SPECTROSCOPIC ANALYSIS OF ORGANIC COMPOUNDS

PART-4, PPT-4, SEM-5, CC-12P

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¹H NMR Spectrum of 1,3-Dinitrobenzene 400 MHz, CDCl₃: δ (in ppm): 9.08, 8.62, and 7.87





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

• Spectrum is recorded in 400 MHz instrument in CDCl₃ using TMS as internal standard

Chemical	Number of	Splitting	Probable	0_+_0 ⁻
shift	hydrogens	pattern	assignment	
(ð in ppm)				
9.08	1H	S	H _a	
8.62	2H	d	H _b	
7.87	1H	t	H _c	

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- 1. δ 9.08:1H, s, H_a , proton ortho to both -NO₂ groups: This proton (H_a) is highly deshielded due to (i) diamagnetic anisotropic effect of the aromatic moiety (ring current effect), ii) diamagnetic anisotropic effect of the N=O of both the -NO₂ groups, and (iii) presence of strongly electron withdrawing -NO₂ groups (with -I and -R effects) that withdraws electron density from the ring and makes the aromatic protons highly electron deficient.
- H_a appears as a *singlet* as it has no neighbouring proton to couple with (*meta*-coupling is ignored).

- 2. δ 8.62: 2H, *d*, *H*_b, proton *ortho* to one -NO₂ and *para* to other -NO₂ group: The proton, *H*_b is also highly deshielded due to (i) diamagnetic anisotropic effect of the aromatic moiety (ring current effect), ii) diamagnetic anisotropic effect of the N=O of the -NO₂ group which is *ortho* to it, and (iii) presence of strongly electron withdrawing -NO₂ (with -I and -R effects) groups that withdraws electron density from the ring and makes the aromatic protons highly electron deficient.
- $H_{\rm b}$ proton appears as a *doublet* as it couples with the proton $H_{\rm c}$ (*ortho*-coupling).

- 3. δ 7.87: 1H, *t*, *H*_c, proton *meta* to both -NO₂ groups: The proton, *H*_c is deshielded due to (i) diamagnetic anisotropic effect of the aromatic moiety (ring current effect), and (ii) presence of strongly electron withdrawing -NO₂ groups (with -I and -R effects) that withdraws electron density from the ring and makes the aromatic protons highly electron deficient.
- H_c proton appears as a *triplet* as it couples with the *two* H_b protons (*ortho*-couplings).

IR Spectrum of 1,3-Dinitrobenzene FT-IR (CCl₄): Wavenumbers (cm⁻¹): 3112, 1605, 1544, 1514, 1346, and 835





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• Spectrum is recorded in CCl₄ solution.

Wavenumbers (cm ⁻¹)	Nature	Probable Assignment	
3112	W	C _{sp2} -H stretching; Aromatic	NO ₂
1605	W	C=C stretching;	
		Aromatic skeletal vibrations	
1544	S	N=O stretching of -NO ₂ ;	
		Asymmetric	
1514	W	C=C stretching;	
		Aromatic skeletal vibrations	н
1346	S	N=O stretching of -NO ₂ ;	
		Symmetric	
835	W	C-N stretching of Ar-NO ₂	

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- 1. 3112: C_{sp2} -H stretching: These absorptions are due to strong C_{sp2} -H bonds of the aromatic moiety. The absorption occurs at a higher 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. 1605 and 1514: C=C stretchings: These vibrations due to the conjugated aromatic system (*aromatic skeletal vibrations*) appear at a lower wavenumber than that of the nonconjugated system due to lowering of C=C bond strength as a result of conjugation.

3. 1544 and 1346: N=O stretchings of -NO₂, Asymmetric and Symmetric: These are the characteristic absorptions for AB₂ type of grouping (-NO₂) 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 -NO₂ group and (ii) -NO₂ group is conjugated with the aromatic ring.

4. 835: 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.

¹H NMR Spectrum of *trans*-Cinnamic acid 300 MHz, CDCl₃: δ (in ppm): 12.70, 7.77, 7.53, 7.37, and 6.43





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• 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	
12.70	1H	br. s	-OH	•
7.77	1H	d	H _d	
7.53	2H	d	H _a	
7.37	3 H	m	$2H_{\rm b}$ and $H_{\rm c}$	
6.43	1H	d	H _e	



- 1. δ 12.7: 1H, *br. s*, Ar-COOH: Deshielding of O-H proton is due to (i) local diamagnetic effect of the attached electronegative oxygen atom, (ii) mesomeric interaction caused by EW carbonyl group and (iii) hydrogen bonding (in the dimer) that decreases the electron density around the proton.
- Carboxylic acid proton appears as a *broad signal* (*br*, *s*) due to (i) chemical exchange, and ii) intermolecular hydrogen bond between C=O and -OH moieties (iii) absence of any coupling partner.
- 2. δ 7.77: 1H, *d*, *H*_d, β -proton of -C*H*=CH-COOH: This vinylic proton is deshielded by the diamagnetic anisotropy of the C=C. Moreover, *H*_d proton is further strongly deshielded due to conjugation with EW carbonyl group (exerting -R effect) which renders β -C of the α , β -unsaturated carbonyl system electron deficient.

- The proton H_d appears as a *doublet* as it couples with adjacent H_e proton (*trans*-coupling).
- 3. δ 7.53: 1H, *d*, *H*_a, protons *ortho* to -CH=CH–COOH group: These two protons are most deshielded among the aromatic protons in this compound which is due to diamagnetic anisotropic effect of (i) the aromatic moiety (ring current effect) and ii) C=C of -CH=CH-COOH system. This proton is further deshielded as it is in close proximity to EW -CH=CH–COOH system.
- They appear as a *doublet* due to coupling with H_b proton (*ortho*-coupling).

- 4. δ 7.37: 3H, m, 2H_b and H_c protons meta and para to -CH=CH-COOH group : These protons are deshielded due to diamagnetic anisotropy of the aromatic ring (ring current effect) and EW effect of -CH=CH-COOH group. However, these three protons are less deshielded compared to H_{a} protons as they do not fall in the deshielding region of C=C bond because of greater distance from it. The weakly EW -CH=CH-COOH group does not produce too much difference in electron density around m- and pprotons. Therefore, $H_{\rm h}$ and $H_{\rm c}$ protons have almost identical chemical shift.
- H_b protons couple with H_a and H_c (both are *ortho*-couplings) and H_c proton couples with two H_b protons (*ortho*-coupling). So, even if weak *meta*-coupling is ignored, each of them appears as a *triplet* and these *triplets* are close enough and appear as *multiplets*.

- 5. δ 6.43: 1H, *d*, *H*_e, *a*-proton of -CH=CH-COOH: This vinylic proton is deshielded by the diamagnetic anisotropy of the C=C and C=O, and EW effects of -COOH. Due to larger distance from the benzene ring, *H*_e is less deshielded compared to *H*_d.
- H_e appears as a *doublet* as it couples with adjacent H_d proton (*trans*-coupling).

IR Spectrum of trans-Cinnamic acid

FT-IR (**CCl**₄): Wavenumbers (cm⁻¹): 3200-2700, 3067, 3027, 1686, 1631, 1580, 1490, and 1285





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- **1. 3200-2700: O-H stretching of the dimer:** This broad absorption band for O-H bond centres near 2925 cm⁻¹. 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). Broad signal is due to H-bonding. Hydrogen bonding causes lengthening of the original O-H bond and it becomes weaker. Hence force constant of O-H bond decreases.
- 2. 3067 and 3027: C_{sp2} -H stretching: These absorptions are due to strong C_{sp2} -H bonds for aromatic/ethylenic unit. The absorption occurs at a higher 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.

- **3. 1686: Conjugated C=O stretching:** Carbonyl group is conjugated with C=C which in turn conjugated with the aromatic moiety. 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. 1631: Ethylenic C=C stretchings: The vibration due to the conjugated ethylenic system (conjugated with C=O on one hand and with the aromatic moiety on the other). Therefore, vibration due to this bond appears at a lower wavenumber than that of the nonconjugated ethylenic system due to lowering of C=C bond strength.

- **5. 1580 and 1490: Aromatic C=C stretchings:** 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.
- 6. 1285: C-O stretching of -CO-OH: 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.