Concepts of Chemistry for Engineering
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Lecture 69
Representation of Three Dimensional Structures

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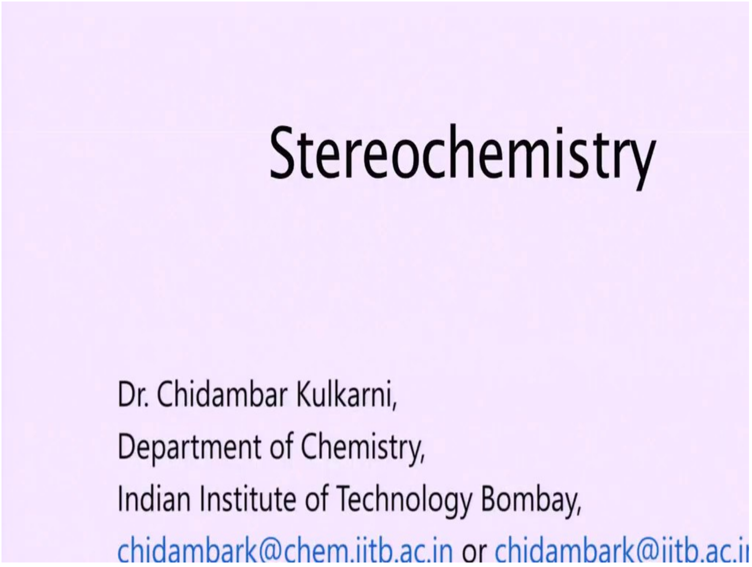

Hello, everyone. Welcome to the module on Stereochemistry. I am Chidambar Kulkarni, at the Department of Chemistry, IIT Bombay. In this module we are going to look at how do atoms arrange in space, and what are the consequences of it, and how do we go about understanding this.

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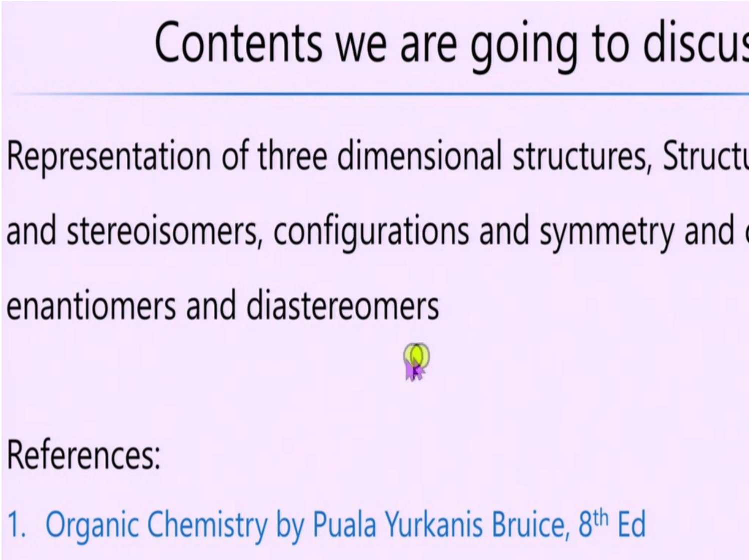

This, the contents we are going to discuss are as follows. First, we would look at the three dimensional representation of organic structures or molecules in space. Why is that important? How did that come about? Followed by, we shall look at, what are called a structural isomers and stereoisomers. What do we mean by this, and what are the different properties, examples and the significance of this.

Following this, we will go a bit deeper and look at configuration, symmetry and chirality, and what is the consequences of these aspects. And then we further delve into what are called as an enantiomers and diastereomers.

And what I am going to cover in this module would mostly be found in either the organic chemistry by this, Puala Yurkanis Bruice, eighth edition, or an online resource called as Master Organic Chemistry maintained by Dr. James Ashenhurst. With this theme that is, now let us get into looking at three dimensional structure of organic molecules.

So, I am sure by the, when I say three dimensional structure of organic molecules, you would start imagining something like this, a tetrahedral carbon, with each of these balls representing different substitutes. You would have sort of heard of this or learnt in your 12th standards.

But what we are going to do today is to actually look at a bit of the origin of this because this is something which is already taught to you, or you know a bit about this. But let us first see how did this come about.

So, to do that, let us transpose ourselves back into the mid 19th century, that is, around 1850s to 1870s. Back then, the concept of chemical bonding, that is, something which we show by this solid line with a solid stick here, was actually not, not very completely understood, it was just beginning to form.

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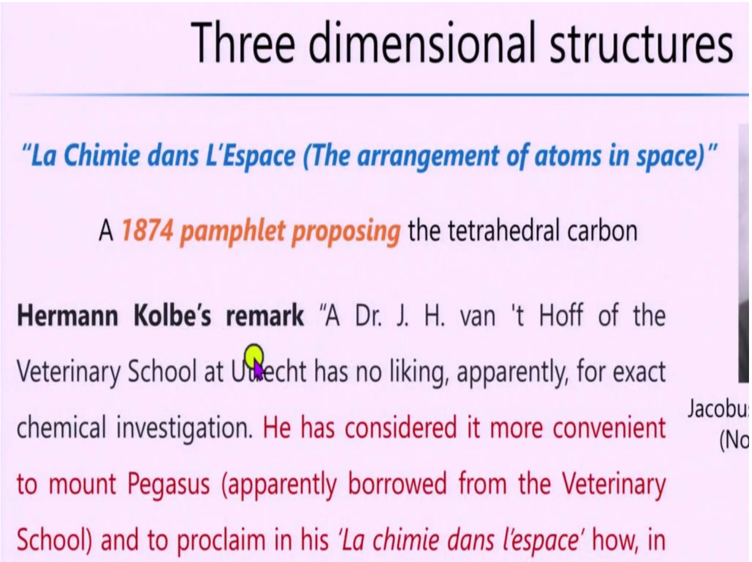

And in and around that time, what happened is that a chemist or a person called Jacobus Henricus van't Hoff from Utrecht in Netherlands, came up with this idea of La Chimie dans L'Espace, meaning or translated to English as the arrangement of atoms in space.

So, what he did was, he looked at various, different kinds of molecules which were being studied at that time, that is tartaric acids, lactic acids and other kinds of systems, and these were mainly extracted from natural products like either grapes, or from meat or from some other natural sources. And what people were trying to do in the 1850s was to actually take, extract compounds out of these and look at the various properties, both physical as well as chemical.

Interestingly, people found that they had compounds which looked very similar or had very similar properties except one or two. But at that time, they did not know how to rationalize or how to put that into perspective.

So having this knowledge in the literature or having this knowledge around, what van't Hoff did was, he went out and studied this, and he came up with this proposition. So this is not an experimentally proof. So that is what I would like you to appreciate, that he came up with this proposition in a pamphlet.

So please note that this was not even a journal article or a very authenticated source. It was a pamphlet in 1874, when we van't Hoff was just 22 years old, he came up with the idea that carbon has a tetrahedral geometry, that is, the one which I am currently holding now. He came up with this idea when he was 22 years old, and this was just an idea or an unproven concept.

So, as you can imagine, today, if I come up with a very revolutionary idea, which is unproven, you are bound to get some slack for it. And that is exactly what followed later. So a very noted and established German chemist by the name of Hermann Kolbe, he was in Germany, and he and he made this remark, which I will read out to you and try and explain to you this a bit.

Dr. J. H. van't Hoff of the Veterinary School at Utrecht has no liking, apparently for exact chemical investigation. By exact chemical investigation he means to do a proper scientific investigation.

He further says, he has considered it more convenient to mount Pegasus, which is an horse in the Greek mythology, and to proclaim in his La Chimie dans L'Espace how, in his bold flight to the top of the chemical Paranassus, which is a very sacred mountain, mythical mountain, the atoms appear to him to be arranged in cosmic space.

So, what he is trying to do is he is basically criticizing van't Hoff of just being more philosophical, and taking a philosophical view on the tetrahedral carbon, rather than coming up with exact proofs of this. This is a very well established chemist called Hermann Kolbe, criticizing the idea of van't Hoff in 1877. This was in, three years later.

So, what followed later was, people actually looked into this idea, and many people bought this idea that the carbon could be tetrahedral. And that is one of the ways to account for or to rationalize the optical activity observed in systems.

So, following this, van't Hoff, even went off, went on to win the Nobel Prize in Chemistry in 1901, along with a French person called Le Bel, who also came up with the idea simultaneously and independently.

So, what this short story tells us is that, first of all, that even if you are young and still naive, you can actually come up with a bold, but a well thought of ideas, which might shake the current paradigm. So that is what is something to keep in mind as many of you and people would come up with various, let us say, strong arguments are ideas.

And second is, not always the proof comes first. Sometimes the ideas or the propositions come first, and then they get sort of, goes around and people discuss these ideas, then at a later time the proof comes. So these are the two points which I want you to take away from this.

So, having looked at the story behind the tetrahedral carbon and the discovery by van't Hoff, now let us see how are the different ways in which representing a 3D structure. And broadly classified, there are four different ways in which one can represent a three dimensional structure.

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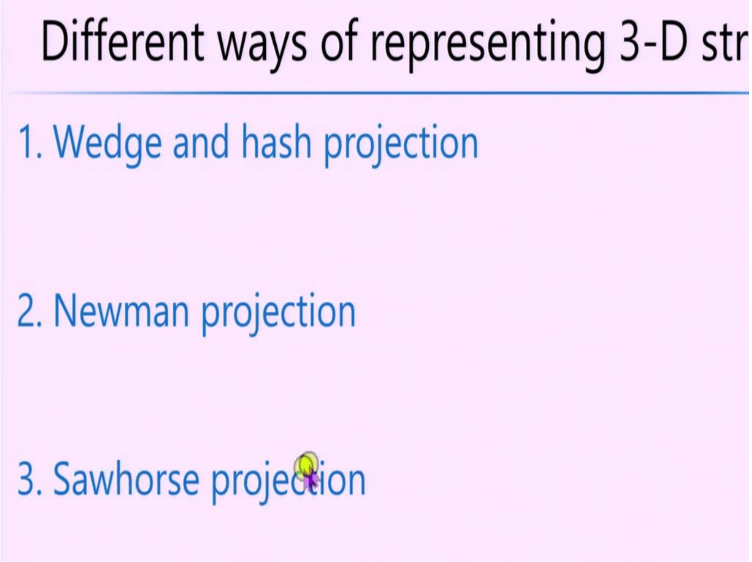

The first one is called as the wedge and the hash projection, which is the most popular, and the second one is called as the Newman projection, which is also quite popular and used, and third is called as a sawhorse projection, and the final one is called as a Fischer projection which was developed by Emil Fischer. So we are going to go into each one of these and look at how do people represent 3D structures in each of them.

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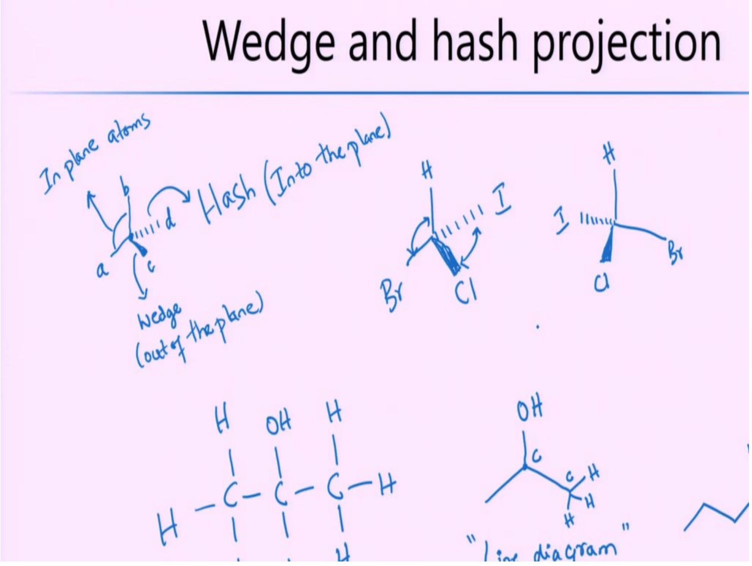

Let us begin by looking at a wedge and a hash projection. So to do that, we are going to take a example here. Say I have central carbon atom which is drawn here, and, and then I have a central carbon atom, which is at this, then I have substituents a, b, c and d. So if you now look at it, I have represented it by two, kinds, three kinds of lines.

One are these two lines which are called as the in plane, in plain atoms. And I have also drawn something which is a bit a solid line, which actually is protruding out. And this is what is called a wedge or a wedge projection. And this is by convention taken to be coming out as a plane towards us. So this is a wedge. And this comes out of the plane. And this dashed, hashed line or dashed line, this is what is called as a hash. And this actually goes into the plane, into the plane of the board.

So just to illustrate this, if we take a, let us say, if I take this particular tetrahedral carbon, which I am showing, I can hold any two of these in the, in one plane, that is, let us say I am having these two atoms are in one particular plane, that is, the green as well as the white or in one plane, then you have the orange, which is product, coming out of the plane towards you, this is the wedge which is protruding out, that is a c substitution. And then on the backhand side, I have another one which is the cyan color, which you can see, it goes back.

So, in it, so if you have a tetrahedral carbon like this, with the central carbon being the black one, what you see is that you can hold any two of them in the plane of the board, on the, in one plane, and then you have two atoms which are either pointing away or behind the plane of the paper.

So, this is what is called as a wedge and hash representation. And in this particular representation, people typically write structures like, if I take tetrahedral carbon, and I put a hydrogen, bromine chlorine, iodine, what this tells me is that I have the chlorine atom, which is actually coming out of the plane of the board or of the screen, and the iodine atom actually goes behind the screen.

And what you would typically notice is that these two, the ones which are in the plane, that is, these two, are typically adjacent to one another. And these two which are either behind or in front of the plane are also adjacent to each other. So this is the most correct way of doing it. And there are many permutations and combinations one can do, that is, you can have, a different way is this.

So, you can have the iodine, you have the chlorine, the bromide and the hydrogen. So in this kind of representation, what you are, all you are trying to show is that the solid lines are in the plane, and the wedges are coming out of the plane and the hash lines are actually going behind the plane.

And another important aspect is that if I take a simple alkane, like let us say if I am trying to write a C, have an OH group here, alcohol, then I have a hydrogen, so a structure like this is usually represented by something like this in most of the organic chemistry, that is, this is called as a line diagram or a line representation of the structure.

And here what is assumed is that the, once the, if I do not show anything that means there is already a carbon here. In this particular atom there is one carbon. And this is also assumed that there is a carbon, and then you have three hydrogens here which are attached.

Similarly, if you want to look at another structure, larger structure, you would do something like this. Let us say I have an alcohol here. In this case, what is assumed is that you have two hydrogens which are attached to each of these corners, which is a carbon atom. And this is what is you, what is usually found in most organic chemistry textbooks. And this hash and the wedge, which I told you a second ago, this is what is usually used to represent the stereochemistry or orientation of molecules in space.

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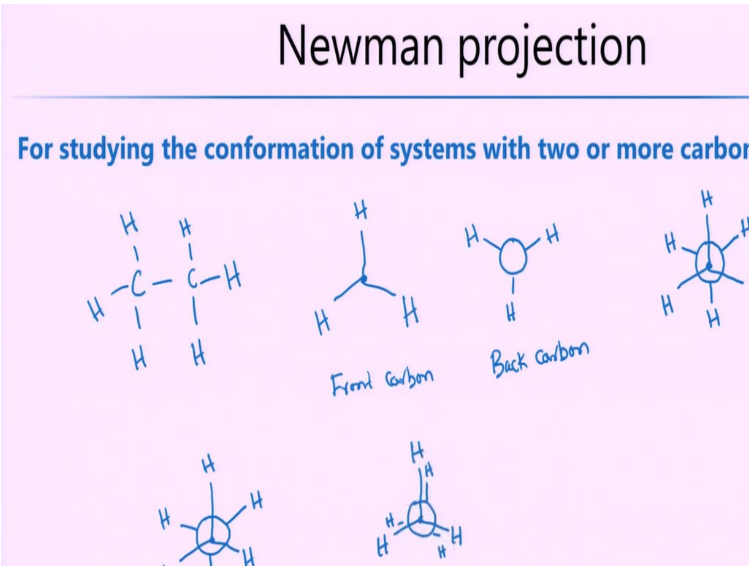

Alright, so now let us look at another important projection that is called as a Newman projection. So, so far what we looked at was a arrangement around a single carbon atom, that is, if I have a carbon atom and four different substituents, like the one I showed you here. So now what happens if I go to more than one?

So, for example, if I go to an ethane molecule, so here you see an molecule of ethane, where I am trying to show where the black ball is the carbon, and the white ones are the hydrogens which are attached to it. So how would one go about writing the conformation or the projections of this?

So, let us first write down the structure of the Ethane. So I have a C C, and then I have three hydrogens attached to it. And if I want to look at it, then there are many different ways one can look about it. But a simple way is that if you now take this particular molecule, and since there is a single bond around the, between these two carbon atoms, this is actually free to move around. It can, I can actually if I hold it like this, I can twist the second carbon atom and I can get different conformations of this.

So, to represent this, what one can do is, if you are looking from the, from your angle, you will only see this particular carbon atom and three hydrogens, you would not see the back carbon atom because that is being masked by the front carbon atom.

So, if you look at it along the C C angle, or the C C bond, bond, bond, what you would see is that you would see the front carbon as the following. This is the front carbon, and you have the hydrogen. This is the first, front carbon, is what I am trying to draw currently.

And if you look at the back, you actually do not see the back carbon, but you only see the hydrogen, that is, if I put it in this conformation, you will only see the three hydrogens. And that is represented by drawing the circle, and these bonds to show that there is an atom which is connected to it.

So, this is the front carbon, and this is the back carbon. And this is when I am weaving along the carbon carbon bond. And if you want to now get the complete picture of this, what we would do is we would just combine these two and then you will have something like this. The front carbon with a dot here and three hydrogens attached to it. And the circle represents the back carbon, and then again, that is attached to three hydrogens.

So, this is what is called as a Newman projection, in which you are actually trying to look at the, trying look at how do two molecules which are, when you look along the C C bond, how you can represent the molecules in a two dimensional picture. And this sort of pictures are typically used to understand the conformations or the conformational analysis of alkanes or other molecules.

And so, to just to show you this, let us say if I, there are two different possibilities of this. One is called as a staggered and another is called as eclipsed. I am going to draw the same picture here, of the circle, and I am writing the front carbon again, and with attached to three hydrogens, and now the back carbons, I am writing at about 60 degrees from each other. And this is called a staggered, staggered conformation.

And if you want to understand this, if you actually now look at this front carbon, you see that these three are here, and the, the other three hydrogens attached to the carbon behind are actually at 60 degrees between them. So what I can do is I can actually go on flipping this, go on turning this, then I would end up in an conformation where you will actually not see from the back carbon, as well as hydrogen, that is, there exactly behind the front carbon. And this conformation is what is called as a eclipsed conformation.

So, I will, so again, I am drawing the circle for the back carbon, the front carbon with the three hydrogens attached to it, and now what I am going to do is I am going to draw just,

just behind it, to show that they are actually eclipsed. So this is one of the ways in which one can use this Newman projections or to look at the conformations of simple organic molecules. And this is actually a widely used technique to see how, how, let us say staggered or eclipsed or gauche, or different kinds of conformations are possible in alkanes.

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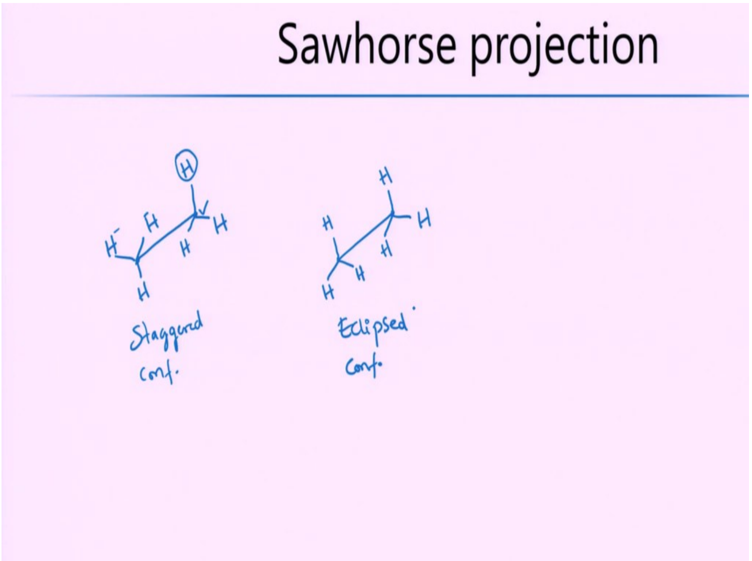

Now we will move on and look at another related projection which is called as a sawhorse projection. So till now what we did was, in the Newman projection, we took this ethane, and we looked along this bond, along the C C bond, just write down the C C bond. Now what we will do is we will actually take a slightly angled view of the C C bond and see how does it look at. So that is what I am going to draw, try and draw now.

So, I will again use the same example. But remember, now I am trying to look at it from a side, not along the C C bond. So in this case, what can happen is, this is one carbon atom, and this is another carbon atom, I am drawing an exaggerated bond here. And then, so this is what you would look as a sawhorse projection, or when you look at it from the side.

That is, if you actually look at it from, from the side, you would see something like this. Let us say in this kind of conformation, you would see both the carbons and you will also see that one of them is up, that is the back carbon here, which is this particular carbon, And, then you have the front carbon in which the hydrogen is down, that is what you see on the screen. And these two are actually up.

But now the only difference between the Newman and the sawhorses is, I am now looking at it a slightly angled version so that I see both the front as well as the back carbon. And this conformation is also used in looking at the conformational analysis. And again, here one can draw both eclipsed and staggered conformations.

As you might have already noted, this is a staggered conformation because you see that this particular hydrogen is now exactly 60 degree between these two hydrogens, on the front carbon.

And if you want to now look at the eclipsed, so I am going to go ahead and draw again our C C, these two carbons and I will put this at the same and two hydrogens. And here I am going to put the same because I am looking at a staggered, eclipsed conformation. So this is the eclipsed conformation of ethane.

So, I hope you can see that this is now, you can see the eclipse much more easily in the, in this particular sawhorse conformation compared to looking at it in a, in a Newman projection because they, both of them are completely one behind each other. So you cannot really see what is happening.

But if we now look at it in this particular fashion, you see that these are exactly identical, both in the way they are arranged. And that is much more evident if you just look at it a slight angle. And this is what sawhorse projections are useful for. They actually tell you a bit more clearly what, how do atoms are arranged in a longer C C bond.

And whatever I told you, both the Newman as well as the Sawhorse projections are extensively used in looking at the conformation of molecules, that is, if I want to look at the barrier between this, that is, if I rotate this particular bond, what is the conformational energy or the penalty I have to pay. To understand this, these models are excellent to understand them.

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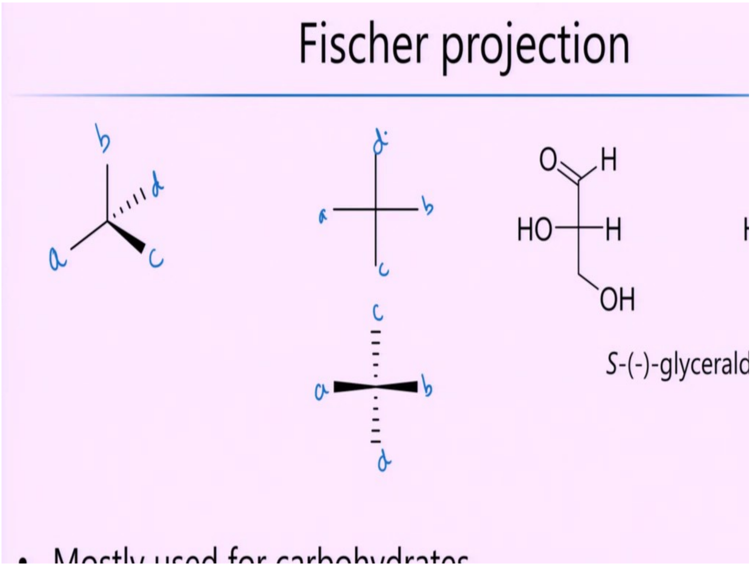

Alright, so now what we will do is we will go ahead and look at one last conformation that is called as the Fischer conformation or the Fischer projection. So here I am going to draw similar tetrahedral structure, which I showed you previously, and then I have placed four different substituents a, b, c, d, which is what we looked at as a wedge hash representation.

However, what people have done is, it is more mostly comes from Emil Fischer, where one can actually draw them as this, that is, you can draw them as, as a cross line. And in this cross line, what you do see is that you have both those substituents which are actually coming out at you, that is, you have a, b, you have a b, and then c, d which are at the back.

And this was done with the purpose because they wanted to study the arrangement of sugars or mostly carbohydrates. And these are ideally suited to study the projections of carbohydrates rather than usual organic molecules.

So here, what you actually do is you take the same tetrahedral carbon, and here what I am going to do is, I will not cut through any of the any of the atoms, I will put, pass a plane which is actually going like this between, along this direction. So then what you see is that I have two substituents at the back, and two substituents in the front.

So, the ones which are actually coming in front to me are labeled as a, b in this particular diagram, and the ones that are actually going back are labeled as c, d, that is, in the vertical direction. So whatever is actually coming towards you, that a, b is shown as a horizontal line, and the substituents which are actually going back is shown as a, it has, as a vertical line.

So just to show the utility of this, here is the structure of S glyceraldehyde monosaccharide. And this is the usual way in which it is represented, the one on, the Fischer projection, which is shown on the left. And if you really want to make it more clear, you can actually put the hash and the wedge. That will make it clear the way in which it is actually represented.

Although these are actually nice representations, Fischer projections, but these are actually mostly suited for carbohydrates, and they are typically not used for most organic molecules. So they have a very limited utility when it comes to organic or bio, biological molecules. So with this, we stop here and in the next lecture, we will actually look at what are the different kinds of stereoisomers and how do we study them. Thank you.