Structure, Stereochemistry and Reactivity of Organic Compounds and Intermediates: A Problem-solving Approach
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Lecture 17
Application of Octant Rule (Contd)

Hello, welcome back to this course on Structure, Stereochemistry and Reactivity of Organic Molecules and Intermediates: A Problem-solving Approach. In the last episode what we have what we are discussing was the application of an empirical rule which is octant rule, in determining the stereochemistry of a molecule. Now, stereochemistry of a molecule means the study of its conformation or a configuration, as the case maybe.

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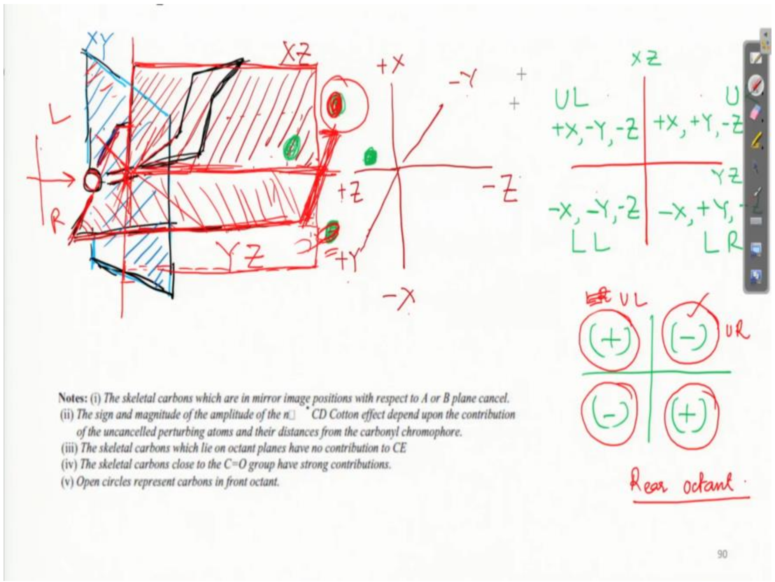

Notes: (i) *The skeletal carbons which are in mirror image positions with respect to A or B plane cancel.*
(ii) *The sign and magnitude of the amplitude of the n□ * CD Cotton effect depend upon the contribution of the uncancelled perturbing atoms and their distances from the carbonyl chromophore.*
(iii) *The skeletal carbons which lie on octant planes have no contribution to CE*
(iv) *The skeletal carbons close to the C=O group have strong contributions.*
(v) *Open circles represent carbons in front octant.*

Now, you remember what was this octant rule is applicable to determine or to predict the sign of the cotton effect. Now, the cotton effect is basically the anomalous behavior that is shown, when the wavelength of light is decreased. And you measure either the either the refractive index that is just what is called the circular birefringence; or you can measure the ellipticity. Because when there is differential absorption; the light becomes elliptically polarized light. So, either this ellipticity, you measure against decreasing wavelength, or the refractive index. The difference of the refractive index between the right and the left circularly polarized light, which can be expressed in terms of rotation, or a molar rotation or specific rotation.

And you see that the what happens that the there is first, there could be this anomalous behavior; that there could be a maxima first. That means the rotation can increase to a maximum and then followed by a rapid decrease; and it reaches a minimum and then again goes up. The same may happen with also in case of the circular dichroism; where the ellipticity goes up and then goes down and then again goes up. So, depending on whether you reach the maximum first, while we decrease the wavelength; and minima followed by the minima is that is called the positive cotton effect.

And the reverse is what is called the negative cotton effect. Now, this cotton effect is basically an experimental measurement that one can measure the sign of cotton effect, exhibited by a chiral molecule with a chromophore. And again I repeat the cotton effect is shown and in the window of the absorption of the chromophore. Now, there are different rules, empirical rules; first we have discussed the axial haloketone rule, specifically the 2 axial haloketone rule; and then we introduced to you the octant rule. Just a quick recapitulate that what is this octant rule all about.

The octant rule is basically that you place the cyclohexanone in such a way, which is shown here this cyclohexanone system and this carbonyl. So, you it is a 3-dimensional space, so you divide the 3 dimensional space by 3 planes; 3 planes namely the XY, XZ and the YZ plane. So, one plane is which is shown here one plane, which is the if you think that this is the z-axis; this is the x-axis and this is your y-axis; the y-axis is going somewhere through here. So, these 3 planes basically segment the space into first of all into front and rear octants. Now, what are those if you have the carbonyl on this side and if you view the carbonyl from this side; then this plane is dividing the space into 2.

One is which is away from the observer and the other is which is lying on the side of the observer. So, if it is away from the observer, then so we are talking about XY plane; if it is lying behind this XY plane. Then that will be called the rear octants, and the plane which is in the side of the observer the viewer; that is the front octant.

Now, that is the first division and then the second division of the space is done by this plane, which is XZ plane and by this what you have done. You have actually if you think of the rear octants; you have dissected the rear octants now into left towards the left of the observer and towards the right of the observer; 2 spaces are created; the same is true for the front octant.

You are dividing the front octants into towards the left space and towards the right another space; and then employing the third plane. Third plane as is shown here this third plane will divide again the left and the right, again into 2 spaces. So, basically what you have? You have 4 spaces at the back that is in the rear, and 4 spaces in the front; so, this is what are called the octant. In 2-dimensional figure we have quadrants when you employ 2 axis or 2 planes perpendicular planes. Here there are 3 mutually perpendicular planes and that will divide the space into 8.

So, that is octants and these octants 4 of them will be behind the observer; the observer is looking in the line of the oxygen carbon, carbon bond and from the side of the carbonyl oxygen. So, that will put that rear octants and the front octants. So, if you look at the rear octants, so this is so something at this point; that means it goes into the if you are thinking that I am standing here. So, my left side will be on this side and my right side will be on this on this. So, this will occupy the to the left, so left or rear left and any any group here on this the side will occupy the rear right.

So, and then because of these other plane that means this plane, which is the; this is the see the planes are this is XZ plane, this is XY plane, this is the YZ plane. So, this YZ plane some space are actually above this YZ plane, some are below the YZ plane. So, depending on that we will call this as the lower, this is called not the lower; because it is above this YZ plane. So, this will be upper left, so this space will be called upper left; and something which is here below this YZ plane that will be and also on the right side will be called the. This is say first of all lower, so this will be lower right; so this will be lower right.

So, depending on that you have now in the rear octants, you have a lower; this is lower, this is upper. Sorry, this is upper right, this is upper left and this is lower left and this is lower right. And the contribution of a substituent which is depending on which octant it is actually; which octant this is occupying that is important. And if you look at the sign of the axis, so if it is plus X minus X; then plus Z minus Z, and this is plus Y and minus Y. And so, any substituent on the lower on the upper right; let us see what is upper right. Upper right is on this side; so upper right will have so the upper right the contribution of the substituent will be plus X. Because that is the that is the sign of the coordinate here x coordinate; then plus Y and minus Z.

You can actually look it from here something which is on this side, something which is on the upper right. Upper right will have plus X definitely, upper right will have plus Y; because it is in the right direction and minus Z. So, if you multiply these if you multiply these contributions, then what will happen? You will get a sign of minus. So, that is why this contributes in a negative sense; that means any substituent in the upper right, rear octant will be will contribute in a negative fashion to the sign of the cotton effect. So, similarly you just carry on with the sign of these axis; if something of the of these coordinates and multiply them.

And that will give you the contribution the sign of contribution towards the cotton effect. So, if you think of upper left, in upper left your Y is negative; your Z is negative, but your X is positive. So, multiplication of this will give positive, positive cotton effect; so that is how it is. Now, it is purely empirical, but interestingly this empirical rule works. There are some different empirical rules you know that this Woodward as a diene rule for calculating the lambda max. So, those are empirical rules, which are derived by looking at several molecules like Woodward did. Look at the lambda max for several dienes and then came out with his famous Woodward dine rule, and then dienophile rule.

Similarly, by looking at the sign of the cotton effect of several ketones, then people have come out with this octant rule; so, this is for the rear octant. Remember in the if something is on the front octant, then this sign of cotton effect contribution of cotton effect will be just the opposite. That means if it is the front octant, then upper right front octant will contribute in a positive sense. So, this is your upper right rear octant, this is your lower right upper right, sorry this is upper left; I am sorry, this is upper left rear octant and that contributes plus. So, if it is in the if it is the front octant, then upper then upper right will contribute positive.

That means it is just the reverse of all this; so you have to remember that. Fortunately, most of the molecules that are there that have been studied have their substituents; mostly falling in the rear octant. But, there are some cases where substituents can also come in the front octant, and then you have to be careful. Just remember that it is just the opposite of what is the sign of contribution for the rear octants.

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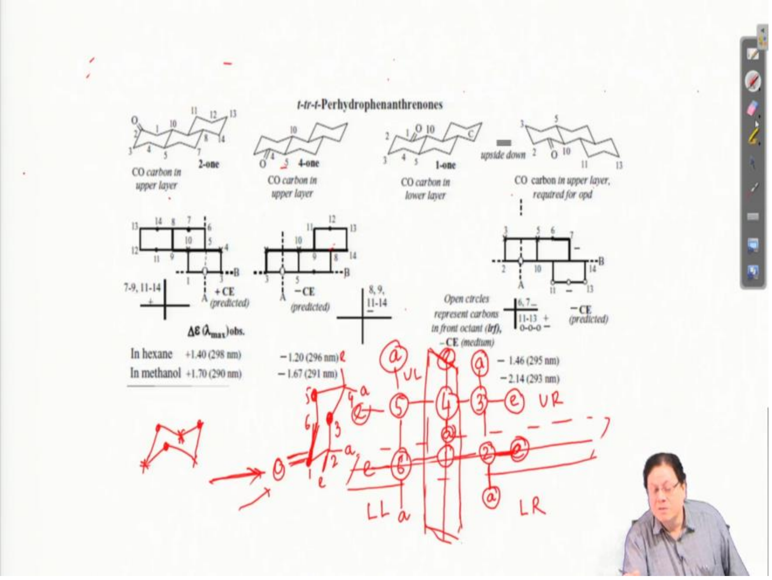

t-tr-t-Perhydrophenanthrenones

Δε (λ_{max})obs.

In hexane +1.40 (298 nm) −1.20 (296 nm) − 1.46 (295 nm)
In methanol +1.70 (290 nm) − 1.67 (291 nm) −2.14 (293 nm)

Now, let us decalone system or even cyclohexanone system simple system, and applied the octant rule. Let me just and then let us check little bit more complicated cases; complicated cases means where the number of cyclohexanone rings are more. Now, remember you should always be very confident in your original understanding of cyclohexanone axial equatorial bonds. Because what you are doing in octant by applying octant rule, is basically taking a projection on a screen which is held at the rear side. And you take a projection of all the substituents of all the atoms on to that screen.

And you should have very clear idea of how the projection looks like for a cyclohexanone system; let me just draw it here the projection again. So, if it is the carbonyl sorry, so if this is the case this is the carbonyl; so this is 1, 2, 3, 4, 5, 6. So, at this so when you take the projection, then what will be the projection diagram look like. C1 is in the central point, you are looking from this direction so 1; then on the right is 2, on the left is 3 6. Here there is one important point that when you talk about a cyclohexanone system, the carbonyl. When you look at the carbonyl, you should make sure that the carbonyl carbon is occupying the head of a chair.

The head of a chair means in the chair, there are certain 3 carbon atoms, which are actually called the head of the chair, like these 3 ones; and these are the leg of the chair. So, the carbonyl has to occupy the head of a chair, which is it is occupying the way I have written here. The carbonyl is occupying because this is a head that is a head and that is the head of the chair; so, carbonyl is in the right position. Then you look through the oxygen carbon bond, and as you look you will see that 1 is in the middle; then 2 then 3. On the right side gets 2, on the left side get 6; and then it goes up. 5 and then 4 and 3 and 3 is connected to 2.

Now, the cross section of the 2 planes of the 2 planes, which is basically I can go back; no, I think that is ok. The cross section of the 2 planes which is basically dividing into these 4 spaces; the rear the 4 spaces at the rear and 4 spaces at the in the front. Their cross section of the 2 planes will be lying like this; 2 lines perpendicular mutually perpendicular to each other. And that means one plane is going through this line, one plane is going through this line; and the other plane is going through this line. So, this is the picture, so what we are drawing is the intersection of the 2 planes; and the projection intersection which is drawn as a projection.

So, now so this is the basic diagram you should remember, and then the substituents; because everywhere there is an equatorial and axial substituent. So, you have to be careful which way these equatorial and axial substituents go. So, what happens the equatorial is you is going in the horizontal direction and the axial goes in the in the vertical, along the vertical direction up or down. So, equatorial 2 equatorial will be on right side, and 3 equatorial will be also on the right side; and then 3 axial will be on the upper side. Remember this when you have completed 3 lines, the 4th is automatically fixed; the 4th group the projection of the 4th group.

So, when you have when you know that the equatorial is on the right; so that means the axial has only one position here that is the top. For the 4th carbon which is incidentally lying in the right in the plane, which plane that means this is the plane, or which is lying at the cross section of the 2 planes. So, this 4 has an axial, 4 has an equatorial here and axial there; so, you can make out from this. I think it is easy to visualize that the equatorial will go up and the axial will go down; so this is the scenario and then 5 and 6. So, 5 equatorial is on the left and axial on that right, and then 6 equatorial on the left and axial on this.

That means this axial is occupying the lower right. These are occupying the upper right and these are occupying the upper left and this is lower left; so that is the scenario. And this you have to be you have to remember at least you have to understand this, how to draw this equatorial axial.

Because when you have more rings, then this is important; because the ring bonds will be either axial or equatorial; so you must know how to draw this.

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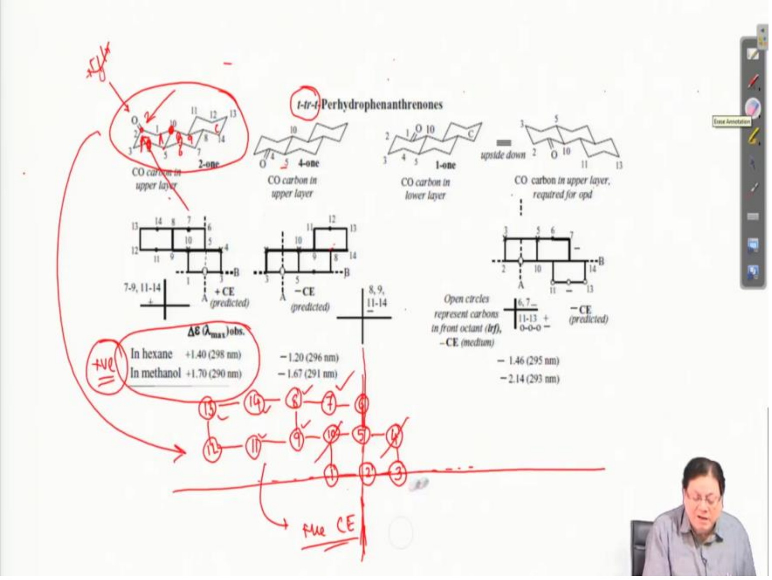

Now, let us come to this system which is depicted here; this is the perhydrophenanthrenone. Now, as I told as I already told you that this cotton effect, this octant rule is utilized to know the conformation, configuration of the molecule. Another important point is suppose, you have a cyclohexanone system, where you really do not know the structure the basic structure. Basic structure means the constitution; constitution means you should know the connectivity of different atoms.

And sometimes what happens, you are not very sure where is the carbonyl; whether it is at the c1 position or c2 position. So, the precise location of the carbonyl is also very important to know, and it is also can be determined with the help of this sign of the cotton effect. So, now there are 3 things that you can know precisely the location of the carbonyl, the conformation of the system as well as the configuration. All these 3 can be verified with the help of cotton effect, sign of the cotton effect.

Now, let us take a molecule which is perhydrophenanthrenones; not only perhydrophenanthrenones you have already read different perhydrophenanthrenenes. And different perhydrophenanthrenenes are expressed in terms of the stereochemistry of the ring junction and the relation between the hydrogen's; which are not ring junction hydrogen's. That means the A and the C ring; the hydrogen's how what is the special relationship. That is expressed as transoid or cisoid; and the ring junction are cis or trans. So, here it is a molecule, like this molecule is written here; this molecule is written here. This is what is that? This is trans, this is first of 5-10 ring junction is trans.

Then 10 and then this is 9 that is not written here; this is 9. So, 10 and 9 they are transoid and then 9 and 8 are again trans. So, this is a trans-transoid-trans perhydrophenanthrenones; so you have a carbonyl. Now, here the question is that if you have a carbonyl at the 2 position of this system, then what will be the sign of the cotton effect?

Now, the sign of the cotton effect has already been experimentally determined that it is positive; experimental is positive. So, if this structure is correct, suppose you have a perhydrophenanthrenone, and if you want to really know whether the carbonyl is at the 1 position or at the 2 position. Then determine the sign of the cotton effect and then predict it with the help of octant rule; and then see what was the experimental observation.

So, let us draw the projection of this in the octants; the octant projection of this 2 perhydrophenanthrenones, in the trans-transoid-trans isomer, so this is the situation. Now, what is done in octant in drawing the octant projection; that you have to look along the oxygen carbonyl, the oxygen of the carbonyl and the carbon of carbonyl; that means OC bond, against the OC bond or along the OC bond. Sorry along the OC bond and then but you have to make sure that you are looking at the carbonyl carbon, when the carbon is occupying the head of a chair. So, in this case there are first of all this is occupying the head of a chair that is not a problem.

Because these are the head of the chair; sorry this one, that one and that one; that means c10, c4 and c2. So, that is first condition is made. The second condition is second condition is that you have to look along the OC axis. However, here because the carbonyl is on the other side; so it is very difficult that you stand here, and then look at this look along this OC bond. So, to simplify the problem, because the way to do it is that, you have to turn it upside down; you have to turn it upside down or turn it in such a way that it comes in front of the observer. Otherwise, the observer has to stand here; the observer has to stand here.

And what I usually do I suggest to the students is that whatever way the carbonyl is written; let it be there. And you also you are comfortable by looking from this direction, because you are on the, you are lying top of the; you are seeing from this side, from the top of the screen. So, you look from this side, the carbonyl is occupying the head of a chair; but you are looking just opposite to what is required for drawing the octant projection. If that be the case then what happens is very simple logic that if you look from this side; whatever comes to the right that will go to the left; and whatever was in the left that will go to the right, so that is the simple logic.

So, if you do that then you know that 2 is in the central point, and then as it appears that 1 is on the right; but then actually it should be on the left. 1 should be on the left and then 3 should be on the right; and then once you fix that it is not a problem. Now, 1 is connected to 10 1 is connected to 10, 10 is connected to 5; and 5 is connected to 5 is connected to 4. So, this is a projection of the ring A containing the carbonyl; so this is your, the 2 cross section of the 2 planes. The intersections of the 2 planes, and now you have to complete the other rings; the projection of the other rings. For that you need to know where are the carbonyls, where are the axial and the equatorial ones.

Now, before that I should have mentioned here that the how the contribution of the each substituents vary, depending on their location. First of all substituents or atoms which are lying along these axis; they do not contribute at all to the sign of the cotton effect. And the substituents which are and the sign is obviously determined at which octant it is occupying; that is we have already told. But, what will be the extent of their contribution that depends on how close it is in towards the; how close it is in comparison to the chromophore. So, if the greater the closeness spatial closeness; so it will contribute more.

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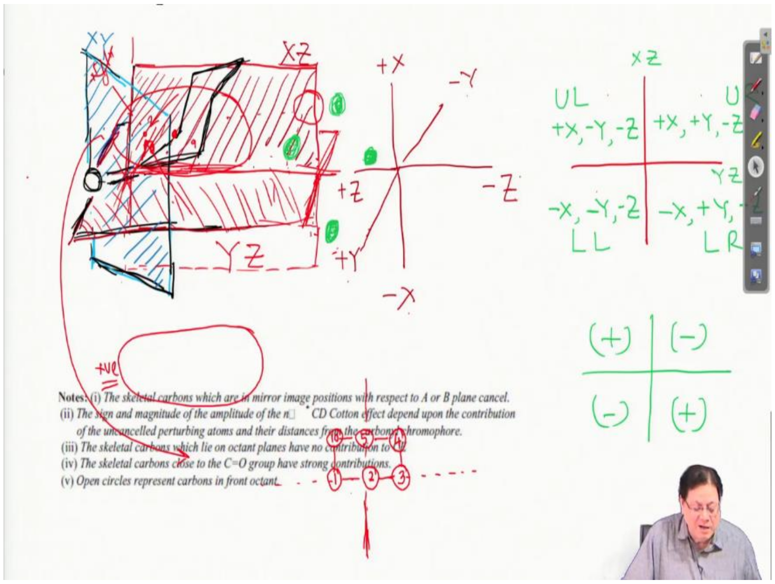

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(iv) The skeletal carbons close to the C=O group have strong contributions.
(v) Open circles represent carbons in front octant.

I think I have certain let me see maybe I missed that; yes, first of all the carbons which are occupying mirror image positions, they cancel each other. The substituents which are occupying mirror image positions, they cancel each other.

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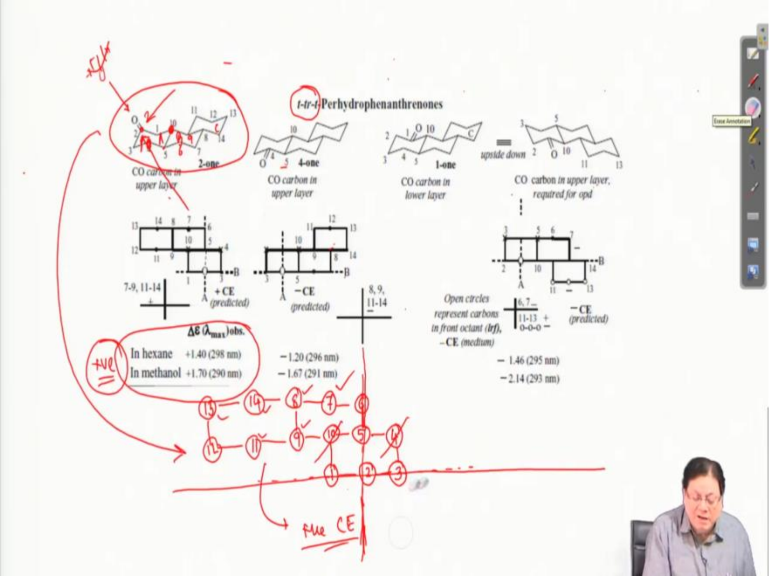

t-tr-t-Perhydrophenanthrenones

CO carbon in upper layer

CO carbon in upper layer

CO carbon in lower layer

CO carbon in upper layer, required for opd

Open circles represent carbons in front octant (lrf), −CE (medium)

Δε (λ_{max})obs.

In hexane +1.40 (298 nm) −1.20 (296 nm) − 1.46 (295 nm)

In methanol +1.70 (290 nm) −1.67 (291 nm) −2.14 (293 nm)

And as I said that the substituents which are lying or atoms lying at the basically in one of the planes, like this plane or that plane. Or, I can say that the projection is right on this the axis; axis is created by the intersection of the 2 planes. Then they do not contribute at all; so these are the important points. So, that means 4 will cancel the contribution of the 10; because both are carbon.

So, they will contribute, they will cancel each other; but let us continue to draw the projection. So, this is the first ring that means the cyclohexanone and then 10 has. 10 you know that equatorial goes in. Sorry, the equatorial goes in this direction, so what is the equatorial bond in to attach to 10 is 9. If you look carefully 9 is equatorial to this ring A, if it is the ring A; so that is equatorial, and the other is the 5. Now, the 5 you have to remember 2 and 5 the plane which is going through 10, is also going through 5. So, 5 your equatorial is at the top, so equatorial means this is 6; so that will be 6.

And so 9, 10, 5, 6; because that is the equatorial one and axial goes at the bottom. If you remember the original diagram, and then once you fix 4 atoms, then it is easy to complete the full picture. So, 9 is attached to 8, you do not have to think much in fulfilling the other atoms; 7 and then that is connected to 6. So, this is the ring B and now the ring C; so, this is suppose B and the ring C. So, ring C starts from 1, ring C is fused to 8 and 9; so you have to see what is the 11 carbon atom that bond 9, 11 bond. Whether it is equatorial or axial, it appears that it is the, it is equatorial.

The bond which is attached to 9 that means the element attached to 9 is equatorial; so 11 will be here. And then 8 what about the 8? 8 also has an equatorial equatorial carbon, which is carbon 14; so, 8 also equatorial. Equatorial will go on this side, so that will be here 14. Now, you have 4 atoms already fixed, so you can complete that; 14 is attached to 13 and 13 is attached to 12; so, this is the complete diagram. Remember do not forget the 2 axis, so this is the axis; so now you see all the 4 cancels 10. The contribution of 4 cancels 10, but you have a huge number of other atoms, which are not cancelled by any. There is no atoms other than 4 on this side.

So, basically you have a strong, you expect that it should show a strong positive cotton effect; and what was the result? Yes, it indeed showed a strong positive cotton effect. So, that is how you draw the projection, and then do the conformation of the position of the carbonyl; because that immediately proves that yes the carbonyl is at the 2 position.

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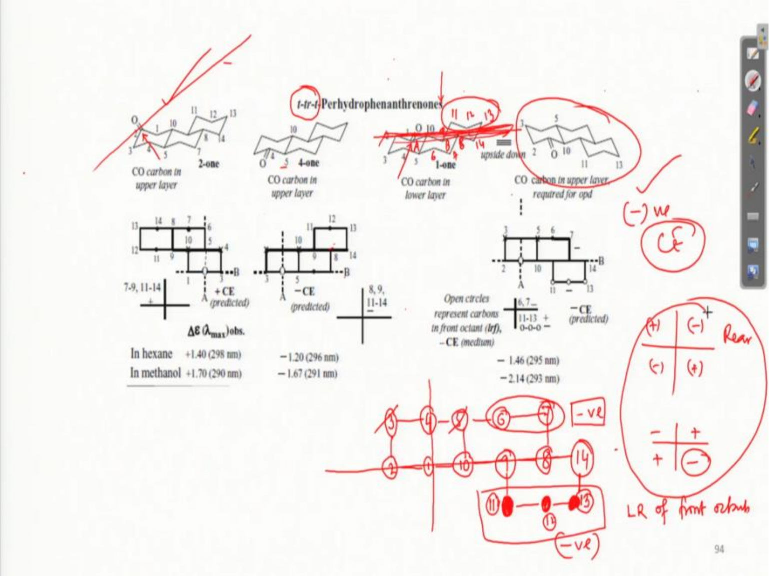
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Let us just quickly do the 1-one because 1-one is little bit more tricky. Here the carbonyl carbon is occupying carbonyl carbon is occupying the leg of a chair, the leg of a chair and also it is on the opposite side of the observe observers view. Otherwise, observer has to go on the back side which is very difficult here; so or you can turn it upside down. What has been done here that turn it upside down; that is one way to do it. If you turn it upside down, the advantage is that the leg of the chair becomes head of the chair.

So, you satisfy that one. Not only that one you also satisfy, you also make it very comfortable for the observing to see from the oxygen carbonyl bond. So, the other way is basically you do not turn it upside down, you do not change the structure as it is represented. On the other hand, you just make a logical, you just put some logic behind your drawing the octant projection.

So, what we do? Like last time for the 2 1 what we did? We looked at the opposite to the oxygen carbon bond. But we are looking from the carbon oxygen bond, because that is the that basically is from the side I am looking at; so, I look from this side. Now, while I look from this side, I am violating the the the direction parameter; that means I am supposed to look from the oxygen carbon direction. But, this is I am looking from the carbon oxygen; so that is one violation. The second one also is the carbonyl carbon is occupying the leg of a chair; so there are 2 variations here.

Unlike in this case of the 2 ketone, where there is only one variation that I am just violating the direction parameter. Here I am violating both the direction parameter as well as the head carbonyl carbon occupying the head of the chair. If that be the case, then I do not have to change anything. Whatever I see from here, right will remain on the right side; left will remain on the left side. So that is the logic that one can put forward while drawing the projection in the octant projection of this molecule, without disturbing the molecule at all. Now, it is up to the up to you what to do, which one is comfortable.

Whether you turn it upside down, bring the carbonyl carbon to the head of the chair, and as well as also bring the carbonyl facing the observer. So, that is that is one approach, but let us adopt the second approach; which is kind of a mnemonic approach put some logic. Again, I repeat if there are 2 violations, then you do not have to change the right left. So, let us draw the projection, this is 1 and 1 is connected to 10; that is not a problem, and 1 is connected to 2 that is also okay. Then you have 3, then you have 4, then you have 5 and you have 10. So, this is the A ring; remember this is the axis, 2 axis.

Now, 5 is connected to 6 and 5-6 bond is equatorial; so that will be here 6. And 10 is connected to 9 and 10-9 bond is also equatorial so 10-9. And then 6 then as you have 4 atoms already fixed; so you can complete it that 6 is connected to 7; 7 is connected to 8 and this. Now, there is another interesting feature of this molecule that you can also.

But this interesting feature can be visualized or can be understood, by looking at the molecule. See when you divide this this space around the carbonyl into the rear and the front octants. So, these the plane that was dividing it into the 2 rear and the front is this plane; the plane which is going through this.

So, this is the plane which is dividing it into rear and the front octants. If you do that you see that we are actually we should observe from this side; so this will be 3, 4, 5, 6, 7 they will fall in the rear octants. But, what about this 11, 12, 13? As you see that that will be on the towards the side of the observer; so that will be in the front octant. So, that is another important change here and you will face that you will you can show it here; that let us complete the C-ring now. So, B-ring we have completed; so, 8 is connected to 14, 8 is connected to 14 and via an equatorial bond, so that is not a problem.

But, now the other joining is 9 to 11; 9 to 11 is equatorial; but it is unlike it is not going into the rear octants. So, it is coming in the front octant and that will be there is a way to show the front octant means there are you have to remember I put circles; I may put dark circles. Of course, you have to put the numbering here that is 11, and then another dark circle that is your 11 a 12; and then 12 is connected to 12 is connected to 13. So, these 3 are the are reciting in the front octant. As you can see from here also, if you dissect it like this with this plane you see; that 11, 12, 13 are in the front octant and that is what is happening here, so this is the situation.

So, if that is the situation, then now 3 can cross out 5; they are in the mirror image positions. However, there is 6 and 7. 6 and 7 contributes, because they are in the rear octants and upper right that they contribute in the negative sense. That is ok and now what about this one which is occupying the lower right of the front octant. Now, remember in the rear octant, this is minus that is plus, this is minus, that is plus; and in the so this is rear. And in the front octant, it will be just opposite; minus, plus, minus. So, this is occupying the lower right of the front of front octant; and so that will also have negative contribution towards cotton effect.

So, the overall it should show the molecule, this 1-one should show negative cotton effect; and that is the case it showed the negative cotton effect. So, you see that sometimes things are little difficult, little tricky; specially when the carbon atoms come into the front octant. But, I will always suggest to do this check that when you have the carbonyl; put a line like this and see, if anything is coming behind coming in front of the line or behind. Nothing is in the front, so there is no atom in the front octant for this molecule. But, for this molecule when you draw this line, you see that 11, 12, 13 are on the side of the observer; so that comes in the front octant.

So, that gives you first indication that ok when I draw the projection, I have to keep that in mind that some atoms are in the front octant. And the other thing you just remember this, the contribution of the substituents in the rear and the front octant. So, I think these examples will clear your doubt or has cleared your doubt; practice it more and more. Because there are even more complicated cases, which are called which are steroid; that means there are 4 rings. And 4 ring systems, your drawing could be little trickier than this; and I will show one molecule here, which is a steroid.

Let me see the molecule maybe drawn here; this is again a perhydrophenanthrenone. We can comeback to this in the maybe in the problem solving session; will do problem solving in the next lecture. And then at that point we will bring in the steroid molecule, and then we will do some projection practice; practice of how to draw the projection and then how to predict the sign of the cotton effect. Thank you.