Structure solving based on IR, UV-Vis, MS, $^1$H and $^{13}$C NMR spectroscopic data

Problem solving session

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Problem 1:
The IR and EI-mass spectra of a para disubstituted aromatic compound are given. IR spectrum gives clue for one of the substitutents and the clue for the other substituent is amply evident from the MS. Deduce the structure of the compound and then make sure that the molecular weight of the deduced structure matches with the m/z of the molecular ion peaks in the MS.

Intense peaks at 1530 and 1345 cm\(^{-1}\) are indicative of NO\(_2\) (nitro) group asymmetric and symmetric stretch.

Peaks at 1600 and 1610 cm\(^{-1}\) indicate aromatic C=C stretch.
In the Mass spectrum doublets at m/z 215/217 (1:1) and at m/z 169/171 (1:1) confirms the presence of one Br atom in the molecule. Therefore the two functional groups are NO$_2$ and Br.

Disubstituted phenyl (76 mass), bromine (79/81) and NO$_2$ (46) add up to 201, 14 mass units less than Molecular ion. This means CH$_2$ group has to be added.

Facile loss of bromine gives base peak at m/z 136. This implies bromine might be present in the side chain rather than on the ring.

The possible structures are:

\[
\begin{align*}
\text{\textbf{Br}} & - \text{NO}_2 \quad \text{\textbf{Br}} \\
& \text{O}_2\text{N} \quad \text{\textbf{Br}}
\end{align*}
\]
Problem 2:
Molecular formula C$_9$H$_9$ClO$_3$ Only IR and $^1$H NMR data are given in this problem.

IR: 3300 to 2400 cm$^{-1}$ broad band and 1714 cm$^{-1}$ intense band

DBE = 5

From the IR it is inferred that 3300-2400 cm$^{-1}$ corresponds to COOH group
And the CO stretch appears at 1714 cm$^{-1}$. The compound is a carboxylic acid?
Look for COOH peak in NMR spectrum

Peak at 11.4 ppm (1H) confirms COOH group
4 aromatic protons imply disubstituted Derivative. para-disubstitution can be ruled out due lack of symmetrical pattern.

One of the substituent must be oxygen (electron rich ring) because three of the proton chemical shifts are below 7 ppm.

7.2 (t, 1H, J = 8) implies aromatic proton with two ortho protons.

6.9 (t, 1H, J = 1.5 Hz) implies aromatic proton with only two meta coupling partners.

Therefore the substitution pattern is meta.
These multiplets imply XCH(CH3)Y group

Y must be either Cl or COOH, most likely COOH

Because of the chemical shift of red H

Moreover if COOH was present in the aromatic ring
The proton chemical shifts of at least one of the Aromatic protons would have been more than 7.5
Due to electron withdrawing nature of COOH

Therefore the structure is
Problem 3:

400 MHz $^1$H NMR spectrum of hydroxycinnamic acid is shown in the next slide. Among the 6 possible isomers identify the isomer corresponding to the spectrum

The six isomers are *ortho, meta and para* isomers of cis and trans cinnamic acid

Look for AB quartet for the two vinylic protons and measure the $J_{ab}$. If the $J$ value is more than 14 Hz then it is trans isomer.

Para isomer can be easily identified by a Symmetrical AA’BB’ aromatic pattern
Signals marked A and B correspond to vinylic protons.

This gap is equal to approximately 15.6 Hz which rules out cis isomer. Therefore the spectrum belongs to one of the trans isomers.
The aromatic pattern is clearly not a AA’BB’ pattern. Therefore para isomer can be ruled out.

**Signal 1** is a triplet with $J = 7.5$ to $8$ Hz approximately. Two ortho protons are implied.

**Signals 2 and 4** also have ortho coupling along with very small Coupling, perhaps meta coupling.

**Signal 3** has only a very small coupling perhaps meta coupling.
Problem 4:

Molecular formula, IR, UV-Vis, MS, NMR data are given.

Molecular formula is $C_9H_{12}O_3S$

DBE = 4

IR is not very informative. No peaks in the OH, SH CO regions. C=C is present (1600 cm$^{-1}$). Peaks at 1350 and 1180 cm$^{-1}$ might be due to S=O?
AA’BB’ pattern in the aromatic region means para-disubstituted derivative

4.1 (q, 2H, J = 7.0) and 1.3 (t, 3H, J = 7.0) means OCH₂CH₃ group

2.45 (s, 3H) means Ar-CH₃ group (there is no COCH₃)(IR)

The balance is SO₂
The following fragments have been identified

\[
\begin{align*}
H_3C & - Y, \quad \text{O-CH}_2\text{-CH}_3, \quad \text{SO}_2 \\
\end{align*}
\]

The structure is \[ \begin{align*}
H_3C & - \text{SO-CH}_2\text{CH}_3 \\
\end{align*} \]

Let is see if the MS and 13C NMR data fit this structure
We need to account for peaks at m/z 172, 155 and 91
The UV spectrum confirms the aromatic nature of the compound, band in the 200-250 region.

The band at 270 nm could be the longest wavelength absorbing band of the aromatic \( \pi-\pi^* \) transition, there is also a possibility of this being the \( n-\pi^* \) transition of the S=O group.

\[
\text{H}_3\text{C}-\begin{array}{c}
\text{O} \\
\text{S} \\
\text{O-CH}_2-\text{CH}_3
\end{array}
\]
Tips for structure problem solving:

Always use logic (not guess work) to solve structure elucidation problems.

Check whether molecular formula is given, use it to find degree of unsaturation.
Depending upon the presence (or absence) of some hetero atoms you can infer the presence (or absence) of certain function groups.
Eg: If N is present, it could be present as NH$_2$, NHR, NR$_2$, CN etc.
If N and O are present, it could be present as NO$_2$.
If S and O are present, it could be present as SO, SO$_2$, SO$_3$ etc (depending on O content).

IR: Extract functional group information from IR by identifying characteristic frequencies of various functional groups. This means you need to familiarize yourself with most important functional frequencies.
NH, OH, CN, various C=O, NO$_2$, C=C are some of the functional groups which can be identified unambiguously from IR spectrum.
Do not try to interpret every peak in the IR spectrum, it will be a waste of time and sometimes misleading.
MS:
Look for the presence of Cl, Br from M and M+2 peaks with appropriate intensities in mass spectrum. Try to ascertain if M+ is seen in the spectrum.

Note whether molecular weight is even or odd
Pay attention to odd and even mass fragments. Even mass fragments do not arise from simple fragmentation processes if molecular weight is even.

Look for loss of familiar simple fragments from molecular ion such as loss of 15 (Me), loss of 28 (CH$_2$=CH$_2$ or CO), loss of 29 (ethyl), loss of 31 (methoxy) loss of 43 (acetyl or isopropyl), loss of 44 (CO$_2$), loss of 45 (ethoxy) etc
Look for familiar fragments such as 77 (Ph), 91 (PhCH$_2$), 43 (Acetyl), 105 (PhCO) etc

Once the structure of the molecule is more or less ascertained then only look for retro Diels Alder and McLafferty fragmentation if such structure permits.
Fragment ions from these processes will have even mass.

Fragment ion with <10% intensity can be ignored
\textsuperscript{1}H NMR:
From a quick glance of the spectrum ascertain the nature of the compound as aromatic, unsaturated aliphatic, saturated aliphatic etc.

You must use all the three parameters, $\delta$, $J$ and integration in problem solving. Check if the number of protons in the mol.formula matches with the total integration

Look for exchangeable protons or broad signals OH, NH type.

If aromatic, can you recognize any substitution pattern? Para is the easiest to identify by a symmetrical AA'BB' pattern. Look for AB and AA'BB' pattern in the aliphatic region, might be due to diastereotopic Protons.
From the splitting pattern try to identify the molecular fragments, ethyl, isopropyl etc
Note sometime septet may look like a quintet, pay attention to look carefully for weak signals
Look for signals corresponding to CHO, COCH\textsubscript{3}, COOCH\textsubscript{2}CH\textsubscript{3} from their characteristic chemical shift and multiplicity pattern.
13C NMR:

Look for carbonyl, CN and acetylenic carbons (they might weak signals, so pay attention!)

Try to count the number of quarternary carbons and carbons with protons attached from the intensity in broad band decoupled spectrum or off-resonance spectrum (if available).
A triplet in the off resonance spectrum in the olefinic region means terminal olefin C=CH₂

Based on the symmetry (asymmetry) of the structure arrived at, calculate the Expected number of peaks in ¹³C NMR and check if they match.
Eg: anthracene 4 signals, phenanthrene 7 signals etc.

After the structure is arrived at try to assign all the carbon atoms to various signals in the Spectrum and see if they match well in number and δ value
After all the fragments are identified you need to connect the puzzle in a logical manner to arrive at the final list of candidates containing one or two structures.

Get back to IR, MS, NMR data and see if the structure fits all the data and not one or two spectroscopic data. This is very important, but often students ignore this advice.

Make sure the molecular formula matches with the given molecular formula.

Please note that familiarity with IR frequencies, NMR $\delta$ and J values come only with Practice. The more problems you solve the more familiarity you will attain.
THANK YOU