SPECTROSCOPIC ANALYSIS OF ORGANIC COMPOUNDS

PART-6, PPT-6, SEM-5, CC-12P

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

 Spectrum is recorded in 90 MHz instrument in CDCl₃ using TMS as internal standard сн₃



Chemical shift	Number of	Splitting	Probable
(δ in ppm)	hydrogens	pattern	assignment
7.88	1H	br. s	-N <u>H</u> CO-
7.36	2H	d	H _a
7.08	2H	d	H _b
2.29	3H	S	ArC <u>H</u> 3
2.11	3H	S	-COC <u>H</u> 3

- **1. 7.88: 1H**, *br. s*, **-NHCO-:** Deshielding of N-H proton is due to local diamagnetic effect of electronegative N-atom and mesomeric interaction caused by electron withdrawing (EW) carbonyl group and aromatic moiety.
- The –N*H* proton appears as a *singlet* as there is no neighbouring proton to couple with. The broadness of signal is due to (i) intermediate rate of proton exchange, and (ii) the protons couple to each other, and (iii) inherent broadening associated with spin active nitrogen nucleus.
- 2. 7.36: 2H, d, H_a , protons ortho to -NHCOCH₃ group: These protons are deshielded by the (i) diamagnetic anisotropy of the aromatic ring (ring current effect), and (ii) diamagnetic anisotropic effect of the C=O group of -NHCOCH₃.
- H_a protons appear as a *doublet* because of *ortho* coupling with the neighbouring H_b proton.

- 7.08: 2H, d, H_b, protons ortho to Br atom: These protons are deshielded by the (i) diamagnetic anisotropy of the aromatic ring (ring current effect) (ii) -I effect of Br-atom.
- They appear as a *doublet* because of *ortho* coupling with H_a proton. ** H_a and H_b protons represent a complex *AA'BB' system* of *p*-disubstituted benzene derivative where substituents are different and so they look like a *quartet* (*AB-quartet*).
- 4. 2.29: 3H, s, ArCH₃: The deshielding of this benzylic methyl protons is due to the diamagnetic anisotropy produced by the aromatic ring as well as the said methyl group is attached to a sp^2 hybridised carbon atom.
- The methyl protons appear as a *singlet* as the three protons of the $-CH_3$ group are equivalent, and there is no adjacent hydrogen to couple with.

- 5. 2.11: 3H, s, -COCH₃: The deshielding of the ketomethyl protons is due to presence of EW carbonyl group (local diamagnetic effect) and diamagnetic anisotropy produced by the neighbouring C=O group.
- This methyl protons appear as a *singlet* as the three protons of the $-CH_3$ group are equivalent, and there is no adjacent hydrogen to couple with.

IR Spectrum of 4'-Methylacetanilide

FT-IR (KBr disc): Wavenumbers (cm⁻¹): 3296, 3126, 2944, 2853, 1684, 1606, 1552, 1512, and 1403





• Spectrum is recorded in KBr disc.

Wavenumbers (cm ⁻¹)	Nature	Probable Assignment
3296	m	N-H stretching
3126	W	C _{<i>sp2</i>} -H stretching; Aromatic
2944 and 2853	<i>w</i> , <i>w</i>	C _{<i>sp</i>3} -H stretchings;
		Asymmetric and Symmetric
1684	S	Conjugated C=O stretching;
		Amide -I
1606 and 1512	<i>s</i> , <i>s</i>	Conjugated C=C stretchings,
		Aromatic skeletal vibrations
1552	S	N-H bending, Amide -II
1403	т	C-N stretching



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- 3286: N-H stretching: N-H bond contains a small atom H, so frequency (v) and hence wavenumber increases by Hooke's law. The bond Absorption occurs predominantly due to monomeric form. A slight broadness implies absorption of the dimer/polymer also. Broadness is due to hydrogen bonding.
- 2. 3126: C_{sp2} -H stretching: This absorption occurs at a higher wavenumber region which is due to the (i) presence of small atom in the bond and (ii) hydrogen atom is attached to a sp^2 hybridized carbon atom, the bond is thus stronger.
- 3. 2944 and 2853: C_{sp3} -H stretchings: Two bands (*asymmetric* and *symmetric* stretching of CH₃ group) 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. 1684: Conjugated C=O stretching, Amide-I:** Carbonyl group is conjugated with nitrogen lone pair. 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.
- **5. 1606 and 1512: Conjugated C=C stretching:** The vibration due to the conjugated aromatic system (*aromatic skeletal vibration*) appears at a lower wavenumber than that of the nonconjugated system due to lowering of C=C bond strength.

- **6. 1552**: **N-H bending, Amide-II:** This absorption is due to a bending vibration (N-H) and appears at a lower wavenumber region than that of C=O stretching. Bending vibration requires lower energy than that of the stretching vibration.
- 7. 1403: 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. However, this bond is relatively stronger as (i) carbon atom is a part of the aromatic ring and (ii) conjugation with the C=O group makes C-N bond partially double bonded.

¹H NMR Spectrum of Mesityl Oxide

300 MHz, CDCl₃: δ (in ppm): 6.09, 2.16, 2.14, and 1.89



ppm

¹H NMR Spectral Analysis of Mesityl oxide



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¹H NMR Spectral Analysis of Mesityl Oxide

 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
6.09	1H	S	H_{a}
2.16	3Н	S	-C <u>H</u> ^b ₃
2.14	3H	S	-C <u>H</u> ^d ₃
1.89	3H	S	-COC <u>H</u> ^c ₃

¹H NMR Spectral Analysis of Mesityl Oxide

- 1. δ 6.08: 1H, s, H^a (olefinic proton): This proton is deshielded due to the diamagnetic anisotropic effect of the double bond. Further deshielding is due to local diamagnetic effect of the electron withdrawing carbonyl group in close proximity.
- It appears a *singlet* due to the absence of any coupling partner. However, slight broadness is due to the weak allylic coupling (via 4-bond) with hydrogens of both the methyl groups of $CH=C(CH_3)_2$.
- 2. δ 2.16: 3H, *s*, -C<u>H</u>^b₃: These allylic protons are deshielded by the diamagnetic anisotropy of the olefinic double bond but the effect is smaller due to greater distance. This proton is further deshielded as this methyl group is attached to the electron deficient β -carbon of an α , β -unsaturated carbonyl system.
- *H*^b protons appear as a *singlet* because these protons are equivalent and there is no neighbouring coupling partner.

¹H NMR Spectral Analysis of Mesityl Oxide

- 3. δ 2.14: 3H, s; -CHd₃: Methyl protons of the ketomethyl group are deshielded by the electron withdrawing carbonyl group (local diamagnetic effect). Deshielding is also due to the anisotropy produced by the carbonyl group which is attached to it.
- These equivalent protons appear as a *singlet* due to absence of any proton on adjacent centre.
- 4. δ 1.89: 3H, *s*, -C<u>H</u>^c₃: These allylic protons are deshielded by the (i) diamagnetic anisotropy of the olefinic double bond but the effect is smaller due to greater distance and (ii) electron deficient β -carbon (of an α,β -unsaturated carbonyl system) to which the methyl group is attached. However, these protons are shielded to some extent as they are exposed to the shielding zone created by the anisotropy of carbonyl group due to closer proximity in space.
- These equivalent protons appear as a *singlet* due to absence of any proton on adjacent centre.

IR Spectrum of Mesityl Oxide

FT-IR: Liquid Film: Wavenumbers (cm⁻¹): 2976, 2939, 2915, 1690, and 1620





• Spectrum is recorded in liquid film.



Wave Numbers (cm ⁻¹)	Nature	Probable Assignment	
2976	W	C _{sp2} -H stretching; Ethylenic	
2939, 2915	<i>w</i> , <i>w</i>	C _{sp3} -H stretching of -CH ₃ ; Asymmetric and Symmetric	
1690	S	Conjugated C=O stretching	
1620	S	Conjugated C=C stretching	

- 1. 2976: C_{sp2} -H stretching: This absorption is due to strong C_{sp2} -H bond of the 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. 2939, and 2915: 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. 1690: Conjugated C=O stretching:** The 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 ~1715 cm⁻¹.
- 4. 1620: Conjugated C=C stretching: The vibration due to the conjugated ethylenic system (conjugated with C=O group) appears at a lower wavenumber from the normal value (~ 1650 cm⁻¹) due to lowering of C=C bond strength as a result of conjugation in the unit C=C-C=O.