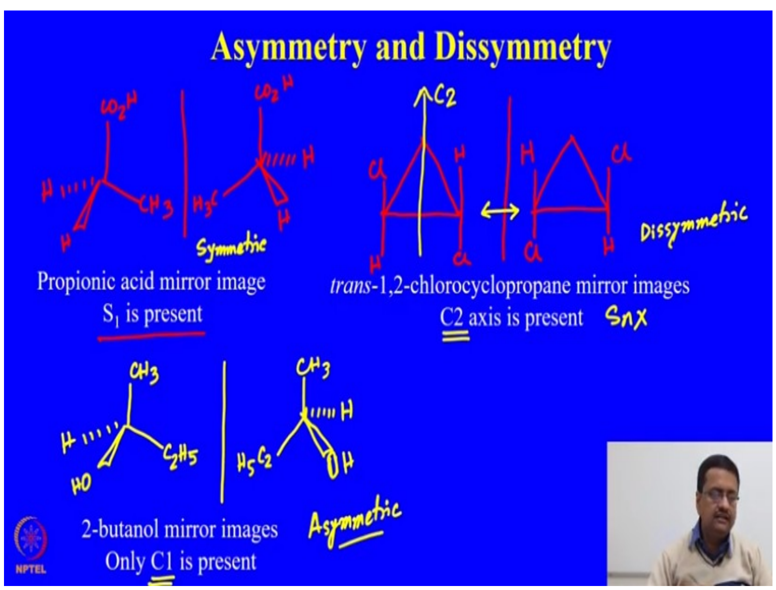

So let us see 3 examples of 3 different types of a molecules here the first one is propionic acid and its mirror image. What is propionic acid? It is a 3 carbon acid with CH2 in between these and the corresponding mirror image can be drawn like this. What we see here is that this molecule has S1 axis that is present. And as a result this molecule is symmetric molecule. Although it does not have; any Cn that is Cn greater than 2 it as C1 of course.

The second molecule that we look at is trans 1, 2-dichlorocyclopropane so let us draw the molecules first. When we say trans that means this 2 groups have chlorine atom at 2 opposite points. So this is the trans 1, 2-dichlorocyclopropane this carbon and that carbon both are chiral centers because each of those have 4 different groups attached to it. And if we take the corresponding mirror image what we get is this one.

What do we see in this molecule? We see that this particular molecule has a C2 axis passing through the middle of the bond and containing the third carbon atom. And what we see about these 2 mirror images? These 2 mirror images are non-super imposable so therefore these 2 are dissymmetric molecule these 2 are enantiomers and they are optically active. So here what we have is a presence of C2 axis but we do not have Sn.

So this is the condition for a dissymmetric molecule that it will not have Sn but it can have any other proper axis of symmetry like C2. Let us see the third case of 2-butanol and its mirror image. So what we see here is that this particular molecule has only C1 there is no Sn and there is no other symmetry element like C2, C3 or whatever. And these 2 mirror images are non-super imposable therefore this molecule is a chiral compound and this is optically active.

So this particular molecule propionic acid is symmetric, this molecule trans 1, 2-dichloropropane is dissymmetric. And this molecule can be termed as asymmetric. Hope you can understand the difference between symmetric, dissymmetric and asymmetric molecules.

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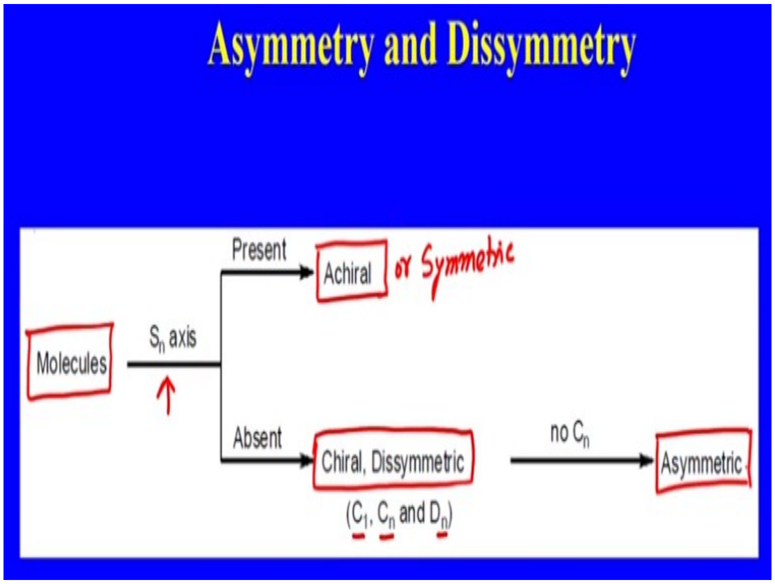

So to simplify this understanding I would like to draw your attention to this flowchart. So when we look at a molecule we first look for the presence of Sn if the molecule contains Sn we call it as an achiral molecule or a symmetric molecule. If the molecule does not have any Sn we call it as a chiral compound but a specific name is given to this compound as dissymmetric. So this chiral compound can have Cn with n = 1 or Cn with n greater than 1 that is 2, 3 and so on.

And can have Dn as well which means if you a C2 you have 3, perpendicular C2's and so on. But if you do not have Cn then it becomes asymmetric compound. So hope this chart clarifies the doubt between the dissymmetric and asymmetric molecules.

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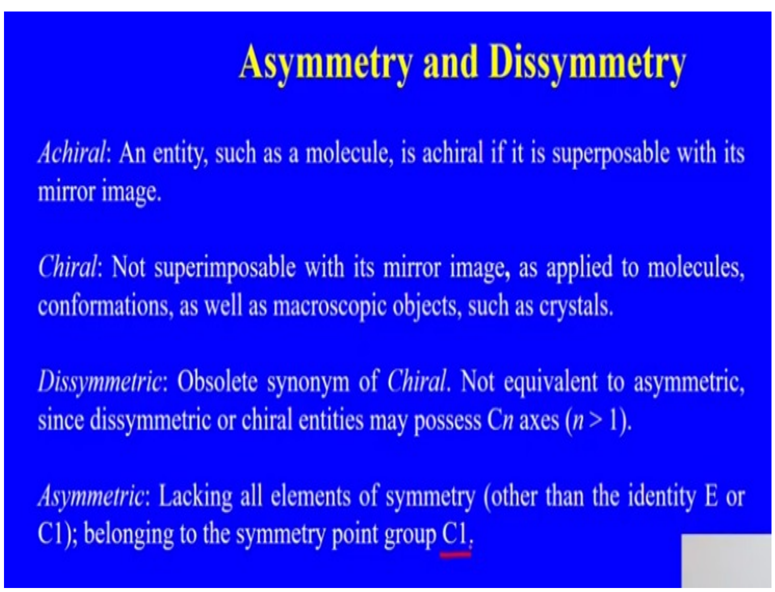

So now if we try to define these terms like achiral, Achiral is assign to an entity such as a molecule which is achiral if it is super imposable with its mirror image. A chiral molecule is not super imposable with mirror image as applied to molecules conformation as well as macroscopic objects such as crystals. When we discuss about the symmetry in this solid state we will see there are chiral space groups that defines different types of crystals.

Then the next type of molecule can be termed as dissymmetric, it is actually an obsolete synonym of chiral which essentially means not equivalent to asymmetric since dissymmetric or chiral entity is may process Cn axes with n greater than 1. The asymmetric molecules are those which are lacking all elements of symmetric other than the identity symmetry or C1 and they all belong to the point group C1.

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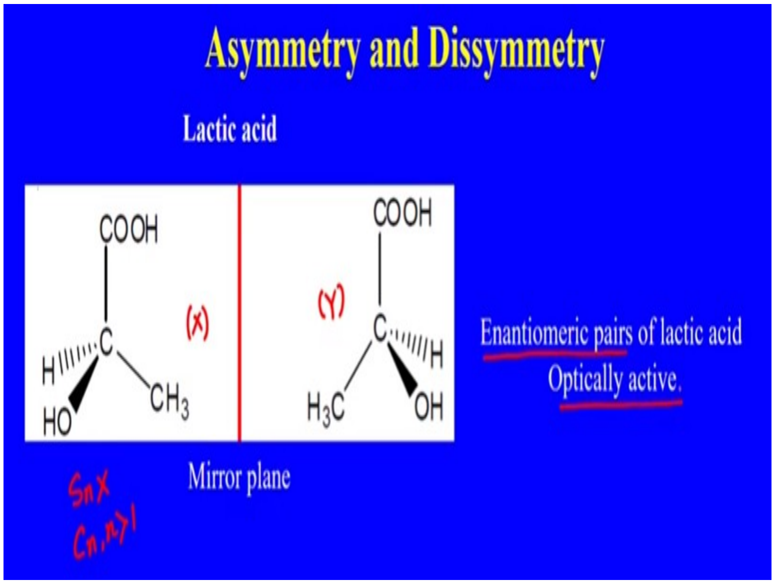

So if we try to look at this molecule lactic acid what we see here that the molecule does not have any alternating axes of symmetric that means there is no Sn. There is no Cn, n greater than 1 so this molecule is an asymmetric compound and the corresponding mirror image is non-super imposable with the original compound. So this one representation X and representation Y are non-super imposable mirror images. So they are enantiomeric pairs of lactic acid hence they are optically active.

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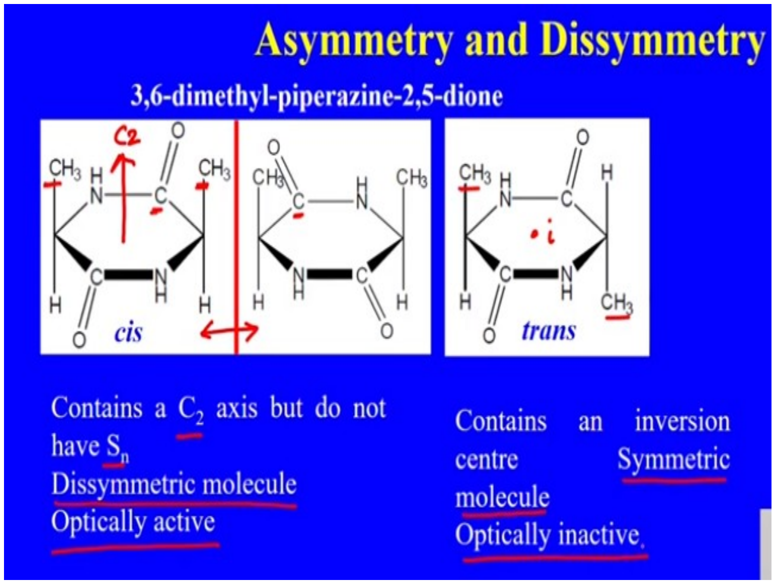

Let us see the case of another molecule 3, 6- dimethyl piperazine 2,5-dione in it is Cis form what we see here is that the methyl groups are upwards and the corresponding mirror image has the Cis form upwards. But this group and that group have changed their positions because of mirror image relationship. So what happens in this we see that contains a C2 axis because this C2 passing through the center of the molecule.

So by rotating this molecule about this C2 axis we get the same orientation of the groups but it does not have any Sn. So we term this molecule as a dissymmetric molecule and hence this becomes optically active because this mirror images are non-super imposable. See the point of optical activity comes from non-super imposability of mirror image. Let us see the case with trans isomer of this particular compound.

So what we see here that the trans compound as methyl groups up and down as a result this molecule contains an inversion center. So this molecule is a symmetric molecule and hence this molecule is optically inactive all symmetric molecule are optically inactive. Therefore in this case we do not need to draw a mirror image and see where they are super-imposable or not.

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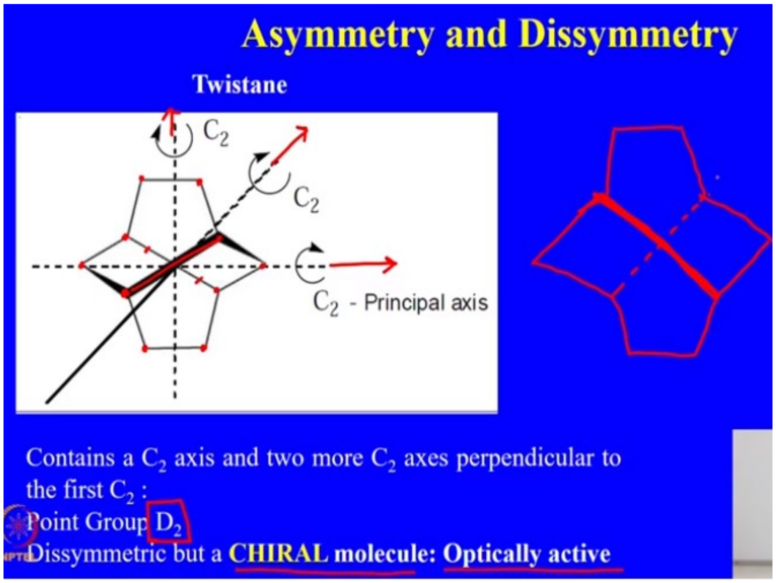

Here we get take one example of a compound called twistane you can easily understand the bonding present here. You have carbon atoms at every point and they are in a twistane conditions and all of them are sp3 hybridized carbon. So what we see in this molecule that there is a C2 axis like this. There is a second C2 perpendicular to the first C2 and there is a third C2 like that perpendicular to the first C2.

So there is one C2 and 2 perpendicular C2's which make it a point group D2 but what we see is that this molecule does not have any Sn axes. So when we do not have Sn but we have C2 and perpendicular C2's make it D2 this molecule is dissymmetric molecule. But is a chiral molecule so this molecule is supposed to be optically active because if you take the mirror image of this compound we will see that the mirror image is non-super imposable with the original compound.

Let us try to draw the mirror image and show it to you. So if I try to draw the mirror image on the right hand side what we should have? They are the groups like this the connectivity that is important between these 2 is now between these 2 groups. The bond which was above of the plane of this paper or above the plane of the projection is now in this orientation. And the bond which was below the plane of projection here is now here and what we see is that this 2 are non-super imposable mirror images. And therefore this compound is chiral and optically active.

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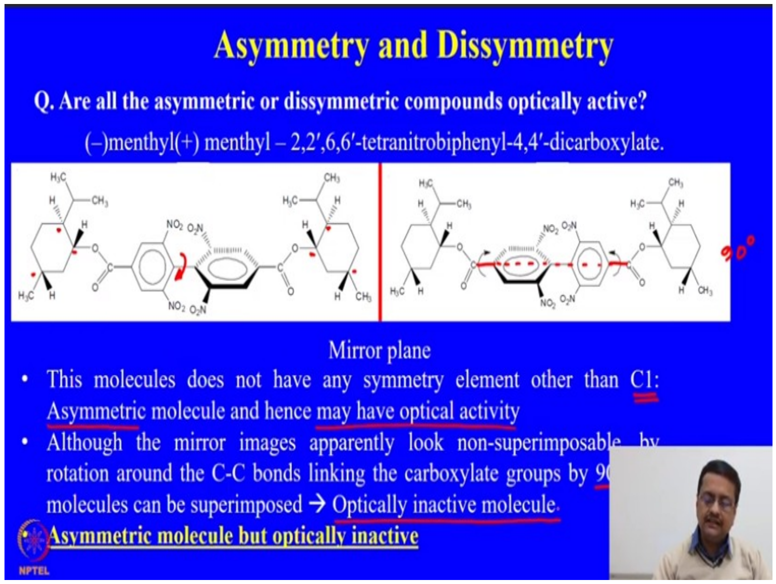

Now the question is we would like to address are all the asymmetric or dissymmetric compound optically active. Let us see with slightly complicated example of a molecule. What we see here in this molecule there are multiple chiral centers on either side. And here we have a restricted rotation about this bond it is a 1, 2 1 prime 2 prime di-substitute tetra substituted bi-phenyl system. And if we take a mirror image of this molecule what we see that you generate this molecule.

So this molecule does not have any symmetry element other than C1 as you can see so this molecule must be an asymmetric molecule. And hence may have optical activity. Now if we look at the mirror images very carefully the mirror images apparently look non-super imposable by rotation around the C-C bond by rotation about this bond by 90 degree the molecules can be super imposed.

If you rotate the molecule about these axes by 90 degree what we see is the same as the left hand side. So by 90 degree rotation of the molecule about that bond makes it super-imposable on one another. Therefore this molecule is optically inactive molecule so this is one example of asymmetric molecule but optically inactive. So we will start discussing about topicity of ligands and faces in the next lecture.