Application of Spectroscopic Methods in Molecular Structure Determination

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Lecture - 32

Structure Solving based on IR, MS, 1H and 13C NMR Spectroscopic Data

Problem solving session – IV

Hello, this is module 32 of the course on Application of Spectroscopic Methods in Molecular Structure Determination. This is problem solving session number 4. We use the data from the infrared spectrum Mass Spectrometry proton NMR and carbon 13 NMR Spectroscopy data for structure elucidation of certain organic, simple organic compounds in this problem-solving session.

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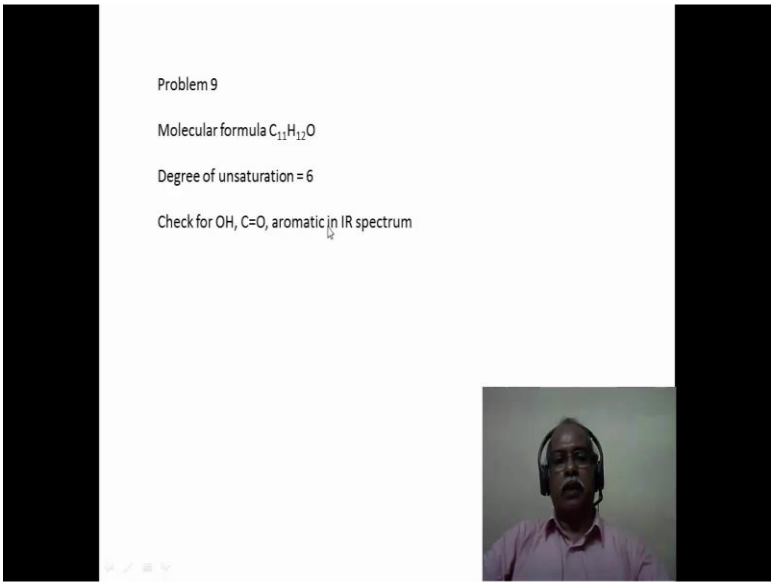

Problem 9

Molecular formula $C_{11}H_{12}O$

Degree of unsaturation = 6

Check for OH, C=O, aromatic in IR spectrum

This is problem number 9. Upto 8 problems we have solved in the earlier modules. The molecular formula of this compound is given as C11H12O from the molecular formula we calculate the degree of unsaturation or the double bond equivalence to be 6 in the particular case. So, this could very well be an aromatic compound because of the large degree of the unsaturation that is present. Because of the presence of the oxygen, let us look at the presence of or absence of OH carbonyl stretching frequency and aromatic stretching frequency in the infrared spectrum of this compound.

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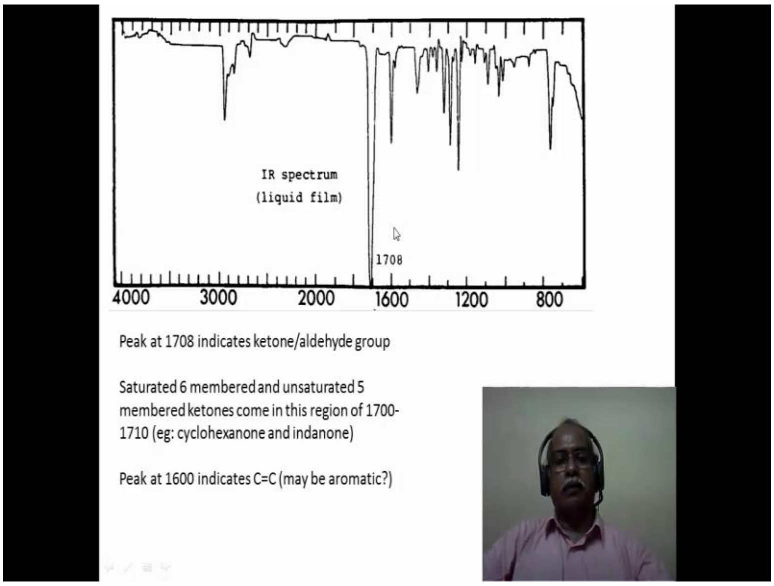

Peak at 1708 indicates ketone/aldehyde group

Saturated 6 membered and unsaturated 5 membered ketones come in this region of 1700-1710 (eg: cyclohexanone and indanone)

Peak at 1600 indicates C=C (may be aromatic?)

This is a infrared spectrum of this compound, the peak around 1708 is a very intense peak. This could be because of an aldehyde or a ketone typically a 6 membered cyclic ketone or an alpha beta unsaturated 5 membered ketone will come in the region between 1700 and 1710. For example, cyclohexanone has the carbonyl stretching frequency around 1710 or so. In the known which is a fused bicyclic system is coming around 1705 or so, in the carbonyl stretching frequency. This is an alpha beta unsaturated system where as, this is a saturated system. So, one need to distinguish whether it is because of a saturated 6 membered ring or an unsaturated 5 membered ring as we proceed we have to see this particular peak. The peak around 1600 might be because of C double bond C which may be due to aromatic in this particular case.

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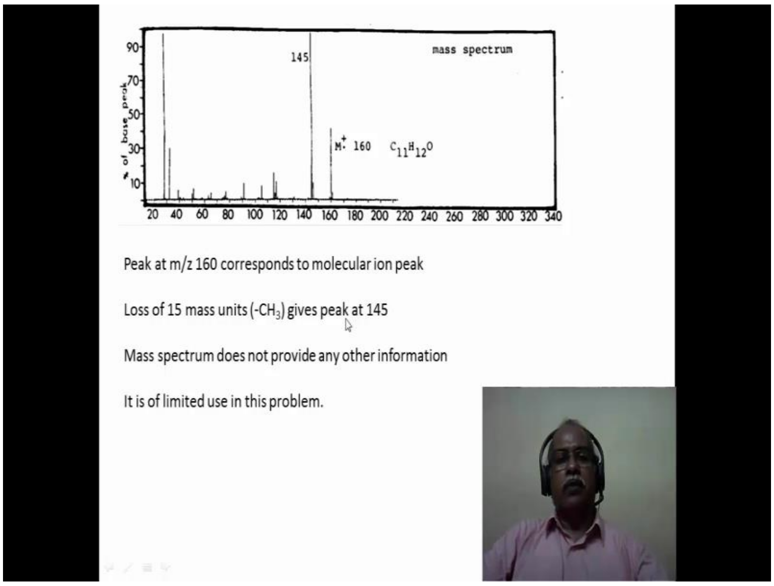

Peak at m/z 160 corresponds to molecular ion peak

Loss of 15 mass units (-CH_3) gives peak at 145

Mass spectrum does not provide any other information

It is of limited use in this problem.

This is the mass spectrum of this compound. The mass spectrum is of limited used in this problem because not much fragmentation is seen here. The molecular ion peak is seen at the m by z value 160 and loss of 15 mass units gives you 145 peak m by z 145 the loss is because of the loss of a methyl group which corresponds to 15 mass unit. Beyond that we do not get much of an information, these are all because of water molecules or carbon monoxide, carbon dioxide kind of molecules which are the in the atmosphere in this particular case.

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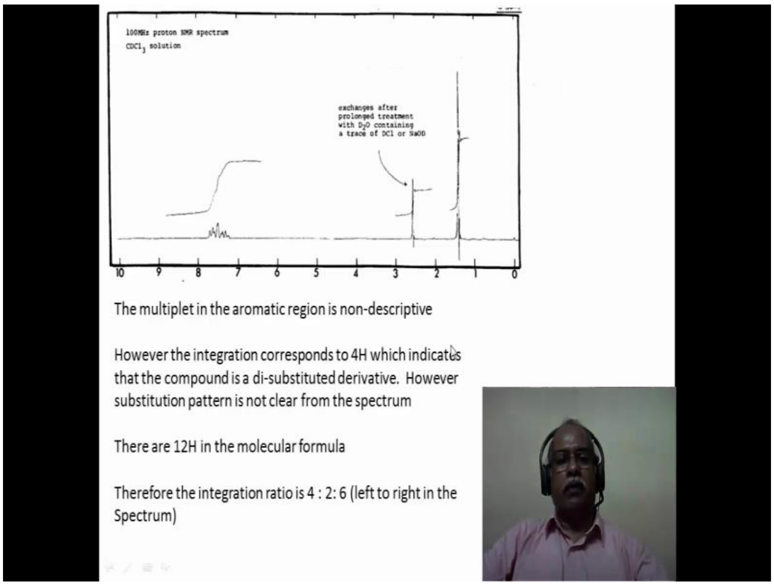

The multiplet in the aromatic region is non-descriptive

However the integration corresponds to 4H which indicates that the compound is a di-substituted derivative. However substitution pattern is not clear from the spectrum

There are 12H in the molecular formula

Therefore the integration ratio is 4 : 2: 6 (left to right in the Spectrum)

So, let us find out from the NMR spectrum what information that we can get. This is a NMR spectrum of the compound right away one sees the D2O exchangeable hydrogen but, this is not ordinary D2O exchangeable hydrogen. The D2O exchange happens only after a prolonged treatment with D2O containing traces of either an acid which is DCL or a base which is sodium hydroxide D; that means, there is a enolizable hydrogen in this molecule. This is not because of AOH in the case of alcohol or phenol or a carboxylic acid kind of a functional group. This is a functional group mainly because of the enolizable kind of hydrogen that is present in the system.

Now, before we go in to that let us look at the aromatic region. Aromatic region is a non-descriptive multiplet is what is seen. So, one cannot figure out from the aromatic signals whether it is a ortho substituted, para substituted or meta substituted the only conclusion we can arrive from the aromatic pattern is because of the hydrogen intensity corresponds to 4 and the total number hydrogens in the molecule is 12. So, out of which you have to now partition this integration for 12 hydrogen if this corresponds to 2 hydrogen intensity and this corresponds to 6 hydrogen intensity and then this would this would correspond to 6 hydrogen intensity and 2 hydrogen intensity. This would essentially correspond to 4 hydrogen intensity. A 4 hydrogen intensity in the aromatic region would only mean, that it is a di-substituted aromatic compound but, unfortunately from the splitting pattern which is a non descriptive splitting pattern, we cannot tell whether it is an ortho di-substituted, meta di-substituted or para di-substituted

So, the integration ratio di-substitute d of 4 is to 2 is to 6 going from left to right this multiplied is 4 hydrogen, this is 2 hydrogen and this is 6 hydrogen is what the information we can get from the proton NMR spectrum. This is a enolizable di-hydrogen. So, it could be that it is adjacent to a carbonyl functional group that is important information that the NMR provides because of the D2O exchange under acidicor basic condition.

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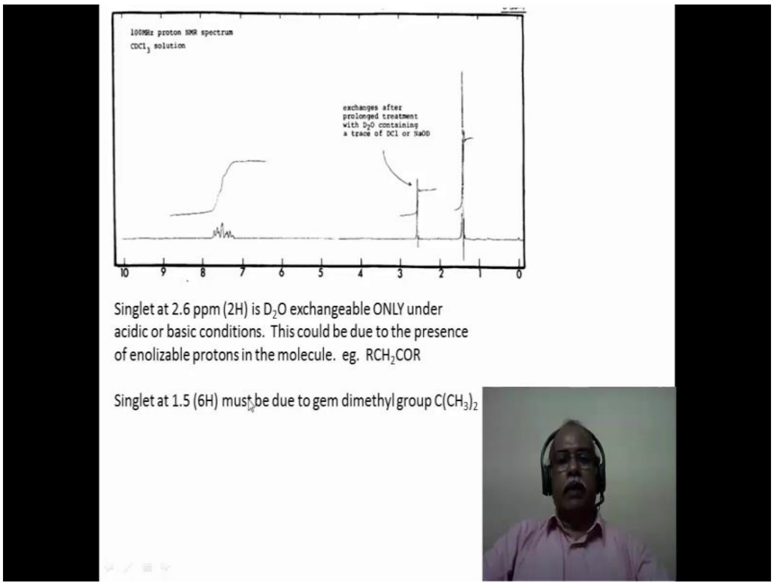

Singlet at 2.6 ppm (2H) is D_2O exchangeable ONLY under acidic or basic conditions. This could be due to the presence of enolizable protons in the molecule. eg. RCH_2COR

Singlet at 1.5 (6H) must be due to gem dimethyl group $C(CH_3)_2$

So, that is what is mentioned here. Around 2.6 ppm, the D2O exchangeable hydrogen only under acidicor basic condition could be only because of the presence of enolizable hydrogen. Like for example, RCH2COR adjacent to a carbonyl functional group. This is the enolizable hydrogen and that is readily exchanged by the presence of an acid impurity or a basic impurity in the presence of D2O.

The singlet at 1.5 ppm is due to gem dimethyl group, because 6 hydrogen intensity of a singlet could correspond to only a gem dimethyl group kind of a functional group in the molecule. So, we have identified CH2CO and a gem dimethyl group and from there proton NMR spectrum we have identified that it is di-substituted benzene derivative.

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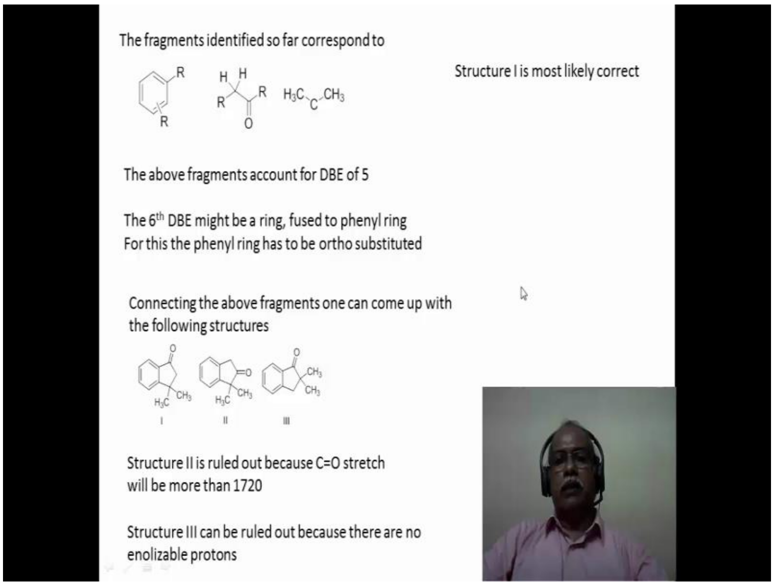

The fragments identified so far correspond to

Structure I is most likely correct

The above fragments account for DBE of 5

The 6th DBE might be a ring, fused to phenyl ring
For this the phenyl ring has to be ortho substituted

Connecting the above fragments one can come up with the following structures

Structure II is ruled out because C=O stretch will be more than 1720

Structure III can be ruled out because there are no enolizable protons

So, we have to put these 2 fragments together, but before we do that if you take these three fragments degree of unsaturation only amounts to 5 but, the actual degree of unsaturation is 6 in this molecule. So, the sixth degree of unsaturation or the double bond equivalence might be actually coming from a ring which is a fused to a ring that is fused to the phenyl ring in other words the phenyl ring has to be an ortho substituted derivative for this to be present.

So, if you put an ortho di-substituted derivative and connect all this fragments together it could be an indanone of this type or it could be an indanone of this type or it could be an indanone of this type. So, the IR stretching frequency matches for these two types of compound number 1 and 3 would match the IR spectrum but, compound number 2 will not match the IR spectrum because this is not a alpha, beta unsaturated system. So, one can straightaway rule out compound number 2 because the CO stretching frequency here will be more than 1720 and not less than 1720 because, it is a 5 membered saturated ring system it is supposed to come around 1740 or so.

Structure number three can be ruled out because there are no enolizable hydrogen in the molecule. Proton NMR very clearly shows that a alpha hydrogen which are enolizable hydrogen. So, the possible structure in this compound is correct structure is probably the structure number one.

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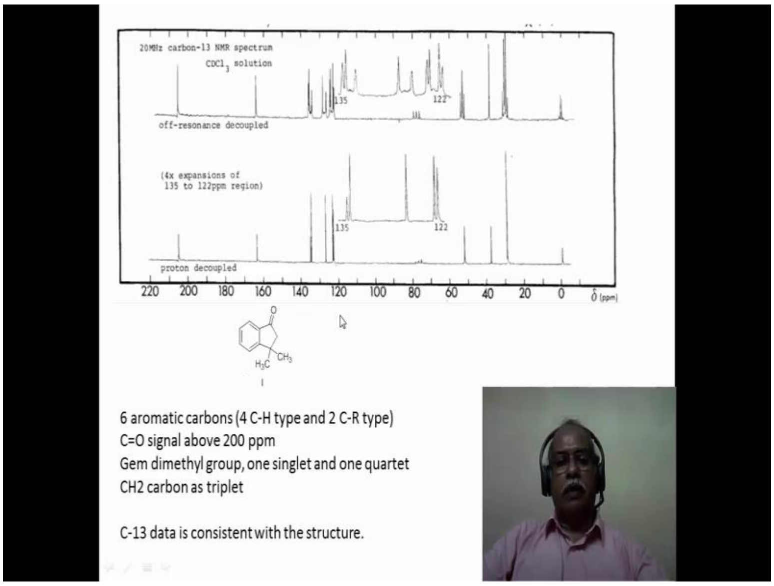

6 aromatic carbons (4 C-H type and 2 C-R type)
C=O signal above 200 ppm
Gem dimethyl group, one singlet and one quartet
CH2 carbon as triplet

C-13 data is consistent with the structure.

Let us see if it is confirmed by the carbon 13 spectrum or so. Structure one for example, has four types of CH carbons which are these 4 unsubstituted CH carbon in the aromatic region and 2 substituted quaternary C, C kind of a carbon quaternary carbon, so one should see 6 carbons in the aromatic region. So, what one sees is carbon number 1, 2, 3, 4, 5 and 6 there are 6 carbons very clearly seen. This region is expanded and shown between 122 and 135 the expanded region is shown here which has the 5 carbons one quaternary carbon and four of the CH kind of a carbon and finally, the sixth quaternary carbon comes around 162 which is because of the presents of the carbonyl functional group in this particular case.

The carbonyl functional group itself comes around 206 or 207 ppm in the carbon 13 spectrum because it is a five membered cyclic ketone it comes around 206 or so in this particular case. So, the carbon 13 data is also consistent if you look at the aliphatic region there is a CH two. So, it is a triplet in the of resonance spectrum. So, this carbon corresponds to the alpha carbon to the carbonyl. Then you have a quaternary carbon which is this particular carbon that is singlet in the resonance spectrum and these two methyl groups come as a quartet in the of resonance spectrum, coming around the 30 ppm or 29 ppm or so for the two methyl groups in here.

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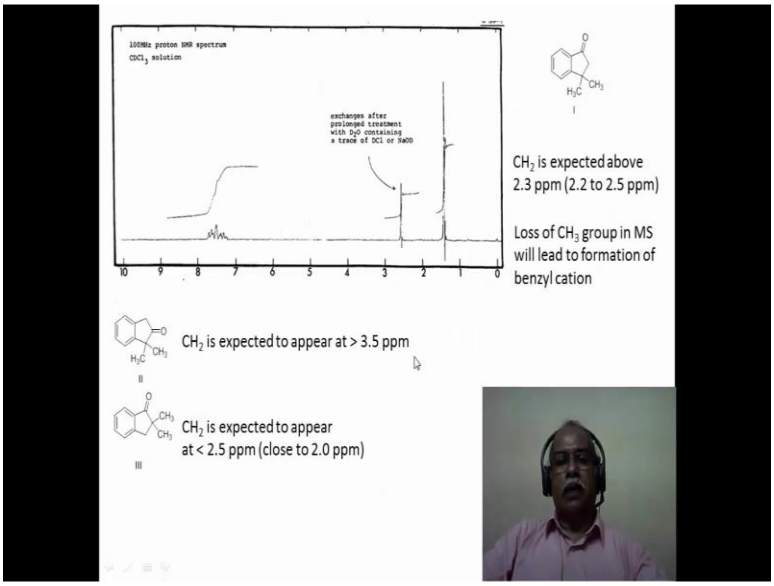

CH_2 is expected above 2.3 ppm (2.2 to 2.5 ppm)

Loss of CH_3 group in MS will lead to formation of benzyl cation

CH_2 is expected to appear at > 3.5 ppm

CH_2 is expected to appear at < 2.5 ppm (close to 2.0 ppm)

So, the molecular structure is solved as this particular structure, one more check one can do after arriving at the structure we have ruled out the possibility of structure number 2 and 3 based on the carbonyl stretching frequency as well as the non enolizable presence of non enolizable carbon adjacent to the non enolizable. There are no enolizable hydrogen in this molecule. So, we ruled out carbo the structure number three also from the consideration in addition to that we can check the CH2 hydrogen resonance this CH2 hydrogen is actually benzylic as well as acetyl kind of a CH2. So, this will essentially come more than 3.5 ppm; however, in the spectrum it comes around 2.7 or ppm or so. This structure can be ruled out based on the NMR spectrum also and in this particular case this CH2 is expected to come around less than 2 ppm but, it is coming more than 2.5 ppm because this is like a tolvin CH2 and that should not be more than 2 ppm or so. So the fact that it is more than 2.5 ppm rules out this structure also.

Where is this particular CH2, which is actually adjacent to a carbonyl functional group is expected to come around 2.2, 2.5 ppm it actually comes around 2.3 ppm or so. In this particular case, sorry coming around 2.6 ppm or so, the loss of methyl group in this particular case will give a stable carbonium ion. So, that is also justified in the mass spectrum fragmentation pattern to give a benzly cation from this particular structure.

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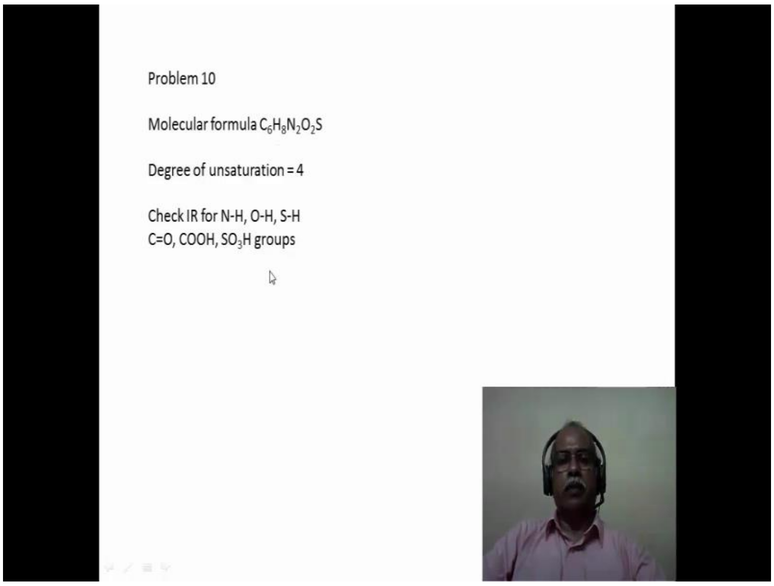

Problem 10

Molecular formula $C_6H_8N_2O_2S$

Degree of unsaturation = 4

Check IR for N-H, O-H, S-H
C=O, COOH, SO_3H groups

Let us move on to the next structure the molecular formula is fairly complex C6H8N2O2S so it is sulphur containing compound. The degree of unsaturation is 4 in this particular case because of the presence of nitrogen, oxygen and sulphur we have check for many functional group in this particular infrared spectrum of this particular compound. One has to check for a N-H namely primary secondary kind of amines or amides as the case be maybe O-H, S-H carbonyl functional group, carboxylic acid functional group even sulphuric acid functional group as to be tested in the infrared spectrum.

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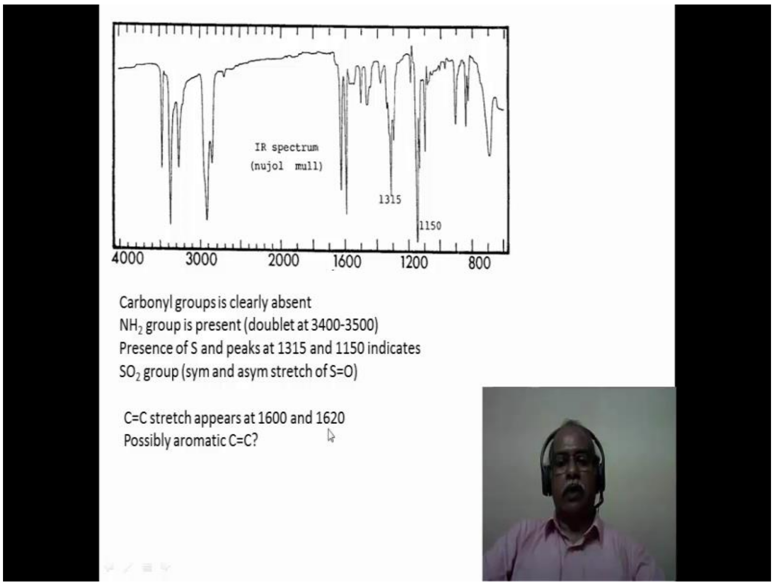

Carbonyl groups is clearly absent
NH_2 group is present (doublet at 3400-3500)
Presence of S and peaks at 1315 and 1150 indicates
SO_2 group (sym and asym stretch of S=O)

C=C stretch appears at 1600 and 1620
Possibly aromatic C=C?

This is the infrared spectrum of this particular compound one can very clearly see the absence of carbonyl functional group in the region between 1650 to 1700 or so. This is not a carbonyl compound that is conformed because of the absence of intense carbonyl peak in this region. What you see here is essentially a C double bond C kind of a stretching frequency is the sharp singlets that you see in this particular region of 1600 not more than 1650 or so. So this cannot be because of the carbonyl functional group. What is important is the NH region. This is NH or OH you can say because it is fact that it is sharp and it is a doublet kind of signal it cannot be a OH remember OH usually gives a very broad signal for a hydrogen bonded and very sharp signal of singlet type for the non hydrogen bonded.

The fact that you have a doublet, clearly tells that NH2 groups are present in this particular system. The presence of sulphur tells us to look for s double bond of o kind of a stretching frequency. 1315 and 1150 are indicated here that is because of the symmetrical and asymmetrical stretching of the SO2 group that is being present in the system. So, the infrared spectrum gives very valuable information that it has a sulfone group SO2 group it also has an NH2 group. So, it could even be a sulfone amine kind of a system in this particular case. As I mentioned the carbon carbon double bond stretching frequency is around 1600, 1620 is the one that is seen here

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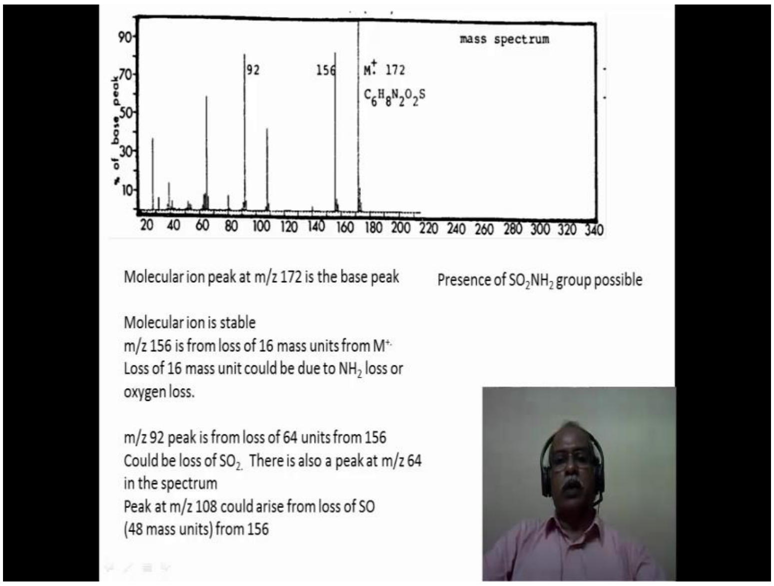

Molecular ion peak at m/z 172 is the base peak

Presence of SO_2NH_2 group possible

Molecular ion is stable
m/z 156 is from loss of 16 mass units from M$^{+\cdot}$
Loss of 16 mass unit could be due to NH_2 loss or oxygen loss.

m/z 92 peak is from loss of 64 units from 156
Could be loss of SO_2. There is also a peak at m/z 64 in the spectrum
Peak at m/z 108 could arise from loss of SO (48 mass units) from 156

Now, let us move on to the mass spectrum. The mass spectrum molecular ion peak is the base peak in other words the molecular ion is very stable in this particular compound and the fragmentation results in the formation of loss of 16 mass unit, which is probably due to the loss of a NH2 functional group in this particular case, NH2 would corresponds to 16. We have already identified that it could be a primary amide or a primary amine and loss of NH2 essentially or the laws of an oxygen atom essential gives 156 m by z value peak in this particular case. The 92 peak actually arises from the loss of 64 mass unit from 156. In other words, if there is an SO2 loss that would account for the formation of 92 in this particular case. The peak around 108 which is this particular peak here could arise from the loss of the SO from the 156.

In other words loss of 48 mass unit corresponding to SO would give this loss of 64 mass unit corresponding to SO2 will give this particular fragmentation in this particular case. So, the presence of SO2, NH2 group is possible in other words a sulfonamide group is possible.

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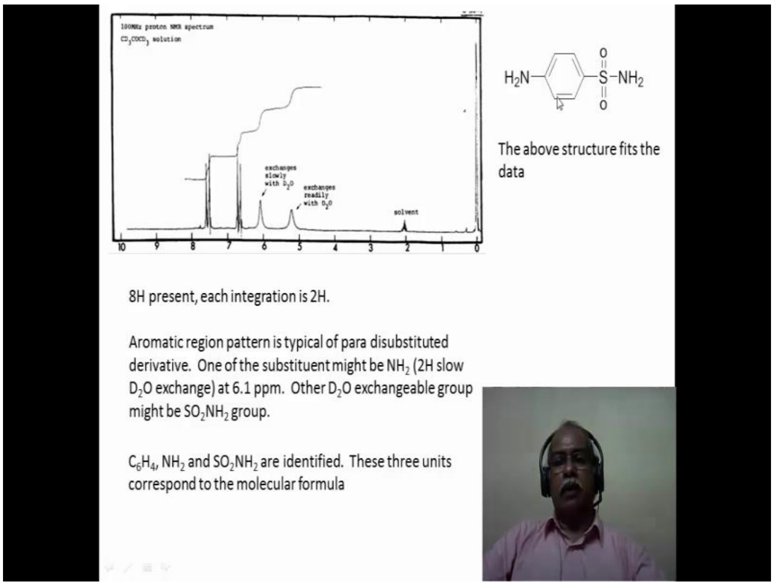

The above structure fits the data

8H present, each integration is 2H.

Aromatic region pattern is typical of para disubstituted derivative. One of the substituent might be NH_2 (2H slow D_2O exchange) at 6.1 ppm. Other D_2O exchangeable group might be SO_2NH_2 group.

C_6H_4, NH_2 and SO_2NH_2 are identified. These three units correspond to the molecular formula

So, one has to look for the kind of changeable if the sulfonamide group is here, this is an exchangeable hydrogen. So, one can look for an exchangeable hydrogen in the proton NMR spectrum. Proton NMR spectrum is very pretty in the sense, that this feature essentially tells you that it is a paradise di-substituted derivative there are 8 hydrogen present of each 2 hydrogen intensity, in other words this is a 2 hydrogen intensity, 2 hydrogen intensity, 2 hydrogen intensity and 2 hydrogen intensity. So, all the 8 hydrogens are taken care of in the molecular formula.

The aromatic pattern is a very typical para disubstituated derivative. One of the substituent might be NH2 because this is a low delta value around 6.8 or so, it might be because of the presence of an NH2 which is an electron donating functional group in the aromatic ring, which increases the electron density in the aromatic ring. And the other group might be SO2, NH2 which is electron withdrawing functional group. So, it comes more than 7.5 ppm or so. The NH2 and SO2NH2 in other words sulfonamide group and the primary amine group are exchangeable to variant degree by D2O exchange. The NH 2 group will exchange very slowly. So, this is probably due to the NH2 group. The sulfonamide group will exchange more rapidly.

And this is probably due to the sulfonamide group. This is a solvent peak in this particular spectrum acetone D6 is used as a solvent it is mentioned here on the top left hand corner acetone D6 is solvent that is used for the proton NMR spectrum. So, this is a residual solvent peak which is because of a acetone D5 kind of a molecule which gives a multiplet around 2 ppm corresponding to the acetone signal. So, one comes the conclusion that it is a phenyl C6H4 di-substituted aromatic para disubstitute the aromatic derivative, NH2 is present. SO2NH2 is present if you put all this 3 units together one gets a para amino benzene sulfonamide as the structure it fits the NMR spectral data. The aromatic region is nicely seen as AA prime, BB prime pattern which is this particular pattern the sulfonamide group and the amino groups are clearly seen also in the NMR spectrum.

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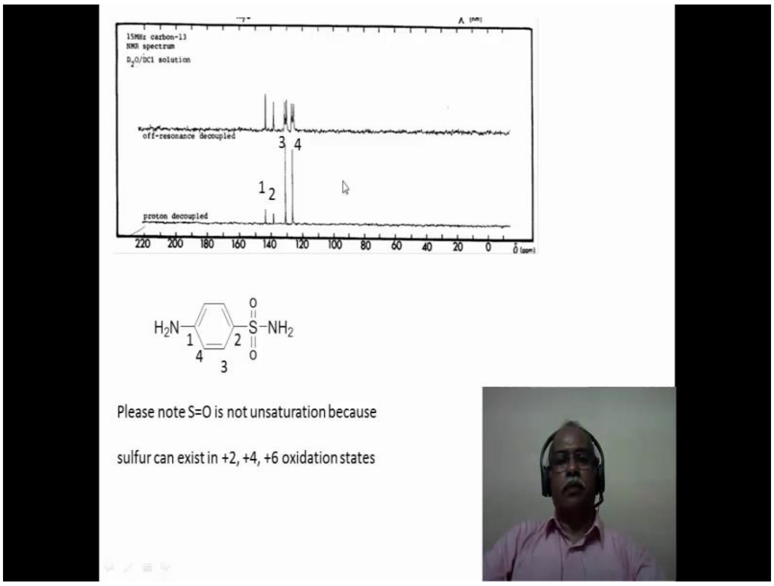

Please note S=O is not unsaturation because

sulfur can exist in +2, +4, +6 oxidation states

The carbon 13 spectrum can be easily assigned, carbon one is this particular carbon will be having the highest delta value because of the electron donating nature of the electron withdrawing nature of the NH2 the nitrogen which is electron negative will deplete the electron density at the IPSO carbon how ever in the ortho carbon it will increase the electron densities. So, that comes at the lowest delta value finally, this IPSO carbon carbon which is coming around 150 or. So, so the 2 IPSO carbons are very clearly seen as low intensity signal and the 2CH carbons are seen as a high intensity signal which also appear as doublet in the of resonance spectrum of this particular compound. Interestingly the carbon thirteen spectrum is recorded in a mixture of D2O and DCL in other words it is measured in aqueous acrylic solution in this spectrum.

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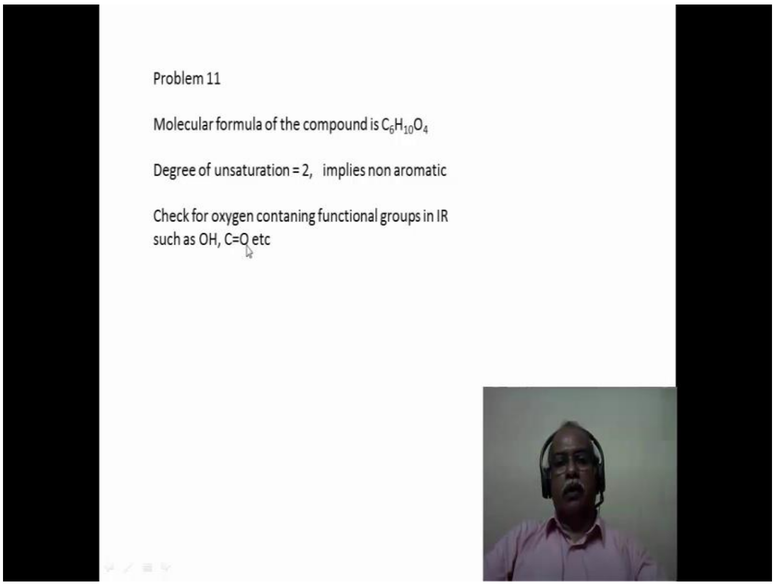

Problem 11

Molecular formula of the compound is $C_6H_{10}O_4$

Degree of unsaturation = 2, implies non aromatic

Check for oxygen contaning functional groups in IR such as OH, C=O etc

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Yes, come to the last problem in this particular module. This is molecular formula C6H10O4 degree of unsaturation is true. So, it implies it is a non-aromatic compound it cannot be an aromatic compound. Check for oxygen containing functional group such as OH and CO in the infrared spectrum of this compound.

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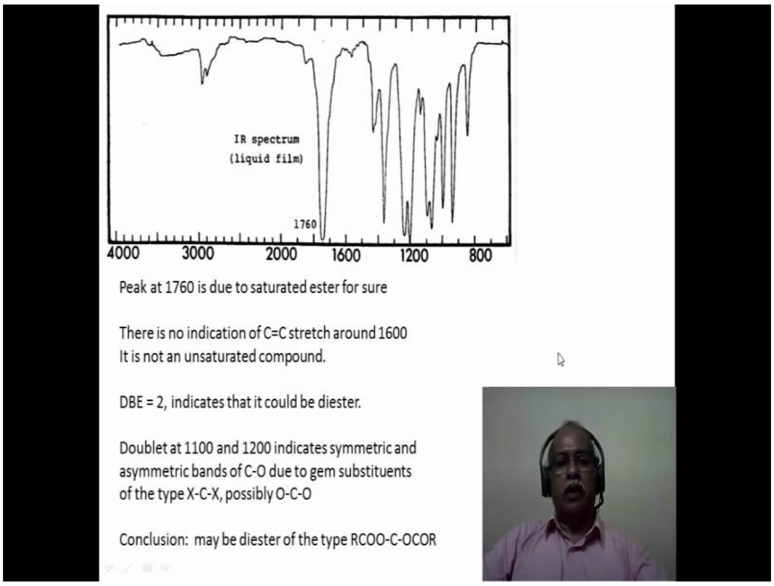

Peak at 1760 is due to saturated ester for sure

There is no indication of C=C stretch around 1600
It is not an unsaturated compound.

DBE = 2, indicates that it could be diester.

Doublet at 1100 and 1200 indicates symmetric and
asymmetric bands of C-O due to gem substituents
of the type X-C-X, possibly O-C-O

Conclusion: may be diester of the type RCOO-C-OCOR

Infrared spectrum is very rich in information here there are no OH functional group present in the system. So, it cannot be a carboxyclic acid, it cannot be a phenyl and it cannot be a alcohol kind of a functional group here. There is a small broadness that you see here is essential in probably due to the moisture of the sample or because of the presence of moisture in the air this peak is seen. But if it is really an alcohol OH functional group, it will be very broad and intern peak in this region.

So, one should not mistake this peak for any kind of OH stretching frequency this is probably due to the residual moisture in the sample or in the atmosphere. The 1760 is definitely due to a saturated ester. Saturated ester comes between 1740 to 178 or so. 1760 is very nice peak, intense peak seen which is due to the saturated ester for sure. There are no indication of any kind of a unsaturation C double bond C stretch is not seen here. However, there are double bond equivalence to which indicates that it could be a diester in other words because there is no C double bond C unsaturation here, the unsaturation can only be accounted for the ester functional group C double bond O present in the ester functional group will take care of the double bond equivalence. So, there must be a diester molecule in this particular system.

The doublet around 1100 and the doublet around 1200 indicates symmetrical and asymmetrical stretching of the carbonyl CO functional group in other words the molecule possibly has a COO kind of a functional group. This is responsible for the symmetric and the anti unsymmetrical stretching frequency which appears as a doublet corresponding to this. This is probably due to the carbonyl bending mode and this is because of the CO single bond stretching mode of the compound that we see. The conclusion is that it is a diester of this nature.

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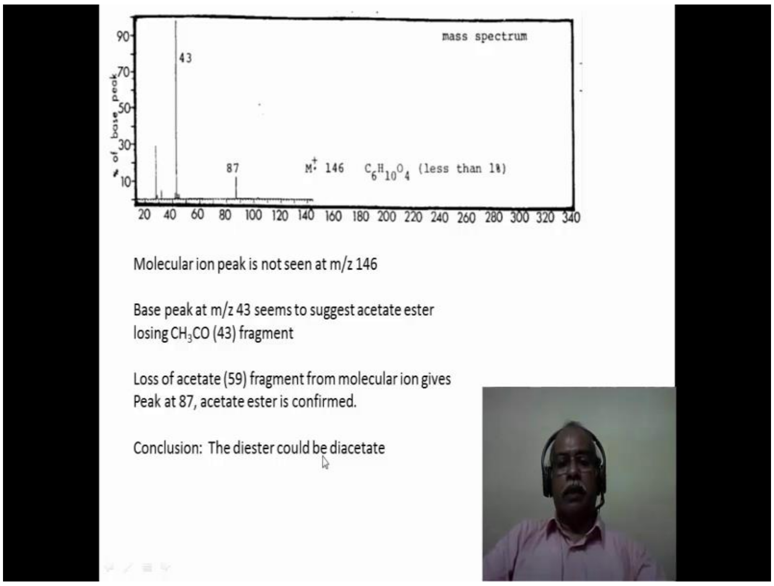

Molecular ion peak is not seen at m/z 146

Base peak at m/z 43 seems to suggest acetate ester losing CH_3CO (43) fragment

Loss of acetate (59) fragment from molecular ion gives Peak at 87, acetate ester is confirmed.

Conclusion: The diester could be diacetate

So, one has to now look at the mass spec and see if further information one can be obtained. The molecular ion peak is very nicely seen at a m by z value 146 the base peak at 43 tells us that it could be a acetate ester because the intense base peak that is seen here is essentially 43 mass unit corresponds to an acetate peak the loss of acetate unit 59 mass unit is from the molecular ion peak, gives you the peak at a 87. So, the acetate ester is very clearly conformed one 46 minus 59 will give 87 for example. So, the conclusion is that it is a diacetate molecule.

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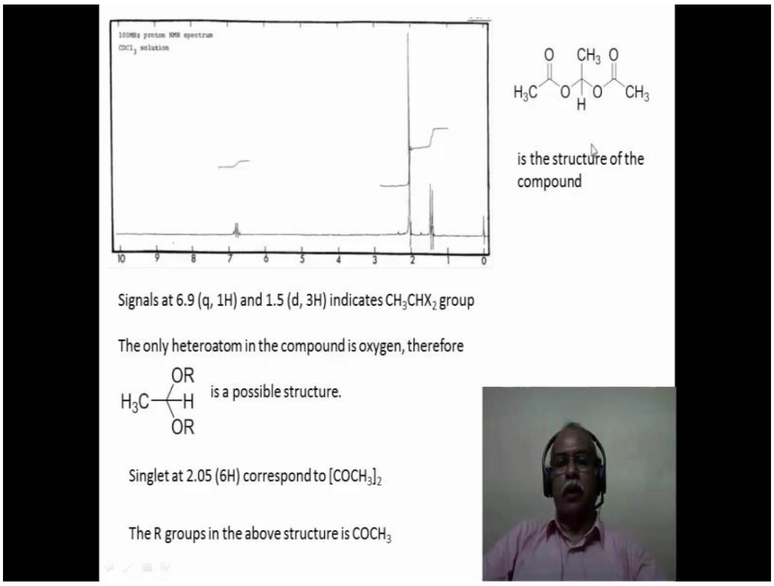

is the structure of the compound

Signals at 6.9 (q, 1H) and 1.5 (d, 3H) indicates CH_3CHX_2 group

The only heteroatom in the compound is oxygen, therefore

is a possible structure.

Singlet at 2.05 (6H) correspond to $[COCH_3]_2$

The R groups in the above structure is $COCH_3$

Now, let us look at the proton NMR spectrum. In the proton NMR spectrum there is a quartet this is certainly not a olefinic or an aromatic kind of the signal because there is no unsaturation we have already seen in the IR spectrum of this particular compound the 6.9 quartet essentially is because of the kind of a group which is a CH3CH kind of a group. The CH3 splits the CH into quartet and the CH interns split the CH3 into the doublet this.

So, the coupling partner is seen here because it is connected to 2 electron withdrawing functional group it comes at a high delta value of 6.8 or 6.9 or so, so the only heteroatom been oxygen the only possible structure is that this has a CH 3CH OR OR, kind of a structure the R group of course is an acetyl group, which is seen here in the infrared in the NMR spectrum as a singlet of 6 hydrogen intensity. So, this is 1 hydrogen intensity, this is 3 hydrogen intensity and this is 6 hydrogen intensity which take care of the molecule all the hydrogens present in the molecular formula. So, the molecule is a diacetate of this hydrated acetaldehyde. So, this is the structure of the compound it consistent with the degree of unsaturation consistent with the mass spectral data, consistent also with the infrared spectrum and a proton NMR spectral data.

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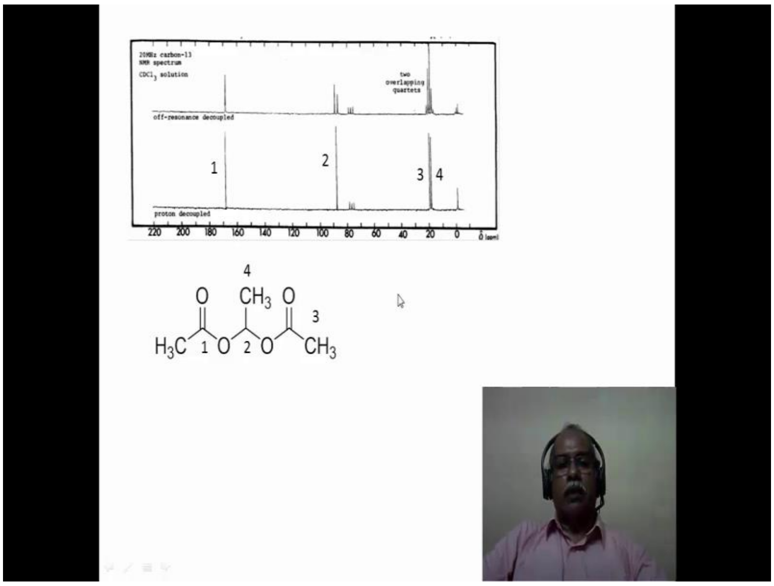

Let us look at the carbon thirteen NMR spectrum, there are 4 carbons present in this system it is a symmetrical molecule the 2 acetative units are symmetrical the CH 3 appears as a quartet which is here for example. This CH 3 also appears as a overlapping quartet. So, 3 and 4 correspond to these 2 methyl groups and signal number 2 corresponds to the CH, which is connected to 2 oxygen. So, it coming around 80, 90, 85 sorry more than 85 ppm or so, finally, the carbonyl carbon comes around 170 ppm in this compound. So, the molecular structure is elucidated based on the NMR and the mass spec.

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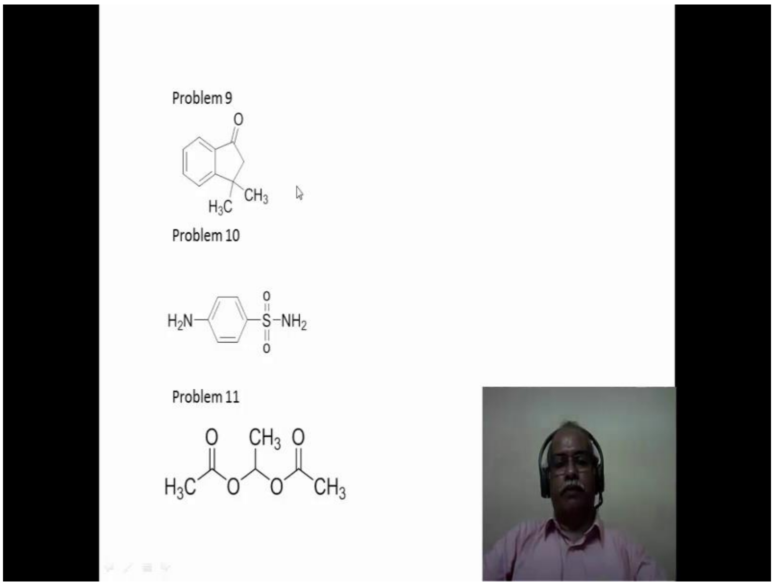

Problem 9

Problem 10

Problem 11

So, we have seen 3 compounds here one is an aliphatic diester compound, it is a special kind of a diester because it is a diester of acetaldehyde hydrate and parameno benzene sulfonamide is other one and an indanone kind of a structure is elucidated based on the spectroscopic data that is provided.

Thank you very much for your attention.