SPECTROSCOPIC ANALYSIS OF ORGANIC COMPOUNDS

PART-1, PPT-1, SEM-5, CC-12P

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¹H NMR Spectrum of 4'-Bromoacetanilide 90 MHz, DMSO-d₆: δ (in ppm): 10.0, 7.54, 7.48, and 2.05





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

• Spectrum is recorded in 90 MHz instrument in DMSO-d₆ using TMS as internal standard



s: singlet br. s: broad singlet d: doublet t: triplet q: quartet m: multiplet

Chemical shift	Number of	Splitting	Probable
(δ in ppm)	hydrogens	pattern	assignment
10.0	1H	br. s	-NHCO-
7.54	2H	d	H _a
7.48	2H	d	H _b
2.05	3H	S	-CH ₃

δ (in	Explanation			
ppm)				
10.0	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 broadness of the signal is due to (i) moderate rate of chemical exchange,			
	and (ii) intermolecular hydrogen bond between C=O and -NH moieties. The			
	-NH- proton appears as a <i>singlet</i> as there is no neighbouring proton to couple			
	with.			
7.54	2H, d, H_a , protons ortho to $-NHCOCH_3$ group: These protons are			
	deshielded by the (i) diamagnetic anisotropy of the aromatic ring (ring current			
	effect), (ii) diamagnetic anisotropic deshielding effect of the C=O group of			
	-NHCOCH ₃ .			
	H_{a} protons appear as a <i>doublet</i> because of <i>ortho</i> coupling with the			
	neighbouring H_b proton.			

δ (in	Explanation				
ppm)					
7.48	2H, d , $H_{\rm b}$, protons ortho to Br: 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 <i>doublet</i> because of <i>ortho</i> 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).				
2.05	3H, s, - CH_3 : The deshielding of the methyl protons is due to presence of EW				
	carbonyl group and diamagnetic anisotropy produced by the neighbouring				
	C=O group.				
	The methyl protons appear as a <i>singlet</i> as the three protons of the $-CH_3$ group				
	are equivalent, and there is no adjacent hydrogen to couple with.				

IR Spectrum of 4'-Bromoacetanilide

FT-IR (CCl₄): Wavenumbers (cm⁻¹): 3300, 3115, 2930, 2860, 1680, 1600, 1540, 1460, 1396 and 689



Wavenumbers (in cm⁻¹)



• Spectrum is recorded in CCl₄ solvent.

Wavenumbers (cm ⁻¹)	Nature	Probable Assignment	
3300	medium (m)	N-H stretching	
3115	weak (w)	C _{sp2} -H stretching	
2930	strong (s)	C _{sp3} -H stretching;	
		Asymmetric	
2860	S	C _{<i>sp3</i>} -H stretching; Symmetric	
1680	m	Conjugated C=O stretching;	
		Amide -I	
1600	m	C=C stretching, Aromatic	
		skeletal vibration	
1540	m	N-H bending, Amide -II	
1460	m	C=C stretching, Aromatic	
		skeletal vibratuion	
1396	m	C-N stretching	
689	W	C-Br stretching	



- **3300:** 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. Consequently a sharp band is observed.
- **3115:** C_{sp2} -H stretching: This absorption occurs at a higher wave number 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.
- **2930-2850:** C_{sp3} -H stretching: Two bands (*asymmetric* and *symmetric* stretching of CH₃ group) that appear in the spectrum are due to the vibrational coupling between two fundamental vibrations.
- **1680: 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.

- **1600, 1460:** C=C stretching: The vibration due to the conjugated aromatic system (*aromatic skeletal vibration*) appears at a lower wave number than that of the nonconjugated system due to lowering of C=C bond strength.
- **1540**: **N-H bending, Amide-II:** This absorption is due to a bending vibration (N-H) and appears at a lower wave number region than that of C=O stretching.
- **1396:** 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.
- **689:** C-Br stretching: Absorption is due to the weak C-Br bond present in the molecule. Lower wave number is due to (i) C-Br bond is weak, (ii) masses of both the atoms are higher, hence reduced mass is higher.

¹H NMR spectrum of 2-Bromo-4'methylacetophenone

90 MHz, CDCl₃: δ (in ppm): 7.90, 7.27, 4.30 and 2.34



ppm

¹H NMR Spectral Analysis of 2-Bromo-4'methylacetophenone



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¹H NMR Spectral analysis of 2-Bromo-4'methylacetophenone

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



Chemical shift	Number of	Splitting	Probable
(δ in ppm)	hydrogens	pattern	assignment
7.90	2H	d	H_{a}
7.27	2H	d	$H_{ m b}$
4.30	2H	S	-CH ₂ Br
2.34	3Н	S	-CH ₃

¹H NMR Spectral Analysis of 2-Bromo-4'methylacetophenone

δ (in	Explanation
ppm)	
7.90	2H, d , H_a , protons which are <i>ortho</i> to -COCH ₂ Br group: These two protons are deshielded due to diamagnetic anisotropy of the aromatic ring (ring current effect) and also by the EW effect and diamagnetic anisotropy of the carbonyl group. H_a protons appear as a <i>doublet</i> as they couple with adjacent H_b protons (<i>ortho</i> coupling).
7.27	2H, d, H_b , protons which are ortho to $-CH_3$ group: These protons are less deshielded compared to H_a protons as they are meta with respect to the EW C=O group and in close proximity to the nearby electron donating methyl group. H_b protons appear as a doublet as they couple with adjacent H_a protons (ortho coupling).
4.30	2H , <i>s</i> , -COC <i>H</i> ₂ Br : This methylene protons are deshielded due to EW effects of both C=O group and Br atom. Methylene protons appear as a <i>singlet</i> as there is no adjacent hydrogen to couple with.
2.34	3H , <i>s</i> , - CH_3 : The deshielding of this benzylic methyl protons is due to the diamagnetic anisotropic deshieding effect of the aromatic moiety. The methyl protons appear as a <i>singlet</i> as there is no adjacent hydrogen to couple with.

IR Spectrum of 2-Bromo-4'methylacetophenone

FT-IR (CCl₄): Wavenumbers (cm⁻¹): 3050, 2975, 1700, 1600 and 687





• Spectrum recorded in CCl₄ solvent.

Wavenumbers (cm ⁻¹)	Nature	Probable Assignment
3050	W	C _{sp2} -H stretching; Aromatic
2975	W	C _{sp3} -H stretching; Asymmetric
1700	S	Conjugated C=O stretching
1600	m	C=C stretching, Aromatic Skeletal Vibration
687	m	C-Br stretching



- **3050:** C_{sp2} -H stretching: These absorptions are due to strong C_{sp2} -H bonds. The absorption at a higher region 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.
- 2975: C_{sp3} -H stretching: This absorption occurs at a higher wave number region which is due to the presence of small atom in the bond, consequently reduced mass is lower.
- **1700: C=O stretching:** Carbonyl absorption occurs mostly at the normal region though the carbonyl is attached to a conjugative group (conjugation decreases wave number of C=O bond), yet it is shifted upward to a normal position due to the presence of electronegative Br-atom.

- **1600: C=C stretching:** The vibration due to the conjugated aromatic system (*aromatic skeletal vibration*) appears at a lower wave number than that of the nonconjugated system due to lowering of C=C bond strength.
- 687: C-Br stretching: C-Br absorption is due to the weak C-Br bond present in the molecule. Lower wave number is due to (i) C-Br bond is weak, (ii) masses of both the atoms are higher, hence reduced mass is higher.

¹H NMR spectrum of Vanillin

300 MHz, CDCl₃: δ (in ppm): 9.8, 7.45, 7.35, 7.05, 6.7, and 3.85



ppm

¹H NMR Spectral Analysis of Vanillin



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¹H NMR Spectral analysis of Vanillin

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

Chemical shift	Number of	Splitting	Probable	он
(ð in ppm)	hydrogens	pattern	assignment	H _c OCH ₃
9.8	1H	S	-CHO	
7.45	1H	d	H _b	H _b H _a
7.35	1H	S	H _a	ОН
7.05	1H	d	H _c	
6.7	1H	br. s	-OH	
3.85	3H	S	-CH ₃	

¹H NMR Spectral Analysis of Vanillin

δ (in	Explanation			
ppm)				
9.8	1H, s, -CHO: Aldehydic proton is highly deshielded due to the diamagnetic			
	anisotropic deshielding and electron-withdrawing effects of C=O group.			
	This proton appears as a <i>singlet</i> as there is no adjacent hydrogen atom to couple			
	with.			
7.45	1H , d , $H_{\rm b}$: This aromatic proton is deshielded most in vanillin. The deshielding is			
	due to the (i) diamagnetic anisotropic deshielding effect of the aromatic ring			
	(ring current effect), (ii) -I and -R effects of -CHO group which is ortho to it.			
	$H_{\rm b}$ proton appears as a <i>doublet</i> as it couples with the neighbouring $H_{\rm c}$ proton			
	(ortho-coupling).			
7.35	1H, s , H_a : This aromatic proton is deshielded by the (i) diamagnetic anisotropic			
	deshielding effect of the aromatic ring (ring current effect), (ii) -I and -R effects			
	of -CHO group. However, it is shielded to some extent by the electron donating			
	–OCH ₃ group which is <i>ortho</i> to it.			
	This proton appears as a <i>singlet</i> as there is no adjacent hydrogen atom to couple			
	with.			

¹H NMR Spectral Analysis of Vanillin

δ (in	Explanation
ppm)	
7.05	1H, d , H_c : Though this aromatic proton is deshielded by the diamagnetic
	anisotropy deshielding effect of the aromatic ring, yet, it experiences some
	shielding by (+R) effect of –OH group which is ortho to it.
	$H_{\rm c}$ proton appears as a <i>doublet</i> as it couples with adjacent $H_{\rm b}$ proton
	(ortho-coupling).
6.7	1H, br. s, -OH: Proton of Ar-OH is deshielded due to anisotropy of the benzene
	ring, local diamagnetic effect of electronegative O-atom and resonance that takes
	away electron density from the oxygen of the -OH group.
	This proton appears as a <i>broad singlet</i> (<i>br</i> , <i>s</i>) due to intermolecular hydrogen
	bonding and moderate to faster rate of chemical exchange.
3.85	3H , <i>s</i> , -OCH ₃ : Methoxy protons are deshielded by the local diamagnetic effect of
	electronegative O-atom and resonance that takes away electron density from the
	oxygen of the -OCH ₃ group.
	This protons appear as a <i>singlet</i> as they have no neighbouring hydrogen to
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IR Spectrum of Vanillin

FT-IR (CCl₄): Wavenumbers (cm⁻¹): 3540, 3030, 2940, 2830, 2725, 1700, 1600, 1510, 1260 and 1030

Wavenumbers (in cm⁻¹)

• Spectrum is recorded in CCl₄ solvent.

Wave Numbers	Nature	Probable Assignment	
(cm ⁻¹)			
3540	m	O-H stretching; <i>monomer</i>	ОН
3030	W	C _{sp2} -H stretching; Aromatic	н ј.осн,
2940	W	C _{sp3} -H stretching of –CH ₃ ; Asymmetric	
2830	w	C-H stretching of –CHO; one of the	
		doublets (Fermi resonance)	H Y Y
2725	W	C-H stretching of –CHO; one of the	сно
		doublets (Fermi resonance)	
1700	S	Conjugated C=O stretching	
1600	S	C=C stretching, Aromatic skeletal	
		vibration	
1510	S	C=C stretching, Aromatic skeletal	
		vibration	
1260, 1030	S	C-O-C stretching; Asymmetric and	
		Symmetric for Ar-O-CH ₃	

- 3550: Non-hydrogen bonded O-H stretching vibration for the monomer: Vibrational frequency associated with the O-H bond is very high because (i) O-H bond is very strong and (ii) this bond contains a small atom hydrogen (reduced mass decreases, frequency increases).
- **3030:** C_{sp2} -H stretching: These absorptions are due to strong C_{sp2} -H bonds for the aromatic moiety. The absorption occurs at a higher wave number 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.
- **2940:** C_{sp3} -H stretching: This absorption occurs at a higher wave number region which is due to the presence of small atom in the bond, consequently reduced mass is lower.
- 2830, 2725: 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.

- **1700: C=O stretching of -CHO:** Strength of C=O bond decreases to some extent when it is attached to phenyl group (conjugation decreases the C=O absorption from the normal value of 1715 cm⁻¹), i.e. conjugation with aromatic ring decreases double bond character of the C=O. Presence of electron donating -OH group at the *para* position further enhances the conjugation.
- **1600 and 1510: C=C stretchings of the aromatic moiety:** The vibration due to the conjugated aromatic system (*aromatic skeletal vibration*) appears at a lower wave number than that of the nonconjugated system due to lowering of C=C bond strength.
- 1260, 1030: C-O-C stretching for Ar-O-CH₃ moiety: Aryl alkyl ethers display two strong vibrations in these regions due to vibrational coupling. Resonance, which results in strengthening of the C-O bond, is responsible for the shift in the asymmetric absorption band.