

Composite Spectral Problems

7.1 AIDS TO STRUCTURAL INFORMATION

7.1.1 Determination of Molecular Formula and the Related Structural Information

The elucidation of structure of an unknown compound by spectroscopic methods can be simplified by examining the molecular formula of the compound. Important useful terms concerning the determination of molecular formula and the associated structural information are described as follows:

7.1.1.2 DETERMINATION OF MOLECULAR WEIGHT (HIGH RESOLUTION MASS SPECTROMETRY)

"Low resolution" mass spectrometer measures m/z values to the nearest whole number mass unit. However, "High resolution" mass spectrometers measure m/z values to three or four decimal places and thus, provide an extremely accurate method for determining the molecular weights.

The determination of accurate molecular weight is possible because the actual masses of the atomic particles (nuclides) are not integers. For example, a molecule whose molecular weight is 32 could be O_2 , N_2H_4 or CH_3OH . However, these molecules have the following precise masses.

$$O_2 = 2 \times 15.9949 = 31.9898$$

$$N_2H_4 = 2 \times 14.0031 + 4 \times 1.00783 = 32.0375$$

$$CH_3OH = 12.0000 + 4 \times 1.00783 + 15.9949 = 32.0262$$

Thus, a high resolution mass spectrometer, capable of measuring mass with an accuracy of 1 part in 40000 or better, can easily distinguish among these three molecules and consequently, provides information regarding the molecular formulae of these compounds.

7.1.1.3 DETERMINATION OF MOLECULAR FORMULA BY USING RULE OF THIRTEEN

High resolution mass spectrometry gives information about the molecular mass from which exact molecular formula can easily be determined. When the exact molar mass information is not available, it is often useful to generate all the possible molecular formulae for a given mass. These molecular formulae can be distinguished by applying various types of spectroscopic information. A useful method for generating possible molecular formulae for a given mass is the Rule of Thirteen¹, which is illustrated as follows:

¹J.W. Bright and E.C.M. Chen, "Mass Spectral Interpretation Using the Rule of 13", Journal of Chemical Education, 60 (1983) 557.

- (i) The first step pertaining to the rule of thirteen is to generate a base formula which contains carbon and hydrogen only. The base formula is obtained by dividing the molecular mass, M , by 13 (the mass of one carbon plus one hydrogen). This calculation provides a numerator, n , and a remainder, r .

$$\frac{M}{13} = n + \frac{r}{13}$$

The base formula thus becomes



which is a combination of carbons and hydrogens that has the desired molecular mass, M .

7.1.1.4 DETERMINATION OF THE INDEX OF HYDROGEN DEFICIENCY (UNSATURATION INDEX)

The index of hydrogen deficiency, U , can easily be calculated by applying the following relation:

$$U = \frac{(n - r + 2)}{2}$$

In order to derive a formula that includes other atoms, besides carbon and hydrogen, the mass of a combination of carbons and hydrogens that is equal to the masses of other atoms must be subtracted from the base formula. For example, if the compound contains carbon, hydrogen and one oxygen only, then the new formula containing one oxygen may be obtained by subtracting one carbon and four hydrogens (mass equivalent to oxygen atom = 16).

Table 1.1 includes a number of C/H equivalents for replacement of carbon and hydrogen in the base formula by the most common elements generally encountered in organic compounds.

Table 1.1 Carbon/hydrogen equivalents for some common elements

S.No	Add element	Subtract Equivalent	Add ΔU
1.	H ₁₂	C	-7
2.	C	H ₁₂	7
3.	O	CH ₄	1
4.	O ₂	C ₂ H ₈	2
5.	O ₃	C ₃ H ₁₂	3
6.	N	CH ₂	$\frac{1}{2}$
7.	N ₂	C ₂ H ₄	1
8.	S	C ₂ H ₈	2
9.	³⁵ Cl	C ₂ H ₁₁	3
10.	⁷⁹ Br	C ₆ H ₇	-3
11.	⁷⁹ Br	C ₅ H ₁₉	4
12.	F	CH ₇	2
13.	Si	C ₂ H ₄	1
14.	P	C ₂ H ₇	2
15.	I	C ₉ H ₁₉	0
16.	I	C ₁₀ H ₇	7

Note: In Table 1.1, the equivalents for chlorine and bromine is determined assuming that the isotopes are ³⁵Cl and ⁷⁹Br, respectively. Always use this assumption while applying this method.

The rule of thirteen is illustrated by taking into consideration the following examples:

- (a) Consider an unknown organic compound with the molecular mass equal to 94 amu. Application of equation (1) provides

$$\frac{94}{13} = 7 + \frac{3}{13}$$

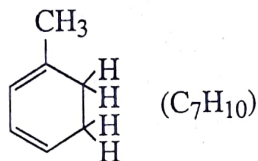
The value of $n = 7$ and $r = 3$

∴ The base formula becomes C_7H_{10}

The index of hydrogen deficiency is

$$U = \frac{(7 - 3 + 2)}{2} = 3$$

∴ The substance, consistent with this formula, must contain some combination of three rings or multiple bonds. A possible structure might be



- (b) We now consider that the substance has the molecular mass 94 amu but contains one oxygen, besides carbon and hydrogen, so that the molecular formula would become C_6H_6O .

This formula is derived according to the following scheme:

(i) Base formula = C_7H_{10}

(ii)
$$U = \left(\frac{n - r + 2}{2} \right) = \left(\frac{7 - 3 + 2}{2} \right) = 3$$

(iii) Add + O (oxygen)

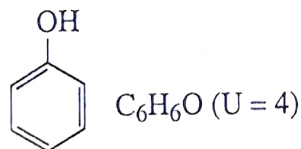
(iv) Subtract (-) CH_4

(v) Change the value of U : $\Delta U = 1$

(vi) New formula C_6H_6O

(vii) New index of hydrogen deficiency: $U = 4$

A possible compound, consistent with the data mentioned above, is



- (c) The additional possible molecular formulae that conform to the molecular mass equal to 94 amu are depicted as follows:

$$C_6H_8N, U = 3\frac{1}{2}$$

$$C_5H_2O_2, U = 5$$

$$C_3H_2S, U = 5$$

$$CH_3Br, U = 0$$

The formula, C_6H_8N , which contains an even number of hydrogen atoms but an odd number of nitrogen atoms, leads to a fractional value of U , an unlikely choice.

- (d) Any compound with a value of U less than zero (i.e., negative) is an impossible combination. It indicates that the molecular formula, in general, contains oxygen or nitrogen atom.
- (e) When there are not enough hydrogens, we can subtract one carbon and add twelve hydrogens (and make the appropriate correction in U). This procedure works only if a positive value of U is obtained.

Alternatively, if the value of U is greater than 7, we can obtain another potential molecular formula by adding one carbon and subtracting twelve hydrogens and incorporating appropriate correction in the value of U .

7.1.2 Determination of number of Double Bond and/or Ring Equivalents (DBE) from the Molecular Formula of an Organic Compound.

The number of double bond and/or ring equivalents (DBE) can easily be calculated provided the molecular formula of the compound is known and thus the structure of the compound, fabricated on the basis of spectroscopic data, can easily be confirmed.

The number of DBE in a variety of organic compounds can be determined from the molecular formula as per the following equation:

$$DBE = 0.5 (2n_4 + n_3 - n_1 + 2)$$

where n_4 , n_3 and n_1 are the number of tetravalent, trivalent and monovalent atoms present in the compound.

(a) *Compounds containing carbon and hydrogen only*


If the compound is a hydrocarbon with the general formula C_xH_y , then

$$DBE = x + 1 - \frac{Y}{2}$$

For example, if the molecular formula of the compound is C_6H_6 . The number of DBE is given by

$$DBE = 6 + 1 - \frac{6}{2} = 4$$

Some possible structures consistent with the given molecular formula are given below

(i) ; three double bonds and one ring

(ii) $H_2C=CH-C\equiv C-CH=CH_2$; two double bonds and one triple* bond.

(b) *Compounds containing carbon, hydrogen and divalent atoms(s).*

If the compound, besides carbon and hydrogen, contains one or more divalent atoms (oxygen, sulphur etc.), the presence of divalent atom(s) may be ignored while calculating DBE.

*A triple bond may be regarded as equivalent to two double bonds. The presence of a triple bond ($C\equiv C$, $C\equiv N$ etc.) in a compound can easily be detected in its infrared spectrum.

Consider an organic compound having the molecular formula $C_3H_8O_3$. Then, the number of DBE will be equal to

$$DBE = x + 1 - \frac{y}{2} = 3 + 1 - \frac{8}{2} = 0$$

(c) *Compounds containing carbon, hydrogen and monovalent atom(s)*

The calculation of the number of DBE in an organic compound containing some monovalent atoms (such as Cl, Br, I etc.) may be achieved by considering each monovalent atom equal to one hydrogen atom.

For example, if the molecular formula of the compound is $C_xH_yX_z^{**}$, then the number of DBE will be given by the following relation.

$$DBE = x + 1 - \frac{y + z}{2}$$

Consequently, the number of double bond and/or ring equivalents (DBE) for such a compound having the molecular formula, $C_{10}H_7Br$, is given by the following equation:

$$x + 1 - \frac{y + z}{2} = 10 + 1 - \frac{7 + 1}{2} = 11 - 4 = 7$$

(d) *Compounds containing carbon, hydrogen, nitrogen atom or some trivalent phosphorus atom(s).*

If the compound contains nitrogen atom or some trivalent phosphorus atoms, then the number of DBE can be calculated by subtracting the number of trivalent atoms from the number of hydrogen atoms present in the molecular formula.

For example, if the molecular formula of the compound is $C_xH_yN_z$, then the number of DBE in its structural formula is given by the following relation:

$$DBE = x + 1 - \frac{y - z}{2}$$

Consequently, the number of double bond and/or ring equivalents (DBE) for such a compound having the molecular formula, $C_{12}H_{12}N_2$, is given by:

$$x + 1 - \frac{y - z}{2} = 12 + 1 - \frac{12 - 2}{2} = 13 - 5 = 8$$

In case of pentavalent phosphorus, three hydrogen atoms corresponding to each phosphorus atom, are subtracted from the number of hydrogen atoms given in the molecular formula for calculating DBE.

7.2 APPLICATION OF SPECTROSCOPIC TECHNIQUES TO STRUCTURAL ELUCIDATION.

7.2.1 Introduction

The elucidation of molecular structure by spectroscopic methods assumes a basic knowledge of chemistry and a familiarity with various areas of spectroscopy to be used. By using the wealth of

**X represents halogen atom.

tabulated information available in the literature for searching out data as well as for cross checking, one gradually assimilates the basic values for various chemical functional groups and because more and more self sufficient in problem solving.

The approach adopted in this text has been to extract as much information as possible from the individual spectra and then to assemble it in an appropriate manner. It is found that the infrared and nuclear magnetic resonance spectra give most of the information whereas the ultraviolet and mass spectra are used to reinforce the information gathered from IR and NMR.

7.2.2 Structural Information Obtainable from Different Types of Spectra

The characteristic and readily obtainable structural information from each type of spectrum is described below.

(a) *Ultraviolet spectrum*

The following structural information can be obtained from a ultraviolet spectrum:

- (i) The nature of the conjugated system and substituents, from the empirical rules for calculation of λ_{\max} of (a) polyenes, (b) enones and (c) aromatic carbonyl compounds.
- (ii) The presence of benzene ring from the bands at λ_{\max} 184, λ_{\max} 204 and λ_{\max} 256.
- (iii) Identification of the nature of chromophoric unit by comparing the shape of the spectrum of the unknown with that of the known compound.
- (iv) Weakly absorbing chromophores such as simple ketones, sulphides etc., or $n \rightarrow \sigma^*$ or $n \rightarrow \pi^*$ transitions are identified by weak bands in the absence of strong chromophores.

(b) *Infrared spectrum*

The infrared spectrum of an unknown compound is extremely useful in the detection of functional groups. The characteristic absorption frequencies of various functional groups in organic molecules are recorded on pages (215–234) and are useful for the detection of functional groups. Some important functional groups which may be detected using infrared spectroscopy are as follows:

- (i) —OH, —COOH;
- (ii) —NH₂, —NH—, —CONH₂, —CONH;
- (iii) >C=C<, —C≡C—, —C≡N, >C=C=C<;
- (iv) Aromatic rings and pattern of substitution on the ring;
- (v) Carbonyl groups;
- (vi) Enes and their cis-trans stereochemistry;
- (vii) Alkyl units such as —CH (CH₃)₂; —C (CH₃)₃.

The absence of absorptions in the infrared spectrum is also important because if a functional group is present, it must absorb at certain wavelength in the infrared spectrum. The vibrations never stop.

(c) *Nuclear Magnetic Resonance spectrum*

¹H-NMR spectrum gives the following structural information:

- (i) The number of different types of protons and also regarding the nature of the immediate environment of each of them. The decoupling experiments identify the neighbouring group of protons.
- (ii) The number of groups of equivalent protons and hence of the nature of carbon atoms in the chain (whether CH₃, CH₂, CH etc). The integration gives the number of protons in each group of equivalent protons.

- (iii) The value of the coupling constant (J) gives information on the relative positions of the coupled protons within the molecule. The J values together with NOE display stereochemistry.
- (iv) Paramagnetic shift reagents simply complex spectrum

(d) ^{13}C -NMR spectrum

The following information can be obtained from a ^{13}C -NMR spectrum:

- (i) In proton-decoupled ^{13}C -NMR spectra, the number of signals exhibits how many different carbons or different sets of equivalent carbons are present in the molecule.
- (ii) In proton off-resonance decoupled ^{13}C -NMR spectra, the splitting of a signal indicates the number of hydrogen atoms attached to the carbon, giving rise the signal.
- (iii) The values of the chemical shifts indicate the type of hybridization (sp^3 , sp^2 or sp) at each carbon.
- (iv) Carbon of a carbonyl group absorbs far downfield (~ 200 ppm).

The NMR spectrum is most useful for structural elucidation because it displays the complete structure of the unknown compound which may need only the marginal information for confirmation.

(e) Mass spectrum

Mass spectrum provides the following structural information.

- (i) Accurate molecular weight and molecular formula can be determined by an application of "high resolution" mass spectrometry.
- (ii) The nature of the carbon skeleton from the fragmentation pattern.
- (iii) The class to which a unknown compound belongs can be determined from M^+ abundance and the general appearance of the spectrum.
- (iv) Functional groups from heavier m/z peaks and characteristic ion series.

7.2.3 Procedure for Elucidation of Molecular Structure by Spectroscopic Methods

The following sequence of steps may be assumed as a model for the structure elucidation of an organic compound:

1. Determine the molecular formula from the accurate molecular weight (high resolution mass spectrometry) and the elemental analysis of the compound. When accurate molecular weight is not known, several formulae will have to be considered.
2. Calculate the number of double bond equivalents (DBE) from the molecular formula using the following equation.

$$\text{DBE} = 0.5 (2n_4 + n_3 - n_1 + 2)$$

where n_4 , n_3 and n_1 are the number of tetravalent, trivalent and monovalent atoms present.

3. Note carefully all the parameters obtainable from different types of spectra. The easiest to examine is the infrared spectrum from which the position of absorption bands (absorption frequency in cm^{-1}) and their approximate intensity can be obtained directly. In the case of ultraviolet spectrum, some difficulty may arise in identifying weak and coalescing bands. The values of the chemical shifts (δ , ppm) and the coupling constants [J (Hz)] can easily be extracted from the NMR spectrum. Recognising important peaks from the large number, obtained in the mass spectrum, requires practice. Generally, high m/z abundant, metastable and characteristic series of peaks are important.

- Examine the infrared spectrum of the compound to determine the nature of functional groups and to deduce whether the compound is saturated, unsaturated, aromatic or a composite of these. NMR and UV spectra may also be used for their confirmation.
- The chemical shift will reveal the chemical environment of the protons present and the spin multiplicity [coupling constant, J (Hz)], the relationship of neighbouring protons. From the integration of various signals in the NMR spectrum in conjunction with the molecular formula, the number of each type of protons can easily be determined. Expand the part structures obtained from infrared.
- Examine the ultraviolet spectrum either qualitatively (λ_{\max} position and application of Woodward-Fieser or Scott rules where appropriate) or quantitatively (λ_{\max} and extinction coefficient) to confirm the validity of deductions made in (4) and (5). In some problems, it will play a decisive role in distinguishing between isomeric structures.
- The mass spectrum fragmentation pattern is very useful when the type of the compound is known. Attempt to determine the mode(s) of fragmentation using known processes. Recognition of fragment ions will confirm earlier predictions.
- Attempt to assemble all the extracted information into a rational structure.

7.3 COMPOSITE PROBLEMS WITH SOLUTIONS (SET I)

Problem 1

An organic compound A (Mol. formula $C_9H_{10}O_2$) exhibits the following spectral data:

IR: 1745 cm^{-1} (s), 1225 cm^{-1} (br, s), 749 (s); 697 cm^{-1} (s);

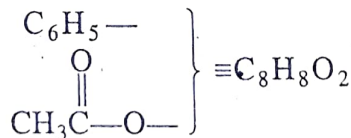
UV: λ_{\max} at 268, 264, 262, 257 nm.

^1H NMR: δ 1.96 (3H, s); 5.00 (2H, s); 7.22 (5 H, s)

Deduce the structure of the compound:

Solution

- The absorption at 1745 cm^{-1} in the IR spectrum suggests the presence of an ester group.
- The broad band at 1225 cm^{-1} is due to C—O—C stretching, characteristic of an acetate.
- Absorptions at 749 cm^{-1} and 697 cm^{-1} indicate monosubstituted benzene ring.
- λ_{\max} values clearly exhibit that the carbonyl group is not conjugated.
- Thus, the compound has the partial structure



Molecular formula of the compound = $C_9H_{10}O_2$

Molecular formula of the partial structure = $C_8H_8O_2$

The remaining group to be accounted for = CH_2

A two-proton singlet at δ 5.0 suggests that the remaining CH_2 group must be present in between the carbonyl group of the ester and the phenyl ring. Hence the structure of the compound A will be:

