Structures, Stereochemistry and Reactivity of Organic Compounds and Intermediates: A Problem-Solving Approach
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Lecture No. 12
Revisiting Conformational Analysis of Perhydrophenanthrene

Hello everyone, welcome to this course on Structure Stereochemistry and Reactivity of Organic Molecules and Intermediates: A Problem Solving Approach. Today, we will be again solving some problems on topics which have already been covered in earlier lectures, last time we solved or clarified some of the important points and issues that were there in while describing a molecule in terms of the point groups and then how to calculate the symmetry number as well as the order of the point group.

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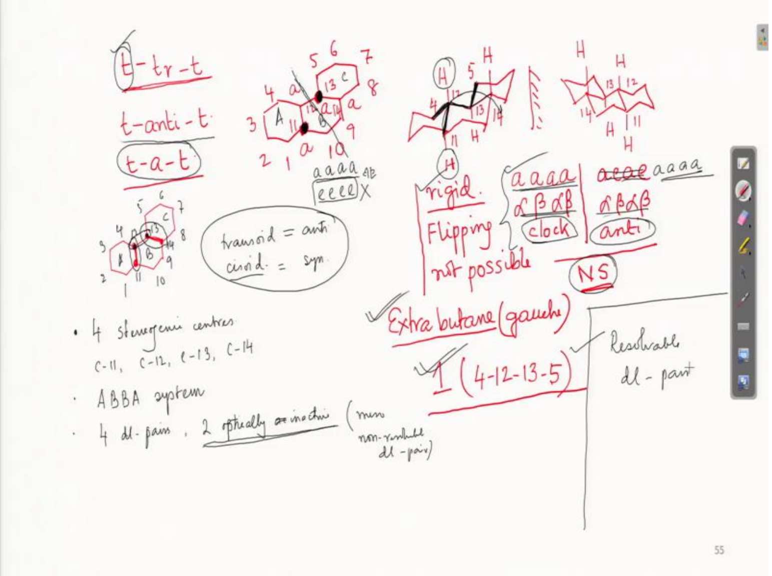

Today, what we will be doing is confirmation analysis, again we will just go back and take those polycyclic, polycyclic system cyclohexane systems, you remember that we have covered or we have discussed the confirmations of two types of tricyclics systems, one is the perhydrophenanthrene and the other was perhydroanthracene, today we will just again revisit those confirmations and then make it more concise and easily understandable and bring this salient features and if a problem comes how to solve it.

So, now you if you remember that paerhydrophenanthrene is basically the reduced form the total completely saturated form, which is obtained from phenanthrene by hydrogenation. Now, how many the question is, while this hydrogenation has taken place one has created 4 stereo-genic centres, which are represented by the carbons which are the ring fusion which is basically forming the ring fusion bonds.

Now, here the perydrophenanthrene nucleus is already there let me again write it perhydrophenanthrene is basically this is the skeleton, what are the ring fusion bombs? These other inclusion bonds. What are the infusion carbons? The ring fusion carbons are this one that one this one and that one. And if you again remember the numbering the numbering is given in such a fashion that is given in such a fashion that your these two which are called the B regions they get the numbering of 4 and 5.

So, if you remember that it will be easier to give the numbering. So, this is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 and then 11, 12, 13, 14, so the first question is, how many stereogenic centres it has? It has got 4 stereogeneic centres. What are they? c11, c12, c13 and c14, then the next question comes is that, what type of system it is? Because systems can be described in terms of AAAA where they are 4 stereogenic centres, so you can have similar stereogenic centres present, so it could be AAAA or ABBA or there are several possibilities, all maybe different ABCD.

So, if you look at these 12 and 13 are basically similar stereogenic centres and the 11 and 14. So, this actually is a ABBA system, ABBA system and when you have this similarity in stereo generosity, then your number of isomers the number of isomers reduces gets reduced, gets reduced as you have seen starting from your tartaric acid when there are similar stereogenic centres the number of stereoisomers is 3 instead of the 4, that you get from the formula 2 to the power n.

2 to the power n is when n is basically when all the stereogenic centres are different, so you apply that 2 to the power n formula, otherwise it will be reduced. There are still formulas to get the numbers, but we are not going into that what we are basically revisiting whatever we have you have been told in terms of perhydrophenanthrene, so we know in perhydrophenanthrene. there are 4 dl pairs and 2 optically inactive, inactive, optically inactive.

I am not writing it meso, because in meso there are again classification true meso and something which is known non-resolvable dl pair that is not a true meso. So, that so it is better that you have optically inactive isomers, optically inactive means you will not be able to separate into any component so it could be either a meso or it would be non-resolvable dl pair, these are the possibilities.

Now, you have to when you are asked to draw the confirmation or find out the isomers you have to go in a stepwise fusion systematic fusion and you also I like to again remind you that here the ring junction is there is a relative stereochemistry between the ring junction stereochemistry and that is it could be trans or it could be cis this 11 12 can be trans or it could be cis, so also 13 14, it could be trans or cis.

Now, the relation between 12 and 13 is expressed in form of either transoid or cisoid, because they are not actually being shared by only two rings 12 is shared only between suppose this is ringing A and B and this is C AB and 13 is shared between BC, so they are not the ring junction between two shared by two rings. So, here you cannot it is basically the relationship is defined by either you call it transoid or you call it cisoid or you can call it anti and you can call it syn.

So, this is the terminology, so when you define a particular stereoisomer so you have to say what is the relationship between 11 and 12. Suppose it is trans, then what is the relationship between 12 and 13? Then 12 and 13 that means the stereochemistry of 12 and 13, so it could be either cisoid or transoid and what is the relationship between 13 and 14, so all these have to be described in order to define a particular stereoisomer.

So, let us start from just we will discuss few of these again because time is short we cannot discuss all but I think two or three examples molecules if we discuss that will clear any doubt if you have in your mind. So, the first one we take is it is already written there t-tr-t, so these t means that means the relationship between 11 and 12 is trans, the stereochemistry setreochemical relationship is trans, then you have transoid, so that means remember these carbons actually apart from this bonds carbon-carbon bonds you have a hydrogen attached to each of these centres.

So, I told you that if your hydrogen is beta then you put a darken circle and if the hydrogen is alpha you do not have to write it, that is the notion that is the accepted notion that if you do not show the stereochemistry of the hydrogen that means if you do not have this bold dot, then you cannot that means that hydrogen is alpha.

So, let us see this is t trans then you have to make 12 13 transoid and 13 and 14 trans. So, you can call it as t-tr-t that means trans transoid trans, you can also call it because transoid is anti so you can call it as t anti trans anti trans and abbreviated as t-a-t, so tat, tat is trans anti trans, but today the it is usually said about the anti and syn they are not used they are not no longer in use because the modern stereochemistry books, they are mentioning it as transoid and cisoid were however for simplicity I am still retaining those old and nomenclature that t-a-t trans anti trans.

So, how do you draw the confirmation of this trans anti trans? First you draw the planer for were planer structure, although it is not a planar molecule, but you draw the plane hexagon structure. So, I have this perhydrophenanthrene and since it is trans, so if I make it hydrogen up then the next hydrogen 12 is alpha 13 is beta and 14 is alpha. So, that is the situation, now if you look at these this is nothing but if you forget about the other rings say this is A ring this is B ring suppose this is C ring, so if you forget about the C ring the AB constitutes say decalin in system and BC also constitutes another decalin system.

And all together they form a perhydrophenanthrene system, the AB if you want to make a trans decalin you know the hydrogen's have to be the hydrogen's want to if you want to make two substituents attached to a cyclohexane which are having 1 2 relationship and to make it trans so the substituents have to assume either axial-axial orientation or equatorial-equatorial orientation. 1 2 trans means either di-equatorial or di-axial.

So, here if we think that this hydrogen is axial, so there is a possibility that this hydrogen is let us write it here, see if you start from this 11 hydrogen as axial, then 12 hydrogen has to be axial. So, axial axial and then you have to have because it is again a trans relationship and this is also again 1 2 because if you considered the only the B ring, so 12 and 13 are basically having a 1 2 relationship if you consider the B ring so it is trans means the next one has to also be axial and then the 13 14 stereochemistry is also trans, so the 14 hydrogen has to be axial.

Now, the other possibility is that you have equatorial equatorial equatorial equatorial, but this is not permissible because a trans, remember trans decalin trans decalin is a rigid molecule with the hydrogen's at the ring junction can assume only di-axial confirmation, you know the reason because you cannot make a ring if the hydrogen's are di-equatorial, so it has to be di-axial, if you want to make a trans decalin.

So, I think this is not permissible, so what is permissible is all four axial, if it is not permissible that means this is actually inter-convertible by flipping because axial goes to equatorial equatorial comes to axial, so flipping is not also possible, so this must be a rigid molecule. If you go back to my lectures what I said as a rule of thumb that if the perhydrophenanthrene if the relationship between any two ring systems is that it is a trans ring junction any one of these, then the system becomes rigid. Because trans ring junction cannot be cannot be changed it has to be di-axial, so that means this is rigid molecule, so that is correct, we understood that.

And then the next question is see there are issues when you draw a conformation first draw the preferred confirmation, I have drawn their all chair conformation and then the next question is whether it is optically active or not. And the third one is basically the energetics the energetics of this system. The extra so that is basically when you are forming this perhydrophenanthrene whether you are incorporating any extra butane unit, gauche butane unit or equally spirit unit, whatever it is.

So, let us first try to find out the extra butane extra gauche butane unit in this system. The trans decalin in order to when you make a trans decalin, you are actually not incorporating any extra gauche butane you need as compared to the as compared to two cyclohexanes basically, when you refusing to cyclohexanes, you are not incorporating any extra gauche butane unit. So, trans because there are two trans decalin in system is present here, so you are not incorporating any extra coming arising from trans decalin system, that is basically 0. But there is one extra butane in that you incorporate when you form the perhydrophenanthrene is this one. This is the extra butane unit and this butane unit is in the gauche confirmation.

How do you know? First of all, you know that the anti bond to this 13 5 is this 11 12, so there can be only one anti bond anti carbon-carbon bond, so this has to be then in the gauche form, if it is not anti the other possibility is in the gauche bond. So, this is in the gauche form and so you have one extra butane unit and that is basically the which one? 4 12 13 and 5. Now, this 4 12 13 5 this unit is present in all the perhydrophenanthrene or whether it is in the gauche form or whether it is in the anti form or if there is any possibility (())(16:22) form you also check that. So, in this case this t-a-t molecule, you have one extra gauche butane unit.

So, in all the perhydrophenanthrene you have this extra butane unit plus the other butane units you have to consider if there is a cis ring junction, because trans ring junction does not incorporate any extra butane in it. So, energetics we know that there is one extra gauche butane unit and you know the energy of one gauche butane. And the next question is whether it is optically active or not.

Now, if you check the if you check the planer formula you are seeing that there is basically what was possible here was the plane of symmetry going through this, but here since this is beta and that is beta, so they are not the mirror images this mirror image of this centre is this one, so it is it does not have this plane of symmetry, so it is from planar formula the conclusion is that it should be optically active. So, it should exist as a dissolvable dl pair.

Now, if you do it try to prove it by drawing the actual conformations which are the packet forms the three chair forms, so I have drawn the this one and then you draw the mirror image the best way to know the optical activity resides or not is to just check the mirror image relationship between the mirror image and the original and then see whether they are same or not or they are different.

So, remember the mnemonic that we have introduced in our earlier stereochemistry course, so you can extend that that here so what we are doing you are just checking the your checking this the axial or equatorial nature of these hydrogen's the ring junction hydrogen's and then what is done in this mnemonic is basically you go from one hydrogen from the end to the other hydrogen at the end that means you go from either 11, then go to 12 then 13 to 14 or you go from 14 then 13 then 12 and 11.

So, that is the shortest path, so you are not taking the other path 11 and then this other arm, so you choose the shortest path that is 11, 12, 13, 14 or 14, 13, 12, 11. So, you do that check the actual as you traverse from 11 to 14 or vice versa and see that what is the nature of the bonds that was axial equatorial and what is the nature of the alpha-beta nature of these bonds and finally what is the direction that you are taking in your path when you are traversing from one end to the other end.

So, what here it is? It is all axial, so axial axial axial axial, now if you start from this hydrogen c 11 hydrogen going to 14, then this will be alpha, so you are going you are taking a path alpha then beta then alpha then beta and if this is the direction is nothing but it is a clockwise direction, you are basically going in this direction, so this is clockwise. So, that is the 3 parameters and what about the these 3 parameters if you consider the mirror image, so the mirror image is the mirror image is, this is wrong axial axial axial axial all axial because there no flipping it is only a mirror image, so axial equatorial does not change.

Then alpha beta nature, so you try to match this you could have done from here beta alpha beta alpha that also you could do but try to match as far as possible in order to avoid complications. So, I take this alpha beta alpha beta, so these two are same now, this is same that is your fixed this is same and this direction is clockwise and this direction is anti-clockwise. If that be the case, that means they are non-superimposable, they are non-superimposable mirror images, so that means it exists as a resolvable dl pair. So, that is the first example.

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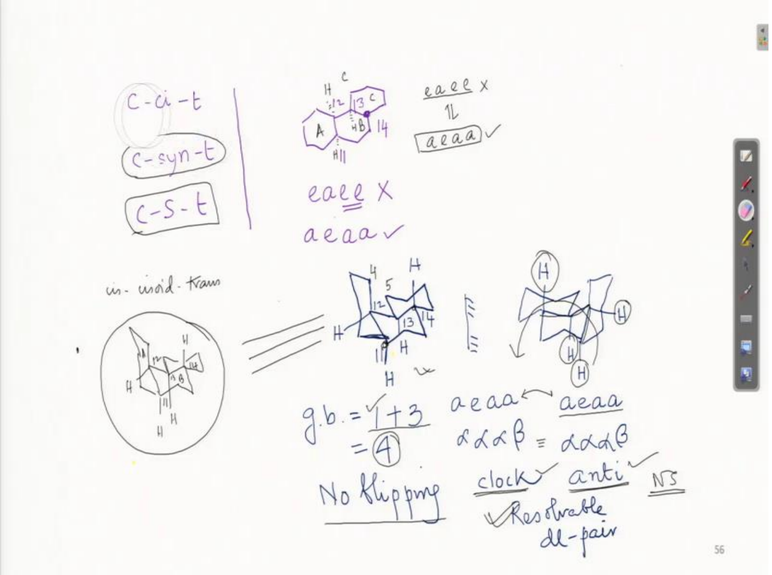

Let me see, let us go another example, which is c that means cis then cisoid then trans, so cis so this is cis cisoid and trans, so you can actually the previous nomenclature system it will be c cis syn trans and then the other abbreviated form is c-s-t, earlier we have done t-a-t, this is c-s-t. So, in the same notion that we have done earlier that you first draw the planer formula and then you have to make it cis so if this hydrogen is alpha, then this hydrogen should be alpha to make it cis, then this hydrogen should be alpha to make 12 13 and cisoid and then this hydrogen will be beta, to make it a trans.

So, it will be then what are the possibilities let us see, so this hydrogen is alpha this hydrogen is alpha and this hydrogen is alpha, so let me just try to draw this hydrogens. So, if this hydrogen C11 hydrogen is having equatorial orientation then because it is 1 to cis the 12 one must be then axial, because 1 2 cis relationship is equatorial axial or axial equatorial, then 12 13 is again cis, so that has to be equatorial and then 13 14 is trans so that has to be now it is trans so either they are 2 equatorial the or they are 2 axial but you are having your equatorial so the 14 hydrogen has to be equatorial.

Now, the question is whether this is possible or not. This is not possible because this is this ring junction is trans the BC ring junction is trans, so these hydrogens have to be axial diaxial but here you are actually having a di-equatorial relationship that is not possible. So, let us see the other one, if you flip this basically, then you have axial equatorial axial axial this is possible. So, if you start from axial then this is equatorial, then this is axial and then that is axial, so that is possible.

So, again what is happening? This is also not favourable, so again the same questions the same set of questions first question, is this molecule rigid? Yes, it is a rigid molecule, why? Because there is a trans decalin system present, because two adjacent rings have trans relationship, so you cannot flip it. And then the third question is what is the preferred draw the confirmation, what are the confirmation possible? So, when you draw the confirmation, what you do? You start from you start from this draw the B ring always the trick is that you draw the B ring this is already written here, but I will just explain how it has been drawn, so you draw the B ring, so the B ring is drawn this is your B ring.

And now remember this is your hydrogen was alpha and axial, so better you have the 11 hydrogen here, if you put the 11 carbon here, then the hydrogen axial is beta but you have drawn something where the 11 hydrogen is alpha, so alpha and axial so in order to satisfy that so this is your 11 hydrogen and this is your 12 hydrogen. So, this is axial that equatorial so you are maintaining the sequence. So, then how the ring looks like the A ring looks like the A ring will look like so this is your A ring.

So, that is your A ring and then so this is A this is B now you have to complete the C ring. Now, so this is your 11 you have to actually better write these numbers otherwise you may be facing problems 13 and 14, so 13 hydrogen is alpha and this is axial, so 13 hydrogen alpha axial and 14 hydrogen is also axial so that is also axial. So, now you complete the ring, so this is the situation that were exactly what was written, so this is exactly the same as this one.

So, now so this is no not flip able so you have drawn the unique confirmation for the structure that you have drawn here. So, now let us try to find out the gauche butane interactions, first of all these this is 1 2 3 4 so this is 4 and this is your 5, so you have to always think of what is the relationship between 4 12 13 5 and that is again in the gauche form gauche butane unit, so that is one plus you have a cis decalin system here, one of these AB relationship is cis and you remember one cis decalin incorporates three additional gauche butane interactions. So, that means it has got 1 plus 3, so that makes it 4 additional gauche butane interactions.

And now the question is so we go have done the energetics we know that it is not flip able, no flipping is allowed and now the question is whether the mirror image is whether it is optically active or not, that is it is a dissolvable dl pair or not. So, you draw the mirror image and then you do the mnemonic again, so again you go from 11 12 see you go from this centre to the carbon 14 so 11 to 14 or vice versa.

So, if you start from 11, so it will be axial equal to sorry axial equatorial axial axial, the orientation in terms of alpha beta this is alpha then this is alpha alpha beta, so alpha alpha alpha beta. And the direction is clockwise, because you are starting from 11 going to 14. And if you do the do the same thing, so here you start from this one axial equatorial then axial and then axial. So, axial equatorial axial so you have to actually basically make these two same and then try to make this also a meso this is not in your hand because you have already fixed this in tune with the first one, so now you have to say what are the alpha beta relationship.

So, this is alpha alpha alpha beta, so alpha alpha alpha beta that means this is also same, earlier it was alpha alpha alpha beta and the direction is anti now, so you are going from here in this direction, so that is your anti direction. So, if it is anti, so that means they are non-superimposable mirror images, so basically it is a resolvable dl pair, so just a second let me erase this and go to the we will take one more example before we finish up this finish of the perhydrophenanthrene systems. So, let us go to the next page.

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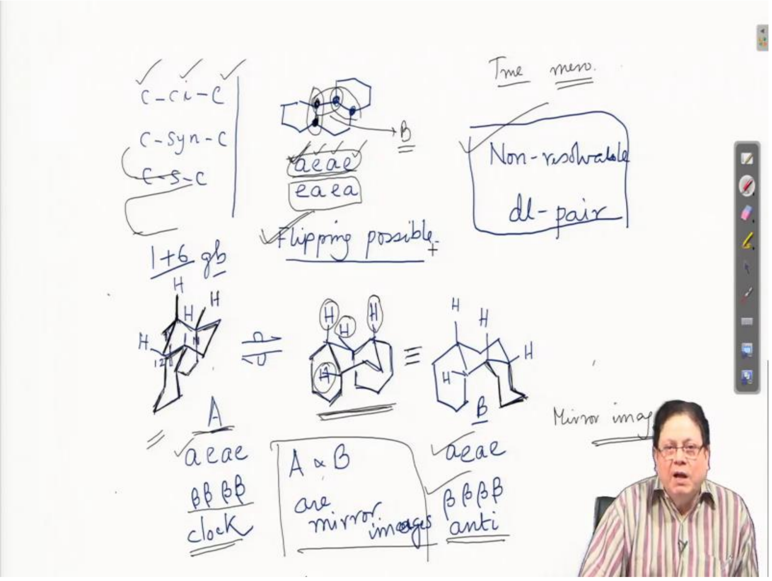

Let me take, possibly this one, this one is quite interesting, this is which form this is the, this is cis cisoid cis, cis cisoid cis that means it is cis syn cis, so that you can say c-s-c. So, if you draw the planer formula, so that will be if you make it beta so there has to be beta in order to make it cis, then in order to make it cisoid you have to have all beta and then in order to make it cis here you have both the hydrogens beta.

So, that means all are beta or it could be other way around all could be alpha. So, we have taken all as beta orientation. So, now let us again do the axial equatorial that check that if you have this axial what will be the axial equatorial nature of the rest of the hydrogens. So, if you start putting is as axial this hydrogen you start considering it as axial hydrogen then the second one because it is 1 2 relationship, so it is cis that means the second one is equatorial, the third one is axial and the fourth one is equatorial.

So, they alternate because this is cis relationship typical of the cis, one to cis relationship. So, this is one possibility axial equatorial axial equatorial or it could be the other way around equatorial axial that means the flipped basically the flipped form, so equatorial axial equatorial axial, since both are possible since both are possible, so what happens is flipping is permissible here. So, this is the situation were flipping is permissible.

So, let us first try to draw the molecule in 3-dimension within the packet form. So, again I said that always draw the, so this is the this is the B ring, so draw the B ring first and then this is the you starting point is 11, so you cannot make this as 11 if you try to follow this arrangement axial equatorial axial equatorial so C11 hydrogen is beta axial, so better pick this 11 pick this carbon as the 11 carbon. So, this is 12 then this is 13 and this is 14. So, now the you put the hydrogen's this is axial this is a equatorial and then form the A ring, so this is you're a ring.

And where is your C ring? Unfortunately first put the hydrogens the hydrogens are all beta, so this is beta axial, yes you are correct beta axial, remember these axial equatorial notation is with respect to the B ring that is important with respect to the B ring, so you put this with respect to the B ring you make this axial beta axial and this is beta equatorial. And now you have the other ring that you have to form the but unfortunately because you are seeing from this side so it looks like that this ring the projection is a just hexagon, but it is actually in the chair form.

And we have seen in many cases that you have to depict it in a hexagon, but they are actually in the chair form, because you are looking at the ring, you are from the middle of the ring or you are looking perpendicular to the average plane of the ring, so that happens the projection formula becomes a plane hexagon. So, this is the confirmation, but since flipping is possible so you flip it and when you flip it then this chair becomes a mirror image chair, so this is your B ring and unfortunately here both the rings have to be the A rings they are projection is basically looks like a hexagon and plane hexagon, everything is hexagon this is also a hexagon, but this is a plain hexagon.

So, this is now the question is that what will happen that during flipping are you getting the same molecule or you are getting the mirror image all you are getting a diastereomer so all these are possibilities. So, let us take all these 3, so this is the original one A, this is the flipped form, this is the flip form, so this is flip from I actually rotated it rotated it by 120 degrees, so that I can show one of the ring in the proper chair conformation, but it is not necessary you can do that, so by 120 degree rotation of the B ring so what you can do you can make this other ring in the chair form look like (()0(34:25) that actual chair form look like the actual confirmation.

Now, by however in order to compare these two you can just go through that apply that mnemonic that you have if you go from this axial that means the 11 hydrogen axial, so hydrogen axial then go to 12 that is equatorial then 13 axial then 14 equatorial and the alpha-beta nature all are beta here beta beta beta beta and the direction is clockwise. If you do the same thing here, so then you have to start from because it is axial equatorial axial, so you start from here axial equatorial axial equatorial, so that is here, then all our beta all our beta but the direction is anti-clockwise.

So, that means these two are mirror images, so they are mirror images, if they are mirror images then what will happen? That means you cannot stop this flipping happening at the room temperature, so they are not so always they will be present as 50 50, because they are energetics remain the same, so they will be present in 50 50 and this is the classic case of what is called non-resolvable dl pair.

So, this is not a true meso remember, a true meso is basically internally compensated, so that is a resolvable, that is no question of resolution comes there, but here you have two conformations which are mirror images of each other and they are inter-convertible by flipping, so you have 50 50 form. And then you cannot separate them because they are energy barrier is too little and that happens all the time at the room temperature. So, that is what is called non resolvable dl pair.

Remember this non dissolvable dl pair is basically we are talking about our ambient conditions that means whatever room temperature that we have that varies that may vary from 20 to 30 or 35 depending on the location where you are deciding, but anyway that or ambient conditions this is not resolvable.

So, this is a an example, so we have covered the 3 this is basically a revisit of what we have done earlier just to clarify if you have any doubt, so I thought that I should repeat it before we go to the another topic, jump to the another topic. So, thank you very much, we will the next one will again do some problems on Perhydroanthracene and then we will jump to the next topic. Thank you.