SPECTROSCOPIC ANALYSIS OF ORGANIC COMPOUNDS

PART-5, PPT-5, SEM-5, CC-12P

Dr. Kalyan Kumar Mandal Associate Professor St. Paul's C. M. College Kolkata

CONTENTS SPECTROSCOPIC ANALYSIS PART-5

¹H NMR and IR Spectral Analysis of

- 1. Diethyl Fumarate
- 2. 4-Nitrobenzaldehyde

¹H NMR Spectrum of Diethyl Fumarate 300 MHz, CDCl₃: δ (in ppm): 6.85, 4.25 and 1.30

ppm



This Lecture is prepared by Dr. K. K. Mandal, SPCMC, Kolkata

 Spectrum is recorded in 300 MHz instrument in CDCl₃ using TMS as internal standard



Chemical shift	Number of	Splitting	Probable
(δ in ppm)	hydrogens	pattern	assignment
6.85	2H	S	H _a
4.25	4H	q	-O-C <u><i>H</i></u> ₂ -CH ₃
1.30	6H	t	-O-CH ₂ -C <u>H</u> 3

- 1. δ 6.85: 2H, s, H_a, olefinic protons: H_a protons are deshielded by the diamagnetic anisotropy of C=C double bond. These protons are deshielded further by the local diamagnetic effect of the electron withdrawing carbonyl group.
- They appear as a *singlet* because both the olefinic protons are equivalent. Therefore, they do not interact with each other. There is no other interacting proton also to couple with.
- 2. δ 4.25: 4H, q, -OC \underline{H}_2 CH₃, oxymethylene protons: These four protons (α -hydrogens of an ester) are deshielded due to local diamagnetic effect caused by adjacent electronegative oxygen atom.
- Methylene (- CH_2 -) protons appear as a *quartet* as they couple with three protons of the neighbouring methyl group.

- 3. δ 1.30: 6H, *t*, -OCH₂C<u>H₃</u>, methyl protons: These protons appear at the normal range of terminal methyl proton of an alkane which is due to the absence of electron withdrawing group in close proximity.
- Methyl protons appear as a *triplet* as they couple with two adjacent methylene ($-CH_2$ -) protons of the ethyl group ($-CH_2CH_3$).

IR Spectrum of Diethyl Fumarate

FT-IR: Liquid Film: Wavenumbers (cm⁻¹): 3078, 2986, 2941, 2908, 2878, 1728, 1645, 1261



Wavenumbers (in cm⁻¹)



• Spectrum is recorded in liquid film.



Wave Numbers (cm ⁻¹)	Nature	Probable Assignment
3078	W	C _{sp2} -H stretching; Ethylenic
2986, 2908	<i>m</i> , <i>w</i>	C _{<i>sp</i>3} -H stretching of -CH ₃ ;
		Asymmetric and Symmetric
2941, 2878	<i>w</i> , <i>w</i>	C _{sp3} -H stretching of -CH ₂ -;
		Asymmetric and Symmetric
1728	S	Conjugated C=O stretching of -CO ₂ Et
1645	т	Conjugated C=C stretching of <i>trans</i> alkene
1261	S	C-O stretching of –CO-OEt

- 1. 3078: C_{sp2} -H stretching of *trans* alkene: These absorptions are due to strong C_{sp2} -H bonds for ethylenic unit. The absorption occurs at a higher wavenumber region which is due to the presence of small atom in the bond on one hand and hydrogen atom is attached to a sp^2 hybridized carbon atom on the other.
- 2. 2986, and 2908: C_{sp3} -H stretchings of -CH₃ group: Two bands (*asymmetric* and *symmetric* stretchings of -CH₃ group respectively) that appear in the spectrum are due to the vibrational coupling between two fundamental vibrations. This absorption occurs at a higher wavenumber region because of the presence of small atom in the bond, consequently reduced mass is lower.

- 3. 2941, and 2878: C_{sp3} -H stretchings of -CH₂- group: Two bands (*asymmetric* and *symmetric* stretchings of -CH₂- group respectively) that appear in the spectrum are due to the vibrational coupling between two fundamental vibrations. This absorption occurs at a higher wavenumber region because of the presence of small atom in the bond, consequently reduced mass is lower.
- 4. 1728: Conjugated C=O stretching of -CO-OEt: The ester carbonyl group is conjugated with C=C. As a result, due to mesomeric interaction (in the unit C=C-C=O), C=O bond assumes single bond character in the charged canonical form. Bond order of C=O bond decreases and hence C=O absorption occurs at lower than ~1750 cm⁻¹.

- **5. 1645: C=C stretching of** *trans* **alkene:** The vibration due to the conjugated ethylenic system (conjugated with C=O of -CO-OEt group) appears at a lower wavenumber than that of the *trans* alkene due to lowering of C=C bond strength as a result of conjugation in the unit C=C-C=O.
- 6. 1261: C-O stretching of -CO-OEt: Appearance at lower wave number of this bond is due to (i) the vibration involves a single bond and (ii) masses of both the constituent atoms are relatively large unlike C-H, O-H, etc. However, this bond is stronger as carbon atom is a part of the unsaturated system.

¹H NMR Spectrum of 4-Nitrobenzaldehyde 300 MHz, CDCl₃: δ (in ppm): 10.17, 8.42, and 8.10





This Lecture is prepared by Dr. K. K. Mandal, SPCMC, Kolkata

 Spectrum is recorded in 300 MHz instrument in CDCl₃ using TMS as internal standard



Chemical shift	Number of	Splitting	Probable
(δ in ppm)	hydrogens	pattern	assignment
10.17	1H	S	-С <u>Н</u> О
8.42	2H	d	H_b
8.10	2H	d	H_{a}

- 1. δ 10.17: 1H, *s*, -CHO, aldehydic proton: Deshielding of aldehydic proton is due to the carbonyl group's diamagnetic anisotropic effect and inductive electron pull (-I effect) i.e. local diamagnetic effect of the electron withdrawing carbonyl group which decreases the electron density around aldehydic proton. Electron withdrawing effect of the nitro group (-I and -R effects) via the ring is also responsible for further lowering of δ -value.
- Aldehydic proton appears as a *singlet* because there is no adjacent hydrogen atom to couple with.

- 2. δ 8.42: 2H, *d*, *H*_b, protons ortho to -NO₂ group: These protons are deshielded by the (i) diamagnetic anisotropy of the aromatic moiety (ring current effect), (ii) diamagnetic anisotropy of the N=O bond of the ortho -NO₂ group, (iii) EW effects viz. (-R, -I) of -NO₂ group which is ortho to it, and (iv) EW effect (-I) of -CHO group which is meta to it. The EW groups decrease electron density around *H*_b protons.
 - These protons appear as a *doublet* due to coupling with adjacent H_a protons (*ortho*-coupling).

- 3. δ 8.10: 2H, d, H_a , protons ortho to -CHO group: These protons are deshielded by the (i) diamagnetic anisotropy of the aromatic moiety (ring current effect), (ii) diamagnetic anisotropy of the C=O bond of the ortho -CHO group, (iii) EW effects viz. (-R, -I) of -CHO group which is ortho to it, and (iv) EW effect (-I) of -NO₂ group which is meta to it. The EW groups decrease electron density around H_a protons. The H_a protons are less deshieded than the H_b protons as EW effect of -CHO group is less than that of the -NO₂ group.
- These protons appear as a *doublet* due to coupling with adjacent $H_{\rm b}$ (*ortho*-coupling).

IR Spectrum of 4-Nitrobenzaldehyde

FT-IR (Nujol mull): Wavenumbers (cm⁻¹): 3105, 2854, 2732, 1705, 1610, 1540, 1475, 1350 and 855





• Spectrum is recorded in Nujol mull.

Wave Numbers	Nature	Probable Assignment	
(cm ⁻¹)			0、 .Н
3105	W	C _{sp2} -H stretching; Aromatic] c
2854, 2732	s, w	C-H stretchings of –CHO; a pair	H H
		of doublets (Fermi resonance)	
1705	m	Conjugated C=O stretching	
1610, 1475	<i>m</i> , <i>m</i>	Conjugated C=C stretchings;	Н
		Aromatic skeletal vibrations	N.+
1540, 1350	<i>m</i> , <i>m</i>	N=O stretchings of -NO ₂ ;	-o´ `o
		Asymmetric and symmetric	
855	m	C-N stretching	

This Lecture is prepared by Dr. K. K. Mandal, SPCMC, Kolkata

- 1. 3105: C_{sp2} -H stretching: These absorptions are due to strong C_{sp2} -H bonds. The absorption occurs at a higher wavenumber region which is due to the presence of small atom in the bond on one hand and hydrogen atom is attached to a sp^2 hybridized carbon atom on the other.
- 2854, and 2732: C-H stretchings of -CHO; a pair of *doublets* (*Fermi resonance*): Two bands are due to Fermi coupling between a *fundamental* C-H stretching of aldehydic group (-CHO) with the *first overtone* of C-H bending of -CHO which normally appears at 1390 cm⁻¹.

- **3. 1705: C=O stretching; Aromatic:** Carbonyl group is conjugated with the aromatic ring in this case. As a result, due to mesomeric interaction C=O bond assumes single bond character in the charged canonical form. Bond order of C=O bond decreases and hence C=O absorption occurs at lower than 1715 cm⁻¹.
- **4. 1610, and 1475: C=C stretching:** The vibration due to the conjugated aromatic system (*aromatic skeletal vibrations*) appears at a lower wavenumber than that of the nonconjugated system due to lowering of C=C bond strength.

- 5. 1540 and 1350: N=O stretchings of $-NO_2$, Asymmetric and Symmetric: These are the characteristic absorptions for AB_2 type of grouping ($-NO_2$) present in the molecule. Two bands are due to vibrational coupling. Being a double bond, this absorption occurs at a lower wavenumber region because N=O assumes partial double bond character due to (i) resonance within $-NO_2$ group and (ii) $-NO_2$ group is conjugated with the aromatic ring.
- 6. 855: C-N stretching: This absorption appeared at lower wavenumber region as (i) it is a single bond and (ii) the bond involves a higher reduced mass.