Concepts of Chemistry for Engineering
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Lecture 70
Structural Isomers and Stereoisomers

Hello, everyone. Welcome to the module on stereochemistry. We will continue our discussion on stereochemistry and three dimensional arrangement of atoms in space. Before we do that, let us just do a quick recap of what we looked at in the last lecture.

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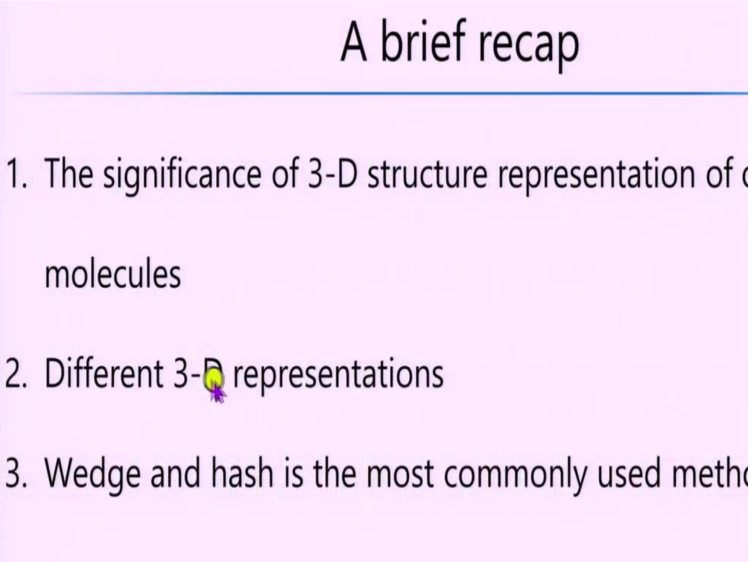

A brief recap

1. The significance of 3-D structure representation of

   molecules
2. Different 3-D representations
3. Wedge and hash is the most commonly used meth

In the last lecture, we first looked at what is the significance of three dimensional structural representation of organic molecules. Here, we had seen the story of van't Hoff and how he came up with this brilliant idea of three dimensional arrangement of organic molecules, and that was consequently proved by experiments.

And we also looked at different ways of representing organic molecules in 3D by using either wedge hash projection or Newman projection, sawhorse projection and finally, Fischer projections. Among this, we had concluded that the wedge hash is the most widely used method to represent organic molecules, and we will take, build on this and look at what are called as isomers in this particular lecture.

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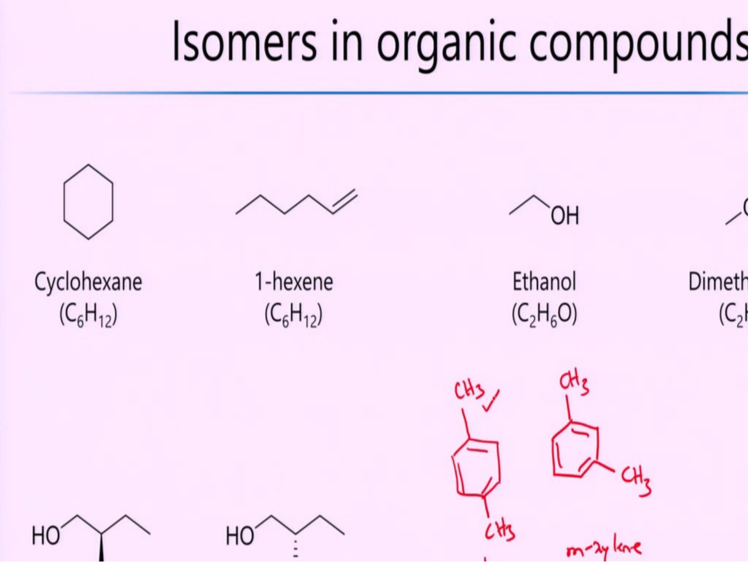

Isomers in organic compounds

So, I am sure you would have come across this idea of isomers in organic compounds or in other branches of chemistry. Like the one shown here, that is, cyclohexane and 1-hexene have both the same empirical formula that is C 6 H 12. But, the way in which the atoms are connected in three dimensional space is totally different between these two organic molecules. So, this is one particular example of, of isomers in organic compounds.

And another is a very simple example where if you take ethanol, that is, C H 3 C H 2 OH, and that is, again has the same empirical formula as that of dimethyl ether which is C 2H 6 O. So, although these compounds have a similar empirical formula, they could have different physical or chemical properties. The properties could be melting point, boiling point, dielectric constant, dipole moment and many other.

And one more example of isomer in organic chemistry is this 2 methyl butanol, which is shown here, where the only difference is in the way in which the carbon is arranged, that is, the CH 3 group on the second carbon either comes out of the plane or goes behind the plane. This is what is also another example of isomers.

So, before we go ahead and look at some of the classification of isomers you might be interested in asking this question of why to study these isomers because this looks very simple and very, very naive. Is there any consequence of this or is there any applications of this?

Just to point to one, there is a very important application, that is, if you take a, if you actually take a simple molecule such as this, which is shown here, which is the xylenes, so there are three different possible isomers. One is the para-xylene, that is, the CH 3, you have. So, this is called a para-xylene. Similarly, you could have an ortho and meta-xylene. So, this is meta-xylene. And finally, one can also have an ortho-xylene.

So, these compounds are actually obtained from, from the cracking of crude oil. And once you get these, these are as, you get them as a mixture of all the three, that is, para-xylene, meta-xylene and ortho-xylene. And it is actually very, very difficult to separate them because they have very similar properties, their chemical and physical properties. They are, they are different, but they are not exactly the same. So, the difference between the properties is minor.

So now what is the consequence of this? So if you actually look at all the water bottles which we use for drinking, that is, the polyethylene terephthalate bottles, they are typically made by, they are made by para-xylene, or para-xylene is one of the starting materials to make these para, PETE water bottles. So, it is a very important commercial starting material to, and it is very important to separate it from the other isomers like meta xylene and ortho-xylene.

So, this very simple idea of isomers can actually have a profound influence on the material properties. So, even today in 2021 there is actually research going on how to efficiently separate para-xylene meta-xylene and ortho-xylene in the crude mixture, because that has a very important consequences for other materials which were, which we use in our day to day life, such as a polyethylene terephthalate bottles.

So, I hope this at least gives you an idea or convinces you of the importance of these isomers. And it is not just an academic interest, it has relevance in our day to day life as well.

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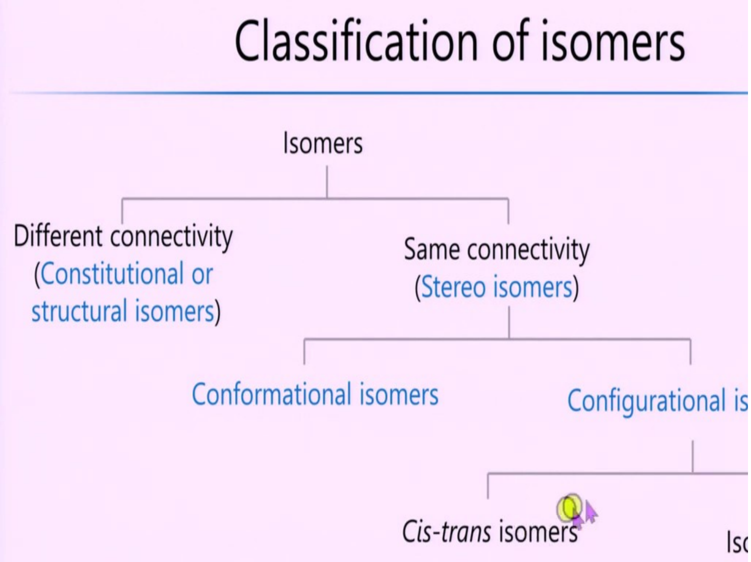

Classification of isomers

Isomers

Different connectivity
(Constitutional or
structural isomers)

Same connectivity
(Stereo isomers)

Conformational isomers

Configurational is

Cis-trans isomers

Is

So, with this, let us get in to now, looking at isomers in a little more detail. And so what do you see is that isomers are compounds which are defined as having the similar empirical formula, but they could have a different chemical as well as physical properties. And these can be further subdivided into two categories.

First one is called as the constitutional or structural isomers, that is, if the atoms are connected in a different manner between the two molecules which we are trying to compare then it is called as a constitutional or structural isomer. And the second one is called as the stereoisomer, that, is the connectivity remains same, but the way they are arranged in space is different. So, the difference between these two may not be apparent at this moment, but we will delve into this in a in a minute to see what is the exact difference.

And the stereoisomers can further be classified into two (pa), two more categories called conformational isomers and configurational isomers. And so very subtle, but an important distinction between these two classes, conformational isomers actually have, do not involve any change in the, do not any, involve any bond making or bond breaking.

Whereas, to go from one isomer to another isomer of a configurational isomer we have to break a bond and arrange it in a different form to get a, another isomer. So, I will show you examples of that as well.

And further these configurational isomers can be again subdivided into two more categories, which is called as a cis-trans isomers, and the other one is the isomers containing an asymmetric carbon. And this is a very, very, both of these are very important classes. And they have a profound influence on our day to day life as well. So, we will delve into that in a bit.

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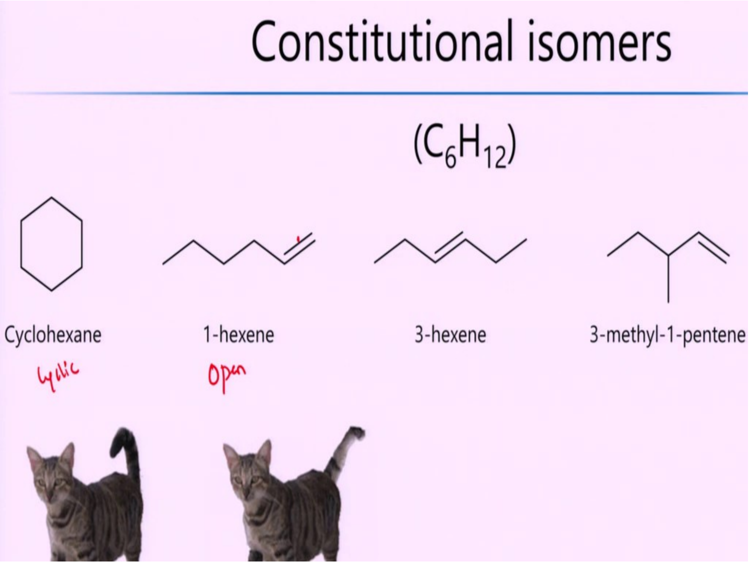

Constitutional isomers

(C_6H_{12})

So, let us just first begin with the constitutional isomers. A few slides ago, you saw that we had looked at cyclohexane and 1-hexene, and we said that they have the same empirical formula, that is, C 6 H 12. But the, if we now look at the chemical connectivity, I hope you see that the chemical connectivity is completely different between cyclohexane and 1-hexene. This is a cyclic molecule, cyclohexane, whereas here you have an open chain system. This is an open chain, and whereas here you have a cyclic.

As a consequence, the properties of these systems will also be different, that is, melting point, boiling point, refractive index and many such properties. And not just these two molecules, you can also draw another isomer of this, which is a 3x-hexene, which is very simply moving the double bond from, double bond from the first carbon. From here, the double bond to the middle carbon here. That is one, you would get a 3-hexene.

And you can also come up with more elegant structures, that is, 3-methyl 1-pentene, that again, has a same empirical formula that is C 6 H 12. And finally, you can also come with a little more innovative ideas like 1-ethyl 2-methy; cyclopropane, as shown here, on the hand side.

So here what you are saying is that with a given molecular formula, you can write many, many different kinds of structures. And all of these are having completely different connectivity, that is, in cyclohexane, it is a, it is a closed structure. Like, for example, here, as you can see in this, it is a completely closed structure of a cyclohexane, whereas if you now go to the 1-hexene, it is an open chain structure. And if you now go to the completely extreme, you have a cyclopropane derivative as well.

So just to make you understand a bit better, if we can take the analogy of these cats. And I hope you can see that the one on the left, which is here, is a, is a normal cat with the four legs and a tail. And to show you the constitutional isomers what we have done or what, what is done here is that you take the same cat, chop off one of the legs, and put it back into its, the position of the tail and take the tail back and put it in the position of a leg.

So, these are classic examples of constitutional isomers because to go from one form to the other, you need to rearrange or you need to break some bonds and make some more bonds at different places. So, I hope this gives you an idea of what do you mean by constitutional isomers.

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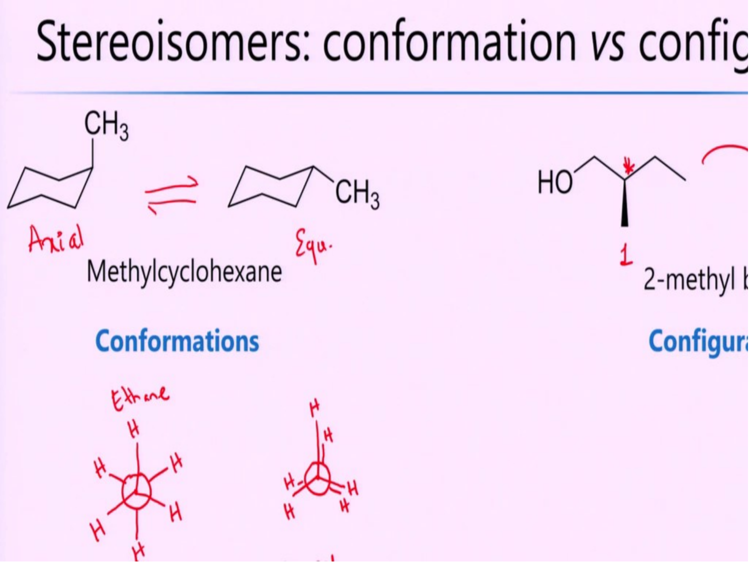

Stereoisomers: conformation vs config

Methylcyclohexane

Conformations

2-methyl b

Configur

So now, let us go ahead and look at stereoisomers in a bit more detail. So, we told that in stereoisomers the arrangement, the, you do not have braking of, you do not have a significant change, but the spatial arrangement is what, what differs. So, in this, there are two categories. One is called as a conformation another is called as a configuration.

So, the first one is, what we are looking at, is a conformation, here. That is, we have a methylcyclohexane. That is, what I am trying to show here is the same thing here. So, I have a cyclohexane which is in the chair conformation, as you can, I hope you can all see this.

There is a cycle exam with the chair conformation, and then I put the methyl group, that is a C, CH 3 in the axial position, here. And I can actually twist this, this boat. And if I twist it then I can actually get this axial back into the equatorial position, which is shown on the hand side. And this can be done without breaking of the bonds.

And this equals, this, let us say, so this conversion between the, between the two forms, that is, the axial, axial CH 3, and the equatorial CH 3 is actually continuously taking place at room temperature. So, you would, typically when you take a bottle of methylcyclohexane, if you buy it from a commercial source, what you would get is you will always have these two forms which are actually equilibrating with one another.

And you cannot actually differentiate to distinguish them unless you go to a very, very, very low temperature, something like minus 50 or even lower, then you might start seeing the signatures of these two different forms, that is, axial and equatorial. So, this is what we call as conformation, that is, the isomers which do not involve a breaking of bonds, they actually undergo conversion between them rapidly without involving a breaking of a bond.

And the next one is what is called as a configurations, that is, if you look at this particular example here, which is shown on the hand side, here what I have taken is a 2-methyl butanol, is what I have taken, and this particular carbon is a stereo center or chiral center.

And to go from this to this form, that is one enantiomer to another enantiomer, I will come back to this term, what do we mean by enantiomer in either this class or the next class, so one has to actually break the bond. You cannot interconvert between these two forms, that is, between, say, form 1 and form 2, by just rearranging the atoms. One has to actually break the bond and again formula a different kind of a bond.

So that is what, and these are actually isolateable. You can, one can actually isolate them. And they have very different, they have different properties, mostly in terms of the way they rotate a plane polarized light. And rest all of the properties of these two forms, that is, 1 and 2, remain the same.

And it is very important to get this distinction between conformations and configurations because both the words look very, very similar. So, please do not get confused between conformations and configurations.

So, to just to illustrate this further, I will show you, I will give you one more example of conformations, which we looked at previously. So, so if you take the example of the ethane, so I would show you in the Newman projection that I have a front carbon which I am not drawing here, I have hydrogens and this is a back carbon. So, this is what we looked at, the ethane staggered configuration. This is the standard configuration.

And now we have also looked at another configuration, that is, conformation, that is, the eclipsed. This is the back carbon, and you have, similarly, so this is the eclipsed. So, these two are actually conformations and not configurations because, if I again go back to my model of ethane, what I have is, I have this, let us say, I start with a staggered configuration, I have, if you look at it from this, along this bond, C C bond, you see that this actually does not, this hydrogen does not coincide with anything at the back.

You clearly see three in the front and three in the back. I can just rotate the back carbon, the back carbon along the C C bond to get to the eclipsed where you actually do not see the back carbon along with the three hydrogens. And this I can do without any breaking. So, I can just rotate freely along this bond, along this C C bond. And this is what is called as a conformation rather than a configuration.

If I have to let us say change something, like for example, if I have to go from particular configuration, say I have a, in this particular example, I have chosen, let us say, in this particular example, I, one atom is in front another is back. If I actually want to flip it, if I want to really flip it and change it or to make another enantiomer, I will have to break the bond. Without that it is not possible. And this is an example of a configuration, and not a conformation. So, please keep this distinction between a conformation and a configuration.

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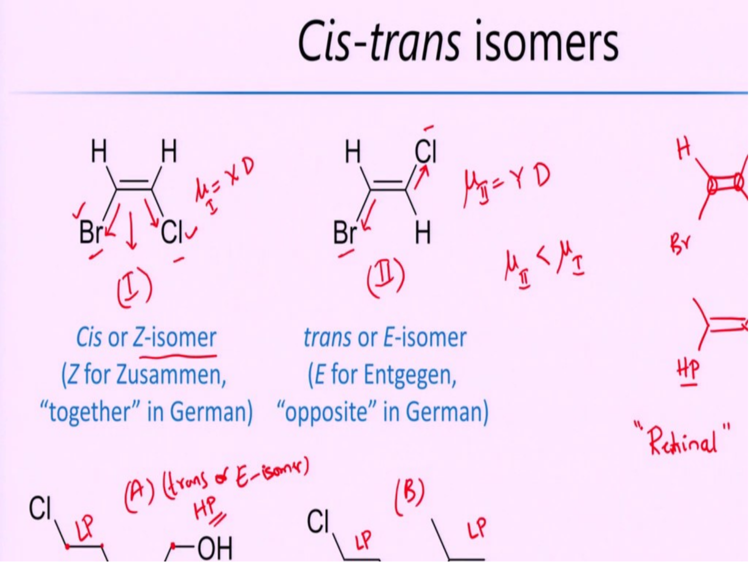

Cis-trans isomers

Cis or *Z*-isomer
(*Z* for Zusammen,
"together" in German)

trans or *E*-isomer
(*E* for Entgegen,
"opposite" in German)

So now let us go ahead a bit in the, in these configurations and look at two different kinds of configurations. In the previous example, here, I hope I have shown you that this particular example on the right hand side is where the stereocenter is different on the carbon which is marked with an asterisk.

But there is also another kind of configurational isomers, and that is called as a Cis-trans isomers. So, in this particular case, what happens is that if I, if I take a, so what, all the while now we were looking at actually a C C single bond. If actually put a, two bonds between the two carbon atoms then this rotation actually is now completely hindered because you have an orthogonal p-orbital, you have p-orbital which is actually bonding between these two. And that will not allow this carbon to rotate freely.

So that is why you only have a free rotation along the C C single bond and not along the C C double bonds or even the triple bonds. So, now once you cannot rotate freely, then you will actually get the isomers based on how you substitute in ethene. And that is what we are going to look at in terms of the cis and the trans isomers.

So, if you now take the, if you now take this particular ethene, let us say for example, which is shown here, and I, it has been now substituted with the bromine, chlorine and the two hydrogens. This is one of the form.

And you can also do it in a slightly different form, that is, you can have the chlorine on the other position, and on the, on the other side of the double bond and the bromine on this side. So, this would actually give rise to two different isomers.

So, these are two different isomers. If you want, I will call them form 1, and form 2. And these are actually completely isolateable, you can isolate them as two different products. They have different melting points, the, they have different boiling points based on whether it is a solid or liquid, and they will have different dipole moments as well.

So, I hope that is, at least the dipole moment part is apparent because here you will have a, this bond is now polarized along this direction, and here you also, you have a polarized along this section because you have electronegative chlorine and bromine. So, in that you will have a vector reduction of the dipole moment which would be somewhere along this direction. However, so thus you will have a, mu would be some number which is, let us say, I am putting x, x Debye.

However, if I go to this form, the form two, I will have one, the vector along this direction, and the other vector will be along this direction, which is the opposite. And if I add these two vectors vectorially, individual dipole moments vectorially, then I would get a, I will call this mu 1, and this is mu 2, I will get a number y Debye.

Because the two dipole moments are opposing you would have the mu 2 being less than mu 1. And this is clearly borne out based on how the atoms are arranged in the space, that is, either they are arranged on the same side or they are arranged on the opposite side of the double bond.

So, and the nomenclature for this is as follows. If you have both of these on the same side, then you call them as a cis, that is, they are on the same side, or you IUPAC nomenclature will be, it is called as a Z-isomer, and this Z comes from the Zusammen, which in German means together, that is, you have both the bromine, as well as the chlorine together. That means they are on the same side of the double bond. So, that is why it is called as a Z-isomer.

And if you now go to the, the structure 2, it is called as what is called as a trans, or they, they are on the opposite side. Or it is also called as, in the IUPAC, E-isomer. Here, E stands for the Enti, Entigegen, which in German means opposite.

So, I hope this gives you an idea of how, by just going from a single bond to a double bond, you can first completely do away the free rotation. Now we have restricted rotation. And that leads to the isomers called as cis-trans isomers. And the way we, way we get to them, I will tell you in a minute.

So let us say if I have a double bond, now, like this, with substituents, say, bromo and H, I am going to just take the same example here, chloro and H. So, to do this, what is typically done is on each of these carbon atoms, that is, this and this, you need to look at the priority of the atoms.

So here, and that is done by looking at the atoms with the highest, highest atomic number will have the higher priority. So, obviously, in this structure, bromine has a higher atomic number, so this would have a higher priority. So, I am just going to write it like this, higher priority. And if I come to this, again, here, chlorine has a higher priority. So, I am going to write it as a higher priority.

So, if I do this, now I see that both the groups on the carbon atoms having a higher priority are on the same side. And then I would name this as a cis or a Z-isomer. You can do the same exercise for the second form, and you would get the trans form. So, this looks obvious because you have hydrogens and chlorines, which are very easy to distinguish.

So now let us look at one example where it is a little more trickier. So, here I have shown you two forms, that is, let us call this A and B. I am going to call this form as A and this form as B. So, now let us go ahead and try to look at the priority first, because based on priority we are going to assign which is the highest priority.

So, let us take the structure A, and let us start from this particular carbon here. So, I have a carbon here, and again a carbon here, so their priority is the same. So, now I need to move to the next carbon, the next atom. So, here I go to the next atom. Here, the next item is again carbon. Whereas, if I move to the next item, this is chlorine. So, obviously this has a higher atomic number. So, this would get the highest, higher priority. Higher priority, lower purity, I am putting it as LP.

Now I am, come on this carbon atom, which is this. If I go to the first attachment, it is again a carbon here, similarly carbon here, so not a lot to distinguish. So, now I need to move to the next atom. And if I move next, here, I have again a carbon, or a carbon. Whereas, on this substituent, if move ahead, I have an oxygen atom, which has a higher atomic number compared to carbon. So, now this would be the highest priority and this would be the lowest priority group.

So, in this case, now what happens is you see that both the groups which have the highest priority are on the opposite side, that is, then this would be a trans or an E, or E-isomer. So, similarly, if you do the same exercise here what you would get is, you would get the highest priorities on this carbon here, and the lowest priority is this, based on the same arguments as on the structure A.

And if you come to the other carbon atom here, you will get the highest priority on the, highest priority group is now actually lower, or it is on the same side as that of the other carbon. And now you have the lowest priority group this side. So, in this case, what you see is that both the groups which has the highest priority are on the same side. That means, this structure is I, cis or you want to call it as a Z-isomer. I hope this gives you at least some idea of what, what do we call it as a cis-trans isomer.

So now, again you must be wondering, what use is this of, or is this just purely for an academic purpose, or just to study? Not really. So, the answer is that these kinds of cis-trans isomers are actually very, very critical and in fact important for the vision which we are all blessed with.

So, the fact that we see different molecules or different colors and things around us is based on this continuous cis-trans cis-trans rotation in our eyes in a molecule called as retinal. And this particular molecule is the one which would, retinal is the molecule which is actually responsible for undergoing continuous cis-trans cis-trans isomerization in our eyes. And this isomerization actually is what is, gives rise to the vision, which we all observe.

So, I hope this gives you an idea that these isomers, which might look very simple, with the structures, which we have shown, actually have a very profound influence both on the materials we come across as well as in the biological processes.

With this, we stop here. And in the next lecture, we will look at a bit more closely on stereoisomers and what are called as enantiomers and diastereomers and what role do they play in various kinds of materials. Thank you.