Structures, Stereochemistry and Reactivity of Organic Compounds and Intermediates: A Problem-Solving Approach

Professor. Amit Basak

Department of Chemistry

Indian Institute of Technology, Kharagpur

Lecture No. 13

Revisiting Conformational Analysis of Perhydroanthracene

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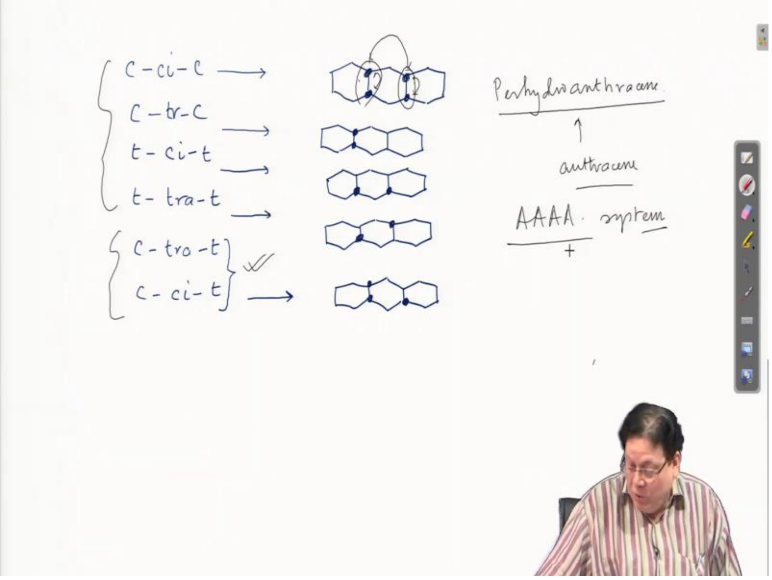

Hello, welcome back to this course on Structure Stereochemistry and Reactivity of Organic Molecules and Reactive Intermediates: A Problem Solving Approach. So, in this lecture we are going to revisit the confirmation analysis of a tricyclic a tricyclic cyclic hexane system that is in this case we are selecting that perhydroanthracene, we have already discussed the confirmations of perhydroanthracene, but just because it is a problem solving approach, so we should again revisit all the concepts has many times as possible during this course.

So, perhydroanthracene in is basically the fully hydrogenated from of anthracene and during hydrogenation what you are doing you are creating forced stereogenics centres as shown here and these force stereogenic centres are all similar that means similar sort of groups are attached, so this system is called AAAA system. Remember perhydrophenanthracene is ABBA system, whereas perhydroanthracene in is AAAA system.

Now, the more similarity you have in a system the there are more chances that you reduce the number of isomers that are possible stereoisomers that are possible. So, here in perhydrophenanthrene which was ABBA system there are 4 dl pairs and two optically inactive forms, one of which is a true Meso another is a non-resolvable dl pair and in case of anthracene it is one less here there are this I have written down that the isomers are c-ci-c c-tr-c and then cis a t-ci-t remember this middle ci mean cisoid middle tr means transoid, otherwise they the two ends the c means cis t means trans.

So, these are the straight cut 4 stereoisomers that I have written in their relationship stereochemical relationship showing their stereochemical relationship and there is one more which is cis transoid and t so c-t-t you can say or c-c-t cis cisoid trans. In this case actually this is basically both are same, so that reduces the number of isomers by one, so there are basically 5 stereoisomers some of which are dl pairs and some of which are meso that are possible.

So, you know that like the perhydrophenanthracene, here what you do while drawing this drawing the confirmation, remember the our target is that we want to answer the following questions, one is first of all, how many stereogenic centres are present? That answer we have got 4. Then is it what type of system it is? It is AAAA system. And then they questioned up the isomers based on this stereochemical relationship at the ring junctions and also across the ring like the relationship between these, the relationship between this and that the relationship between this and that and the relationship between this and that.

Now, this relationship is basically showing the type of decalin that we have and this relationship is also showing the type of decalin that is present in this perhydrophenanthracene and this is the stereochemical relationship across the rings which are not joined together, like this and that one. So, let us start doing one by one we will take a possible in this time frame we can do about 3 examples and we will do a little bit let us be little bit quicker on this.

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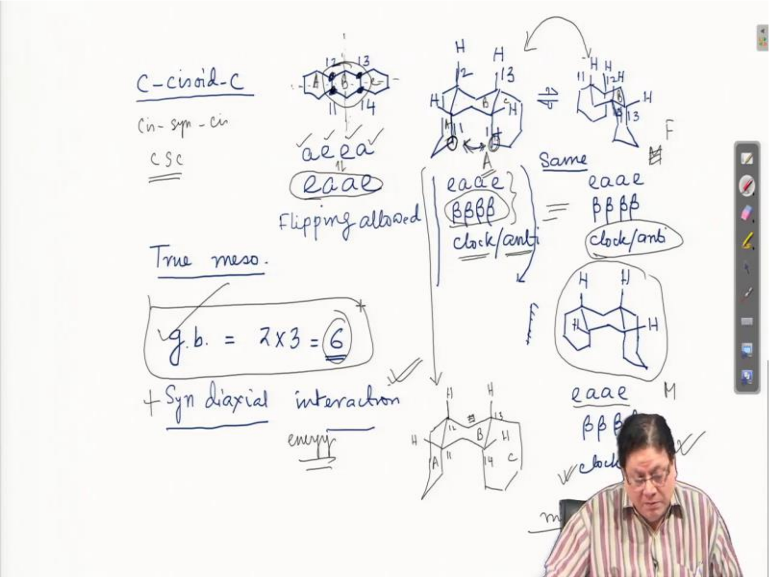

So, the first one is the first one is the let me see whether something is so here I see that the first example that that is shown here is c-c-c so what is basically cis cisoid cis, the other nomenclature is numen creature is cis sync cis, so c-s-c. So, if it is cis cisoid cis that means all could be beta all these hydrogen's or all these hydrogen's could be alpha, these are the two possibilities. So, we have taken all these as beta and we have represented it in the plane or hexagonal formula structure and now we want to assign the axial equatorial nature, before we draw the before we draw the cyclic actual confirmation.

Suppose we start with 11 hydrogen we think that we will start with an axial hydrogen at 11, if that is the case then in order to make a 11 12 cis, so the 12 hydrogen must be equatorial and then this has to be, this is 1 3 relationship if you consider this is as a cyclohexane, cyclohexene 1 3 cis relationship means they have the same nature like the either they could be diaxial or they could be diaequatorial, since you have equatorial here, so that will be equatorial 13 and then this would be axial because that is a cis relation 1 2 cis relationship.

And if you try to flip it which is actually allowed in this case so you will have equatorial if you start so that means H 11 becomes equatorial that is 12 axial and then 13 axial and 14 equatorial. So, now you draw the so draw the actual confirmation A B C, so this is A, this is B, this is C, so first draw the, how to draw it? The way to draw it is that you first draw the ring B and then the

11, so what is drawn here is taking this one as the nature of the bond is axial equatorial nature, so each 11 is taken as equatorial.

Now, this is given a beta orientation, so in order to make it beta equatorial, so this is the 11 hydrogen, so we make it 11 then this 12 this is 13 this is sorry not this is 13, here it is one methylene in between the not this not the perhydrophenanthrene system, so one carbon you skip and then this is your 13 and this is your 14. So, and this is the hydrogen beta hydrogen at C 12 which is it is equatorial which is axial, which is axial with respect to the B ring, so which is axial with respect to the B ring, which is correct.

Now, you complete the A ring this is your a ring and this is your now 13 hydrogen is again axial beta axial and 14 hydrogen is beta equatorial, so now you can complete the other ring. This is actually looks like a hexagon the projection formula is a regular hexagon type. So, this is A this is B this is C. Now, the question is if you flip it so you flip it the B ring looks like a mirror image chair and then your 11 carbon is here now and this is your 12 carbon, so you complete the ring and your 13 14 comes here, so you complete the C ring.

Now, you apply your mnemonic to see the relationship between these two, here also something is drawn here that is the mirror image of this form the original form, so this is A this is a mirror image, not this is not the mirror image this is the mirror image and this is the flip f. So, let us compare all three, so here again the same mnemonic, so what you are doing you are going from equatorial axial axial equatorial, so here you can start from here equatorial axial axial equatorial or is the same if you start from this carbon equatorial axial axial equatorial.

So, and in both the cases it is beta beta beta beta. So, here we write that both the types of direction are possible, if you want to maintain this clock or anti-clockwise both are possible. So, you do the same thing here equatorial equatorial axial so you do this equatorial axial axial equatorial, beta beta beta beta and then here also you can have both possibilities you can start from 13 equatorial axial axial equatorial or from 12 equatorial axial axial equatorial, so both clock and anti are possible.

So, that means these are these are same and if you so basically flipping does not change the molecule, it is not a mirror image anymore, so they have the same molecule you are doing you are looking at and when you draw the mirror image, then you will see, when you draw the mirror image, what is happening? This is equatorial you do the same thing equatorial axial axial equatorial, beta beta beta beta and this is also a clock or anti-clockwise all are possible, so mirror image is also same. So, that means it is a meso compound, it is a true meso, it is a true meso, it is not a non-resolvable dl pair, non-resolvable dl pair will happen if these two are mirror images, but he had these two are same.

And so also the mirror image, so it is a true meso and if you look at this molecule you have a plane of symmetry been through here or going through here the plane of symmetry, apparently there is a plane of symmetry here, but if you look at the axial equatorial nature there is basically this cannot be the mirror image of this, so that is the that is the point to note however this is valid and if this is valid then that also tells that this should be a meso. So, the planer formula says it is a meso and so also the conformational analysis.

Now, regarding the number of gauche butane interactions, so what you do that there are two cis decalin systems here B and C constitute one decalin and A and B the other, each decalin gives 3 gauche butane, so it will be 6 gauche butane units. However, apart from that, there is another interaction that is coming between because when you talk about decalin you are looking only at the relationship between B and C and the relationship and A and B separately, but here is one interaction that is going on that is between the methylene belonging to the A ring and the methylene belonging to the C ring.

So, this syn diaxial interactions energy has to be taken into account. So, it is gauche butane interaction 6 plus it has got this syn diaxial interactions. So, that is one isomer, which is a meso isomer, let us we erase this let us go to the another one which may be a optically active form, let us see which one is that.

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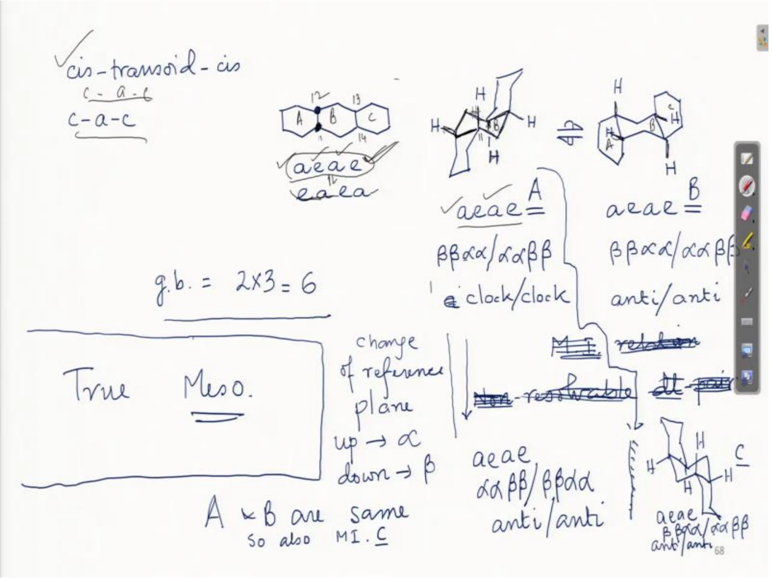

So, let us go to the next, the next one is cis transoid cis, cis transoid cis, so if you that means you can also call it as a or c that is written here, cis anti cis and in order to satisfy that in the planer form structure, so what you do? You draw these three hexagons represent the cyclohexane in form of hexagons and then try to put the maintain the relationship, the relationship is that between 11 12 it is cis, so this is 11, this is 12, so that is cis means both are beta suppose and then there is this 12 13 relationship is transoid or anti that means this is beta so that has to be alpha and then you have a cis one, so 14 is also alpha.

So, if you look at the axial equatorial nature if you start with axial hydrogen at C11 axial then 12 this is 1 2 cis relationship, so that is equatorial that is axial that is equatorial, 1 3 trans means axial equatorial or equatorial axial. So, all you can have a flipping which is allowed here, so that is equatorial axial equatorial axial, so equatorial becomes axial, axial becomes equatorial as simple as that.

Now, you draw the confirmation of the system, so the way to do it is you draw first the B so this is your B, this is your B and then because you have a we have decided to draw it suppose or you have decided suppose you have decided to draw it taking the H 11 as axial, so H 11 then this has to be the 11 carbon beta axial, then this is beta equatorial, then you have this anti relationship between this centre and that centre, so the hydrogen is axial, alpha axial and this next hydrogen

14 hydrogen attached to the C 14 a carbon number 14 is alpha equatorial, that is so this is basically representing that one.

And if you flip it then this is your B ring and this is your A ring, this is your C ring and you see that now it represents the other one that equatorial axial, so equatorial axial equatorial axial and now the question is are they the same or are they the same or are they different. So, let us do it so here axial equatorial axial equatorial, so that is the pathway we are taking, beta beta beta beta beta alpha alpha beta beta alpha alpha or it could be alpha alpha or it would be alpha alpha beta beta, alpha alpha beta beta this remains the same this is equatorial axial equatorial axial, so there are two possibilities here.

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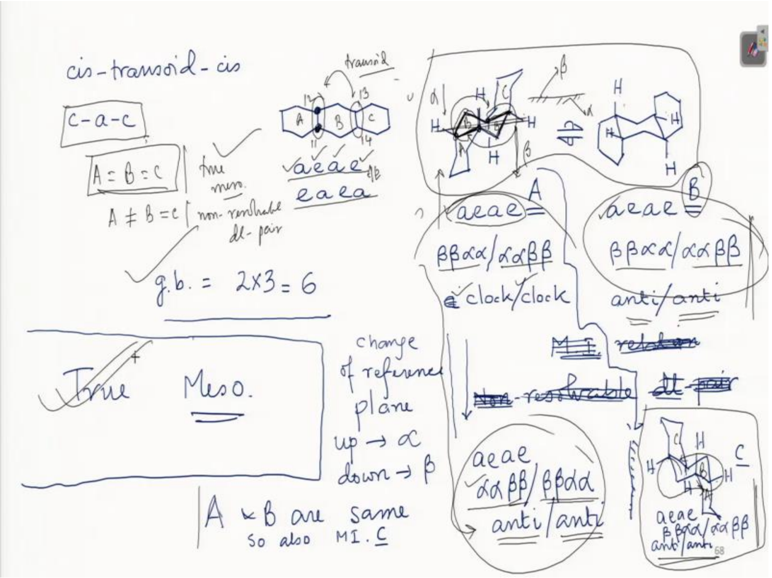

And the direction in both the cases if you go from this, now let us go to another isomer discuss the confirmation of another isomer, which is having the relationships cis transoid cis, so that means the other way to describe it as c-a-c cis anti cis, so in terms of the planer structure you can have because it is cis so you have make it cis both beta then this and that one is transoid, so this is beta so the hydrogen is alpha here and in order to make cis here you have the hydrogen-alpha here, so this is cis that is cis and between this and that you have a transoid relationship. So, that is the planar structure.

Now, the question is before we draw the exact confirmation try to fix the axial equatorial nature of these ring junction hydrogens. So, if you start with the axial hydrogen at this position, then that will be if that is axial then the next one because it is cis that has to be equatorial and then because it is 1 3 relationship in with respect to the B ring so that will be having axial because 1 3 cis relationship is either diaxial diequatorial, 1 3 trans relationship is axial equatorial or equatorial axial.

So, this is equatorial so that has to be axial and then to make it cis, it has to be equatorial. Now, if you flip it which is allowed here, so axial becomes equatorial equatorial becomes axial. So, either it is axial equatorial axial equatorial or equatorial axial equatorial axial. Now, write the confirmation draw the confirmation of the of this system. So, how to do it? First draw the B ring in a chair form, which is down here, so this is the B ring and then your 11 suppose this is your carbon 11, this is 12, this is 13 and this is 14, so to make the carbon the hydrogen at C 11 has beta axial, so you have to choose this as the C 11. And then this is C12 and this is your 13 and that is your 14.

Since flipping is possible, so you flip this B ring and you have the mirror image chair and then you know that now my 11 carbon is here and 12 carbon is here, so you complete the ring and here this is your 13 and this is your 14, so you complete the ring. In this case because you are seeing basically perpendicular to the plane of the plane of the cycle average plane of the cyclohexane ring, so they will look like a plane hexagon that as I said more or less planer hexagon. This is your B and I have drawn the mirror image also, if you draw the mirror image of this it will look like this, so this is your B, this is your C ring and this is your A ring. So, let me write it here A B C. So, up to that point is clear.

Now, first let us see how many gauche butane extra gauche butane interactions are there because there are two cis decalin system are present, so it will be 2 into 3 that is 6, each decalin gives 3. And here there is no interaction that is going on between the bonds in C and the bonds with A, so you do not have any extra here. And then the next question is whether it is optically active or not? Now, how to check that? So, you have already the original and the flip form and you have drawn the mirror image of the original form. So, in order to check the optical activity, we have to find the relationship between ABC.

Now, there are some situations that if A is equal to B is equal to C that means all three are same, then it becomes a true meso, if you think that A is not equal to B, if you find and then B is equal to C that means your mirror image becomes the flip form and the mirror image is non-superimposable then you have a non-resolvable dl pair. So, let us try to apply that mnemonic that we have. So, we have decided that suppose we decide that we will go from an axial and ultimately land to an equatorial, so this will be axial equatorial axial equatorial, so that makes it that makes it beta beta alpha alpha.

But you have to remember that the same axial equatorial axial equatorial type pass way you can generate, if you start from this carbon., equatorial axial equatorial if you start from if you start from this hydrogen sorry, axial equatorial and then axial equatorial. So, this is your now alpha alpha beta beta, earlier it was beta beta alpha alpha, now alpha alpha beta beta and the direction is still the same.

So, earlier you have you are doing this type of direction, now you have started from this one and coming to here. So, both are clockwise and here the same thing you apply axial equatorial axial equatorial there are again two possibilities axial equatorial axial equatorial, so if you do this, so that becomes alpha alpha beta beta, alpha alpha beta beta and then if you start from here axial equatorial axial equatorial, then it will be beta beta alpha alpha that is both are possible and both the directions are anti.

And if you look at the mirror image it is the again you maintain that axial equatorial axial equatorial sequence axial equatorial axial equatorial, so that is beta beta alpha alpha or you can start from here axial equatorial axial equatorial, so that will be alpha alpha beta beta and in both the cases the direction is anti-clockwise, because you are going from here to there or you are starting from this carbon and going to this. So, both are anti-clockwise. So, this is the situation anti anti beta beta alpha alpha, alpha alpha beta beta and this is the same, this you have deliberately fixed.

So, one thing is very clear B and C are same, because all these are matching B and C are same the question is what about A and B or A and C the same thing. So, what you do here in order to check that here there is little bit trick that I change the reference plane, see earlier my alpha beta nature was basically that I have a reference plane which is an average which is the average plane of the cyclohexane in the B ring and then something which is above we call it beta and something which is below we call it alpha.

But now if I change the reference plane that I actually invert myself the observer invert himself so the head is here and the leg is there, so now he is looking at this molecule, so now the reference plane according to the reference plane these bonds which are now earlier which are alpha now that will become beta and the bonds which were earlier beta will become alpha. So, basically now what I am saying earlier the up hydrogens where beta down hydrogens where alpha, now I change the reference plane, so I consider the up hydrogen as alpha and the down hydrogen are beta.

So, basically I am looking from the bottom side. If I look from the bottom side, the direction will also the alpha beta changes as well as the direction, so one which looks like clockwise from the top will look like anti-clockwise from the bottom. So, this can be changed by changing the reference plane that means up as the alpha and down as the beta, then what will happen? This will never change axial equatorial axial equatorial whether you observe from upside or from bottom side, but what will happen this will change beta beta will be alpha alpha and alpha alpha will be beta beta.

So, that will be alpha alpha beta beta or beta beta alpha alpha. And the direction will be anti both anti because the direction changes you are looking from the bottom side, so now if you look at this and if you compare all these, so what will happen? That all these things A B and C are becoming same. So, A B, A equal to B equal to C that means this is a true meso compound.

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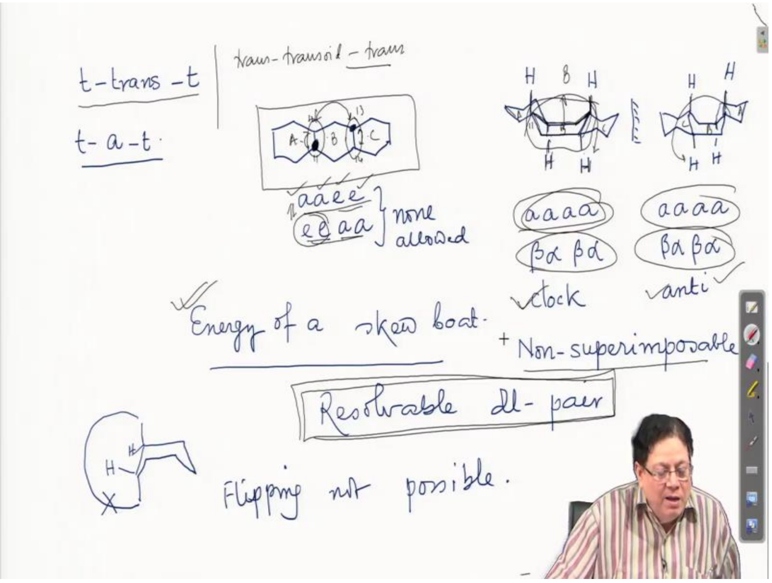

Now, let us go to the next isomer which is written here that is t trans transoid trans. So, trans transoid and trans or you can call it t-a-t trans anti trans. So, again you draw planer structure and to make it trans you if you have this beta then the next hydrogen is alpha and then this hydrogen at 13 position has to be beta in order to make a trans wide relationship and then this has to be alpha in order to make a trans relationship so this is the situation. So, this is beta that is alpha this is beta that is alpha.

Now, let us try to assign the axial equatorial nature, so if you start that this hydrogen as axial that hydrogen that means at C 11 is axial, then what will happen? Then the next hydrogen has to be axial also, because it is trans 1 to 2 trans relationship, then 1 3 trans relationship, so that has to be equatorial and this has to be equatorial, because that has to be trans again diequatorial 1 2 is trans.

Now, if you flip it you get just the just in opposite sequence, so axial will be equatorial and equatorial will be axial, so equatorial equatorial axial axial, so this is a the problem is that this is a trans ring junction that is a trans ring junction, in no cases you can you can have diequatorial orientation of the ring junction hydrogens, but in both the cases here in this or in the flipped one you have diequatorial nature of the hydrogens, so that is not possible. So, that means true chair form B cannot exist in the true chair form.

And that compels it the B to adopt a skew boat type of confirmation where these type of stereochemical relationships you can maintain, so this is your skew board and then you complete this is your 11, 11 earlier hydrogen was axial, so you make it axial with respect to the axial with respect to now the with respect to B ring it is not axial these are the hydrogens the flagpole hydrogen's so then you can call it as if you consider the ring A and C they are axial, but if you consider the ring B, they are the flagpole hydrogen's.

So, pseudo axial, so these are this is also pseudo axial, this is also pseudo axial with respect to the ring B, again I repeat that word. Now, the question is whether this is what is the energy? The energy will be basically now you have the trans decalin system that is not incorporating any extra energy, but what is incorporating the extra energy is the presence of this skew boat, so it will be the energy of a skew board that is the excess energy that you are adding.

And now the next question is whether the it is a optically active? If it is yes, then whether it is resolvable dl pair or are not? So, in order to do that since flipping is not possible here, flipping is not possible because of the trans ring junction, so you draw the mirror image and the best thing is that the mirror image you compare the two structures, so this is the mirror image here, so this is your A ring this is B ring this is C ring, so this is your C ring this is B ring this is A ring.

So, this is again do the mnemonic so instead of writing pseudo axial I am writing axial axial axial axial, so axial axial axial axial and then this is beta alpha beta alpha, beta alpha beta alpha and this is so I am going from here to there so this is a clockwise direction beta alpha beta alpha. And if you do the same thing here axial axial axial axial beta alpha beta alpha if you want to stick to beta alpha beta alpha, then what happens? You have to start from here, beta alpha beta alpha and the direction is anti-clockwise.

So, this is same, this is same, so only difference is here that means they are non-superimposable. So, if they are non-superimposable, that means this molecule exists as a known this exists as a dissolvable dl pair. So, this exists as a resolvable dl pair. So, this is the one which is the t-a-t tat or trans transoid trans molecule. Remember this is a difference from the other ones in the sense that the middle ring is in the skew board conformation. One more isomer and let us see what is there.

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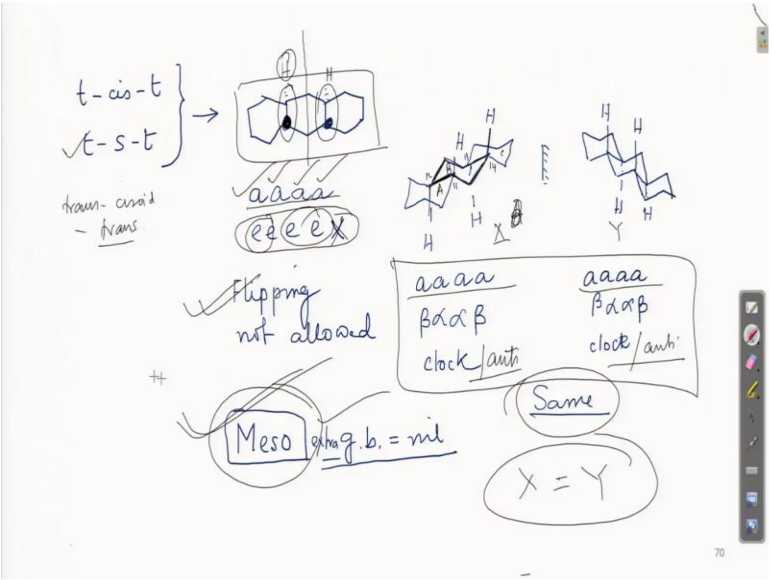

That is t trans cisoid trans, sorry trans cisoid trans, trans cisoid trans or t-s-t, trans syn trans. So, here the planer formula says that if you make it beta in order to make this trans, so that its hydrogen has to be alpha, then 1 3 cis relationship, so this hydrogen has to be alpha and then this hydrogen has to be beta. Now, the axial equatorial nature of these bonds, so if you start from this that this is beta axial, so axial so that has to be axial also alpha axial, then this will be alpha axial because this is 1 3 cis relationship and this is also axial because this ring junction is trans.

So, all are axial and if you want to flip it, then all will be equal to all will become will adopt equatorial orientation and you know trans ring junction di-equatorial is not allowed, so this confirmation will not be allowed, that means flipping is not possible for this molecule. Now, let us before we draw the molecule let us try to adjust first draw the molecule and then at last I will show that how this perhydroanthracene molecule actually look like in model in three-dimensional model and I will show that after we go through this isomer.

So, this is all axial so you write the B always write first write the cyclohexane the B ring first in the chair form and then you draw the other rings A and C, so since you started with beta axial, so this is your 11, so this has to be 11 carbon, this is 12, this is 13 and this is 14. So, this is beta alpha now so first this is the confirmation of this what we have drawn here and this is not flappable because as I already told you that any trans ring junction in fact molecule having trans ring junction cannot be flipped, flipping is not allowed that is the rule of thumb and you know why it is basically flipping gives di-equatorial relationship of the hydrogens which is not permissible.

So, next question is, whether only extra gauche butane unit is present or not. Actually there is no because this is a trans decalin and this is the trans decalin and trans decalin does not introduce any extra gauche butane, then you have to also check that if there are any interaction between ring bonds of A and with the ring bonds of C. In this case it is not there. So, it has got no extra gauche butane unit that is nil. And what about the optical activity? Let us see, in the planer form if you go by the planar from there is a plane of symmetry, so it should be meso, now the question is whether it is a true meso or it is a non-resolvable dl pair let us see.

So, draw the mirror image and then adopt the mnemonic all axial beta alpha, so basically what is doing beta alpha alpha beta, beta alpha alpha beta, now here both are possible you can actually start from here also beta alpha, beta alpha and then alpha beta, so basically here both directions are possible clock as well as anti, if you go from this side or if you come from 14, 13, 12, 11, and in this case also you will have axial are all axial beta alpha beta alpha to possibilities are there either you go from beta alpha sorry beta alpha alpha beta beta alpha alpha beta or you can start from here beta alpha alpha beta, so both directions are possible.

So, now all the parameters are basically same, so if they are same that means a if it is sorry if it is X if it is Y, so X is equal to Y same, so the mirror image is same superimposable, flipping is not allowed, so in that case this constitutes a true meso compound, so this is a true meso compound. Now, I told you that I want to show you how does this molecule look like in three dimensions.

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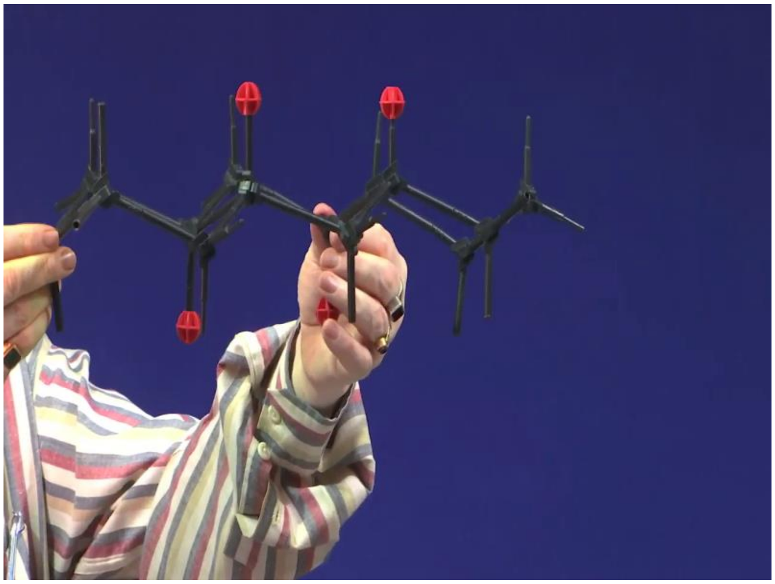

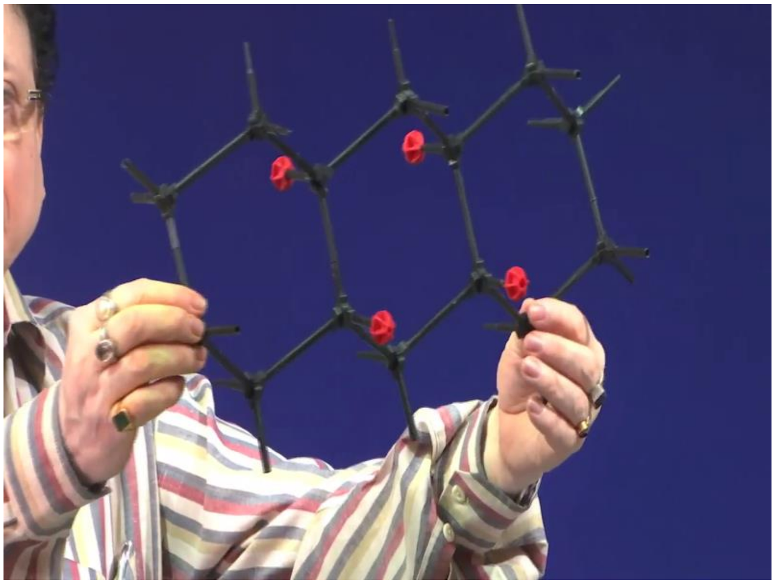

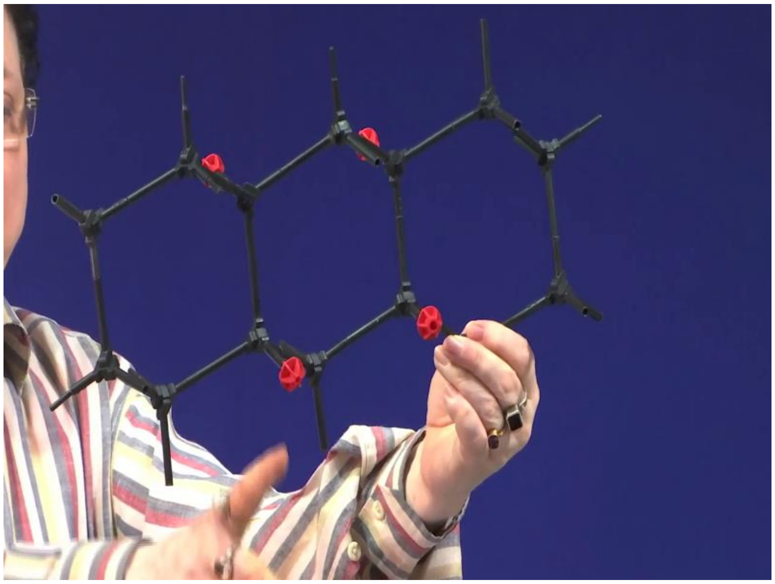

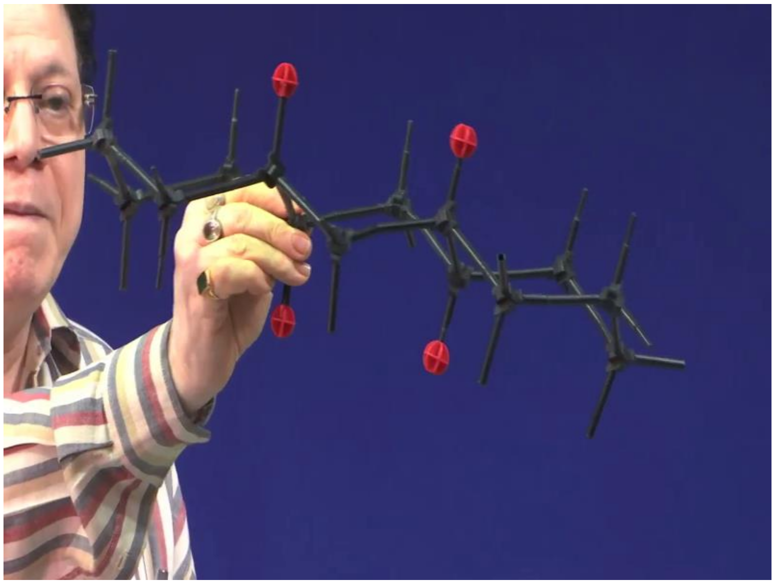

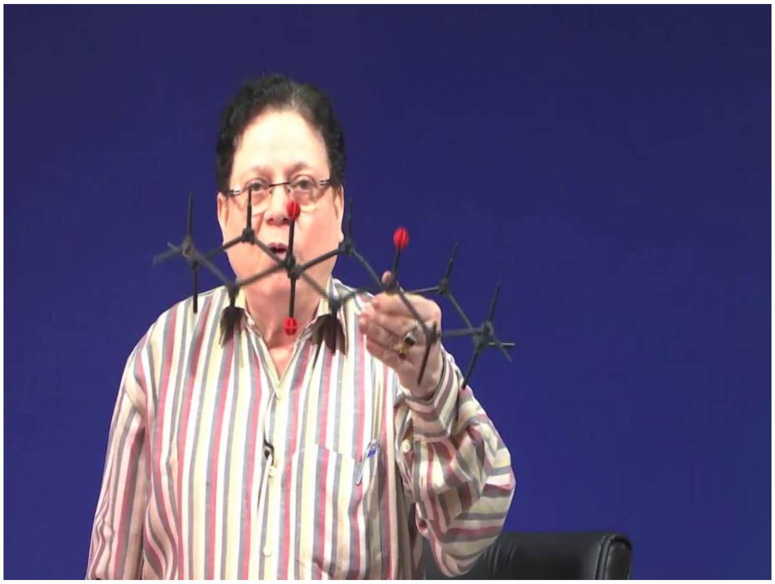

So, in here I have made a molecule which is let us see we will try to assign the relationship between the ring junction as well as across the ring and I want to show you the molecule. So, see this is a if you look from this side this is the hexagon type, if you take A projection you will get 3 rings, 3 hexagons plane hexagons the projection.

Now if you look at the hydrogen's which are marked by the red, so this is one carbon which is common to both these two rings, so this hydrogen is alpha, this hydrogen is beta that means this is a trans ring junction, then you come to the other ring, other ring carbon, which is common to both B and suppose C, so again the hydrogen is in the in your view this hydrogen is beta facing towards the observer this hydrogen is facing towards the observer, this hydrogen is is actually below the if you are looking from this side this hydrogen is below and this hydrogen is below.

So, basically what you have this is a trans ring junction, this is a trans ring junction, one up one down and this is a cis cisoid relationship, so this molecule is trans cisoid trans. So, now look at the confirmation the true picture of it by holding it in this fusion, so if you look at this, you see the 3 chair forms of the cyclohexane, so this is the first ring, this is the second ring and this is the third ring. So, that is how it looks, you cannot flip it that is that is already we know from our analysis that because di-equatorial is not possible here, so you cannot flip it.

And you look at the symmetry aspect if you look at the symmetry aspect there is a plane of symmetry, there is a plane of symmetry going through, let me try to show you the plane of symmetry, the plane of symmetry is basically going through these carbons let me try to find out here. Yes, the plane of symmetry is going through this these two and I will try to hold it properly in a proper fusion. So, this is the that tells you the plane of symmetry. So, going through this let me try to find out this and this one, so this is the plane of symmetry going through this, so that is a true meso.

Because the plane of symmetry is present even in the pocket confirmation because planer confirmation sometimes give wrong information regarding plane of symmetry, because that does not take into account the axial equatorial nature, that is why the you sometimes fail in your interpretation. So, this is the kind of molecule that we are handling. So, there are some natural products which are even bigger than this, there are 3 rings so that can have 5 rings, like those are called triterpenes steroids another class of molecules, which have got 4 rings, the fourth ring is in the is a cyclopentane, but we have triterpenes where all the 5 rings can be in the are 6 member that means there are 5 chairs which are possible for the confirmation of this of the triterpenes.

So, those are all very important natural products that is why conformational analysis your so important and you must understand the brilliance of the care of the scientists who are handling the stereochemistry of these molecules are just making models I think they got the empirically they could derive that what will be the energy what will be the optical activity all these and which are found to be correct later on by spectroscopic analysis or (())(42:17) crystallography studies.

So, I think that takes care of our problem solving on the on the stereochemistry of polycyclic hydrocarbons like perhydrophenanthrene and Perhydroanthracene. I think that takes care of our two things the lecture one the two topics first we have focused on the symmetry and the point group and the second aspect was absolute configuration of stereogenic units, which are not SP3 stereogenic centre axial chirality like axial chirality planer chirality helical chirality and then we discuss the confirmation this is of decalin and then followed by tricyclics system like perhydrophenanthrene and perhydroanthracene.

Now, whatever was any doubt was there that has been cleared in the last 3 or 4 lectures, we have again revisited those things point groups, symmetry number order and then this conformational analysis of tricyclic cyclohexane like perhydrophenanthrene and perhydroanthracene. So, we will move on to another topic in the next class. Thank you very much.