Q.P. Code :18398

[Time: 3 Hours] **[Marks:80]**

Please check whether you have got the right question paper.

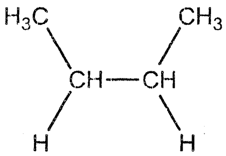
N.B: (1) All questions are compulsory
(2) Figures to the right indicate full marks
(3) Answer all the sub-questions together and in order
(4) Spectral correlation tables are allowed

Q1) a) Answer any four **4**

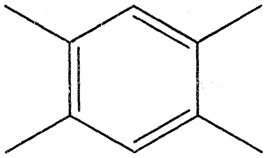
i Predict m/z of base peak of ethyl benzene

ii Calculate Index of hydrogen deficiency for $C_7H_4Cl_2O$

iii Give the number of signals in ^1H NMR of –



iv Give the number of signals in ^{13}C NMR of

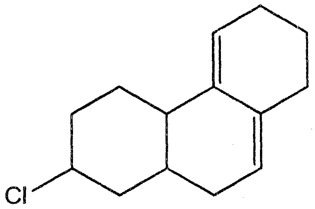


v Predict the IR frequency for the carbonyl group in acetophenone

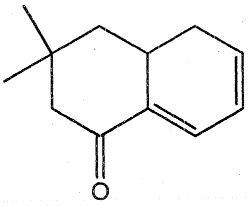
vi Depict a fragmentation pathway for isopropyl alcohol.

Q.1) b) Answer any **eight** (two marks each) 16

i Predict the UV λmax for

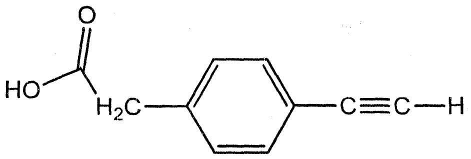


ii Predict the UV λmax for

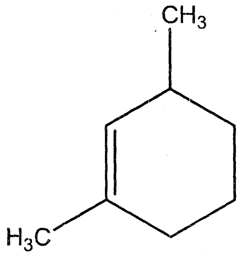


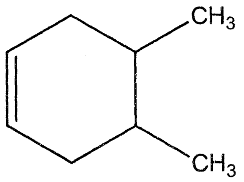
Turn Over

iii Predict the ^{1}H NMR of-



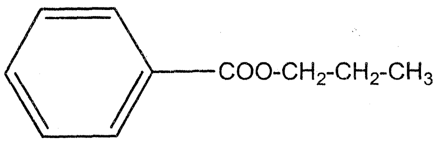
iv How will you distinguish between the following by mass spectrometry?

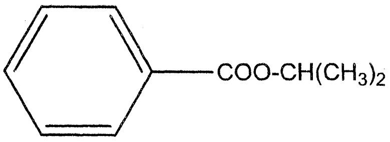




v Predict ^{s}C NMR giving δ value & splitting pattern of the molecule- $CH_3CH_2COCH_2CH_3$. Do not give ranges.

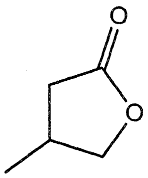
vi How will you distinguish between the following by ^{1}H NMR spectroscopy

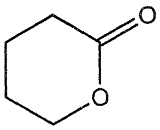




vii A compound with molecular formula $C_6H_{14}O$ gives only two peaks: septet at δ 3.65 and doublet at δ 1.1, predict its structure.

viii How will you distinguish by IR spectroscopy



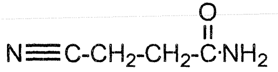


ix Depict one fragmentation pathway involving rearrangement for n-hexanal.

x Predict ^{13}C NMR giving δ value & splitting pattern of the molecule- $CH_3CH_2COCH_2CH_3$. Do not give ranges.

Q.2 **Answer any five questions (5 × 8)** **40**

a) Predict IR spectrum, ^{13}C NMR and ^{1}H NMR of-



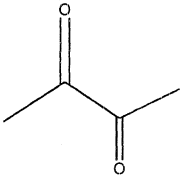
$$N\equiv C\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NH_2$$

Turn Over

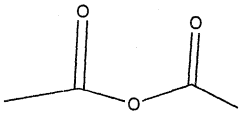
b) How will you distinguish between following compounds using any one spectral technique. Give distinguishing spectral characteristics. If mass spectrometry is used one fragmentation pathway has to be depicted.

i) $CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$ & $CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$

ii)



&



c) A compound with molecular weight 201 has the following spectral characteristics
^{1}H NMR: δ 7.28 (d, 8 Hz, 8 sq.), 6.73 (d, 8 Hz, 8 sq.), 3.93 (q, 6 Hz, 8 sq.), 1.37 (t, 6 Hz, 12 sq.)

Deduce its structure and justify your answer. What would be the m/e value for the molecular ion? Will this compound show McLafferty rearrangement? Give reason.

d) A compound with molecular weight 140 has the following spectral characteristics;
IR: 2960, 2200, 1700 cm^{-1}
^{1}H NMR

δ		
0.88	t	16 sq
1.38	sextet	11 sq
1.5	quintet	10 sq
2.28	t	9 sq
3.7	s	15 sq

^{13}C NMR: δ 13.5 (q), 18.2 (t), 21.9 (t), 29.3 (t), 52.5 (q), 68 (s), 84.8 (s), 210 (s)
Deduce the structure and justify your answer

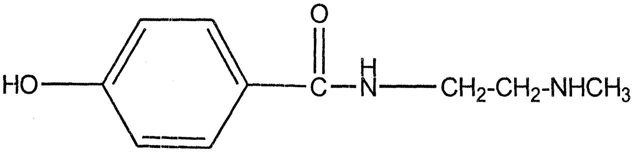
e) An organic compound with molecular weight 164 has IR bands 3060, 2960, 1728, 1225 cm^{-1} and ^{1}H NMR signals at δ 7.8 (m, 21 sq.), δ 7.4 (m, 33 sq.), δ 3.8 (septet, 11 sq.), δ 1.5 (d, 62 sq.). Deduce the structure. Depict any two fragmentation pathways in the mass spectroscopy of the compound, one involving rearrangement.

f) A compound with molecular weight 104 has the following spectral data;
IR: 3125-2857, 1718, 1449 cm^{-1}
^{1}H NMR:

δ		
10.95	s	5.4 sq
4.13	s	11 sq
3.66	q	10.6 sq, J=7.1 Hz
1.27	t	16.2 sq, J= 7.1 Hz

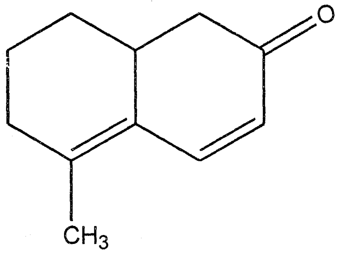
Deduce the structure and depict one mass fragmentation pathway

g) Predict the ^{1}H NMR and mass spectrum of the following compound and depict one fragmentation pathway for the molecule

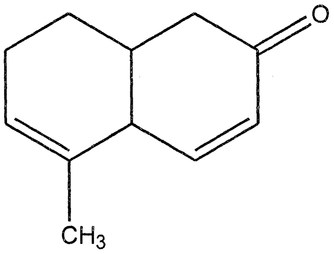


Q.3) **Answer any five questions** **20**

a) Distinguish between the following compounds using a suitable spectral technique



AND



b) Two isomers A and B with a molecular formula $C_3H_6O_2$ display the following characteristics
IR:

A	2860 cm^{-1}	2750 cm^{-1}	1742 cm^{-1}
B	2913 cm^{-1}	1745 cm^{-1}	

^{1}H NMR: δ A: 1.35, 4.25 and 9.15 in the ratio of 3:2:1
B: 3.85 and 2.05 in the ratio of 1:1

Deduce the structure of A & B and justify your answer.

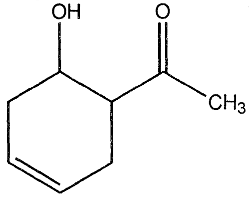
c) An optically active compound with molecular formula $C_5H_{12}O$ shows the presence of a D_2O exchangeable proton. Its ^{13}C NMR is 15 q, 18 q, 25 t, 30 d, 55 t. Deduce its structure and write structure of an isomer for the same and predict its ^{13}C NMR

d) A compound of molecular formula $C_9H_{12}O_3$ has
^{1}H NMR: δ 3.6 (s) and 6.8 (s) in the ratio of 3:1
^{13}C NMR: δ 165, 115 and 55.
Deduce the structure and justify your answer.

e) A compound with molecular formula C_5H_8O shows IR absorption bands at 1695, 1620 cm^{-1} and ^1H NMR shows the following spectral characteristics. Deduce the structure and justify your answer.

δ		
1.95	d	J=4 Hz, 3H
2.2	s	3H
5.85	dd	J=4 Hz, 16 Hz, 1H
6.5	d	J=16 Hz, 1H

f) Depict two mass fragmentation pathways, one fission and one involving rearrangement for



g) A compound of molecular weight 99 containing C, H, O and N shows the following spectral characteristics –

IR (cm^{-1}) : 2250, 1740, 1240

^1H NMR : 3.5 (s, 2H)

3.8 (s, 3H)

Deduce the structure and justify your answer.

SPECTRAL CORRELATION TABLES

Chemical Shifts for Methylene Groups Attached to Two Functional Groups (Y—CH$_2$—Z)

GROUP	-CH$_3$	-C=C	-C≡C	-Ph	-CF$_3$	-CF$_2$	-Cl	-Br	-I	-OH	-OR	-OPh	-OC(=O)R	-C(=O)R	-C(=O)Ph	-C(=O)OR	-C(=O)NR$_2$	-C≡N	-NR$_2$	-NHC(=O)R	-N$_3$	-SR
-CH$_3$	1.17	1.90 2.02	2.14	2.55	1.91	1.84	3.57 3.23	3.43 3.03	3.20 2.52	3.70 3.26	3.40 3.06	3.93	4.25 3.83	2.47 2.40	2.54	2.25 2.25	2.23 2:29	2.40	2.63 2:27	2.97	2.67	2.53 2.34
-C=C		2.60 2.87	3.39 2.99	3.30 3.40	2.76	2.69	4.08	3.93 3.88	3.87 3.37	4.13	3.95 3.91	4.78	4.68	3.25	3.39	3.00 3.10	3.14	3.15 3.25	3.30 3.12	3.82	3.52	3.08 3.19
-C≡C			3.11	3.52	2.88	2.81	4.09 4.20	3.90 4.00	3.49	4.28	4.03	4.90	4.71 4.80	3.37	3.51	3.22	3.26	3.37	3.50 3.24	3.97	3.67	3.31
-Ph				3.87 3.93	3.29	3.50 3.22	4.50 4.61	4.33 4.41	3.90	4.58	4.70 4.44	4.91 5.31	5.08 5.21	3.55 3.78	3.92	3.40 3.63	3.66	3.65 3.78	3.48 3.65	4.34	4.04	3.68 3.72
-CF$_3$					2.63	2.58	3.97	3.76	3.26	4.01 4.01	3.80	4.67	4.57	3.12	3.28	2.99	3.03	3.12	3.01	3.71	3.41	3.08
-CF$_2$						2.51	3.90	3.70	3.56 3.19	3.93	4.73	4.60	4.54	3.07	3.21	2.92	2.96	3.07	2.94	3.64	3.34	3:01
-Cl							4,99 5.29	5.16 5.09	4.99 4.58	5.32	5.40 5.12	5.99	5.89	4.46	4.60	4.05 4.31	4.17 4.35	4.07 4.46	4.37	5.13	4.73	4.40
-Br								4.94 4.89	4.38	5.12	4.92	6.36 5.79	5.69	4.26	4.40 3.40	3.70 4.11	3.92 4.15	4.26	4.13	4.83	4.53	4.20
-I									3.90 3.87	4.61	4.41	5.16	5.06	3.75	3.89	3.60	3.65 3.64	3.65 3.75	3.62	4.32	4.02	3.69
-OH										4.55 4.35	5.13	6.02	5.92	4.49	4.63	4.34	4.38	4.49	4.35	5.06	4.78	4.43
-OR											4.65 4.95	5.81	5.72	4.29	4.43	4.13 4.22	4.18	4.20 4.29	4.15	4.94	4.64	4.23
-OPh												6.69	6.59	5.16	5.30	5.09	4.45 4.05	5.16	5:03	5.86	5.56	5.10
-OC(=O)R													6.46	4.42 5.10	5.20	4.91	4.95	5.10	4.92	5.63	5.37	5.00
-C(=O)R														3.60 3.63	3.77	3.37 3.48	3.52	3.63	3.50	4.10 4.20	3.90	3.57
-C(=O)Ph															3.91	3.62	3.66	3.77	3:64	4.34	4:02	3.71
-C(=O)OR																3.35 3.33	3.37	3.48	3.17 3.35	4.05	3.75	3.42
-C(=O)NR$_2$																	3.30 3.41	3.52	3.39	4.09	3.79	3.46
-C≡N																		3.63	3.50	4.20	3.90	3.57
-NR$_2$																			3.10 3.37	4.07	3.77	3.44
-NHC(=O)R																				4.75	4.45	4.14
-N$_3$																					4.15	3.84
-SR																						3.51

CHARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS[†]

Group	Range μ	Intensity	Range cm⁻¹
A. Hydrocarbon chromophore			
1. C—H STRETCHING			
a. Alkane	3.38–3.51	(m–s)	2962–2853
b. Alkene, monosubstituted (vinyl)	3.29–3.32	(m)	3040–3010
	and 3.23–3.25	(m)	3095–3075
Alkene, disubstituted, *cis*	3.29–3.32	(m)	3040–3010
Alkene, disubstituted, *trans*	3.29–3.32	(m)	3040–3010
Alkene, disubstituted, *gem*	3.23–3.25	(m)	3095–3075
Alkene, trisubstituted	3.29–3.32	(m)	3040–3010
c. Alkyne	~3.03	(s)	~3300
d. Aromatic	~3.30	(v)	~3030
2. C—H BENDING			
a. Alkane, C—H	~7.46	(w)	~1340
Alkane, —CH$_2$—	6.74–6.92	(m)	1485–1445
Alkane, —CH$_3$	6.80–7.00	(m)	1470–1430
	and 7.25–7.30	(s)	1380–1370
Alkane, *gem*-dimethyl	7.22–7.25	(s)	1385–1380
	and 7.30–7.33	(s)	1370–1365
Alkane, *tert*-butyl	7.17–7.22	(m)	1395–1385
	and ~7.33	(s)	~1365
b. Alkene, monosubstituted (vinyl)	10.05–10.15	(s)	995–985
	10.93–11.05	(s)	915–905
	and 7.04–7.09	(s)	1420–1410
Alkene, disubstituted, *cis*	~14.5	(s)	~690
Alkene, disubstituted, *trans*	10.31–10.42	(s)	970–960
	and 7.64–7.72	(m)	1310–1295
Alkene, disubstituted, *gem*	11.17–11.30	(s)	895–885
	and 7.04–7.09	(s)	1420–1410
Alkene, trisubstituted	11.90–12.66	(s)	840–790
c. Alkyne	~15.9	(s)	~630
d. Aromatic, substitution type:[‡]			
five adjacent hydrogen atoms	~13.3	(v, s)	~750
	and ~14.3	(v, s)	~700
four adjacent hydrogen atoms	~13.3	(v, s)	~750
three adjacent hydrogen atoms	~12.8	(v, m)	~780
two adjacent hydrogen atoms	~12.0	(v, m)	~830
one hydrogen atom	~11.3	(v, w)	~880
3. C—C MULTIPLE BOND STRETCHING			
a. Alkene, nonconjugated	5.95–6.17	(v)	1680–1620
Alkene, monosubstituted (vinyl)	~6.08	(m)	~1645
Alkene, disubstituted, *cis*	~6.03	(m)	~1658
Alkene, disubstituted, *trans*	~5.97	(m)	~1675

[†] Abbreviations: s = strong, m = medium, w = weak, v = variable, b = broad, sh = sharp,
~ = approximately

[‡] Substituted benzenes also show weak bands in the region 5.0–6.0 μ (2000–1670 cm⁻¹) which are characteristic of the substitution type. See Fig. 3-30.

CHARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS[†]

2

Group	Range μ	Intensity	Range cm⁻¹
Alkene, disubstituted, *gem*	~6.05	(m)	~1653
Alkene, trisubstituted	~5.99	(m)	~1669
Alkene, tetrasubstituted	~5.99	(w)	~1669
Diene	~6.06	(w)	~1650
	and ~6.25	(w)	~1600
b. Alkyne, monosubstituted	4.67–4.76	(m)	2140–2100
Alkyne, disubstituted	4.42–4.57	(v, w)	2260–2190
c. Allene	~5.1	(m)	~1960
	and ~9.4	(m)	~1060
d. Aromatic	~6.25	(v)	~1600
	~6.33	(v)	~1580
	~6.67	(m)	~1500
	and ~6.90	(m)	~1450
B. Carbonyl chromophore			
1. KETONE STRETCHING VIBRATIONS			
a. Saturated, acyclic	5.80–5.87	(s)	1725–1705
b. Saturated, cyclic:			
6-membered ring (and higher)	5.80–5.87	(s)	1725–1705
5-membered ring	5.71–5.75	(s)	1750–1740
4-membered ring	~5.63	(s)	~1775
c. α,β-Unsaturated, acyclic	5.94–6.01	(s)	1685–1665
d. α,β-Unsaturated, cyclic:			
6-membered ring (and higher)	5.94–6.01	(s)	1685–1665
5-membered ring	5.80–5.85	(s)	1725–1708
e. α,β,α′,β′-Unsaturated, acyclic	5.99–6.01	(s)	1670–1663
f. Aryl	5.88–5.95	(s)	1700–1680
g. Diaryl	5.99–6.02	(s)	1670–1660
h. α-Diketones	5.78–5.85	(s)	1730–1710
i. β-Diketones (enolic)	6.10–6.50	(s)	1640–1540
j. 1,4-Quinones	5.92–6.02	(s)	1690–1660
k. Ketenes	~4.65	(s)	~2150
2. ALDEHYDES			
a. Carbonyl stretching vibrations			
Saturated, aliphatic	5.75–5.81	(s)	1740–1720
α,β-Unsaturated, aliphatic	5.87–5.95	(s)	1705–1680
α,β,γ,δ-Unsaturated, aliphatic	5.95–6.02	(s)	1680–1650
Aryl	5.83–5.90	(s)	1715–1695
b. C—H Stretching vibrations, two bands	3.45–3.55	(w)	2900–2820
	and 3.60–3.70	(w)	2775–2700
3. ESTER STRETCHING VIBRATIONS			
a. Saturated, acyclic	5.71–5.76	(s)	1750–1735
b. Saturated, cyclic:			
δ-lactones (and larger rings)	5.71–5.76	(s)	1750–1735
γ-lactones	5.62–5.68	(s)	1780–1760
β-lactones	~5.5	(s)	~1820

Abbreviations: s = strong, m = medium, w = weak, v = variable, b = broad, sh = sharp,
~ = approximately

ARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS

Group	Range μ	Intensity	Range cm^{-1}
c. Unsaturated:			
vinyl ester type	5.56–5.65	(s)	1800–1770
α,β-unsaturated and aryl	5.78–5.82	(s)	1730–1717
α,β-unsaturated δ-lactone	5.78–5.82	(s)	1730–1717
α,β-unsaturated γ-lactone	5.68–5.75	(s)	1760–1740
β,γ-unsaturated γ-lactone	∼5.56	(s)	∼1800
d. α-Ketoesters	5.70–5.75	(s)	1755–1740
e. β-Ketoesters (enolic)	∼6.06	(s)	∼1650
f. Carbonates	5.62–5.75	(s)	1780–1740
4. CARBOXYLIC ACIDS			
a. Carbonyl stretching vibrations:			
saturated aliphatic	5.80–5.88	(s)	1725–1700
α,β-unsaturated aliphatic	5.83–5.92	(s)	1715–1690
aryl	5.88–5.95	(s)	1700–1680
b. Hydroxyl stretching (bonded), several bands	3.70–4.00	(w)	2700–2500
c. Carboxylate anion stretching	6.21–6.45	(s)	1610–1550
	and 7.15–7.69	(s)	1400–1300
5. ANHYDRIDE STRETCHING VIBRATIONS			
a. Saturated, acyclic	5.41–5.56	(s)	1850–1800
	and 5.59–5.75	(s)	1790–1740
b. α,β-Unsaturated and aryl, acyclic	5.47–5.62	(s)	1830–1780
	and 5.65–5.81	(s)	1770–1720
c. Saturated, 5-membered ring	5.35–5.49	(s)	1870–1820
	and 5.56–5.71	(s)	1800–1750
d. α,β-Unsaturated, 5-membered ring	5.41–5.56	(s)	1850–1800
	and 5.47–5.62	(s)	1830–1780
6. ACYL HALIDE STRETCHING VIBRATIONS			
a. Acyl fluorides	∼5.41	(s)	∼1850
b. Acyl chlorides	∼5.57	(s)	∼1795
c. Acyl bromides	∼5.53	(s)	∼1810
d. α,β-Unsaturated and aryl	5.61–5.72	(s)	1780–1750
	and 5.72–5.82	(m)	1750–1720
e. COF$_2$	5.19	(s)	1928
f. COCl$_2$	5.47	(s)	1828
g. COBr$_2$	5.47	(s)	1828
7. AMIDES			
a. Carbonyl stretching vibrations			
Primary, solid and concentrated solution	∼6.06	(s)	∼1650
Primary, dilute solution	∼5.92	(s)	∼1690
Secondary, solid and concentrated solution	5.95–6.14	(s)	1680–1630
Secondary, dilute solution	5.88–5.99	(s)	1700–1670
Tertiary, solid and all solutions	5.99–6.14	(s)	1670–1630
Cyclic, δ-lactams, dilute solution	∼5.95	(s)	∼1680
Cyclic, γ-lactams, dilute solution	∼5.88	(s)	∼1700

CHARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS†

Group	Range μ	Intensity	Range cm^{-1}
Cyclic, γ-lactams, fused to another ring, dilute solution	5.71–5.88	(s)	1750–1700
Cyclic, β-lactams, dilute solution	5.68–5.78	(s)	1760–1730
Cyclic, β-lactams, fused to another ring, dilute solution	5.62–5.65	(s)	1780–1770
Ureas, acyclic	∼6.02	(s)	∼1660
Ureas, cyclic, 6-membered ring	∼6.10	(s)	∼1640
Ureas, cyclic, 5-membered ring	∼5.81	(s)	∼1720
Urethanes	5.75–5.92	(s)	1740–1690
Imides, acyclic	∼5.85	(s)	∼1710
	and ∼5.88	(s)	∼1700
Imides, cyclic, 6-membered ring	∼5.85	(s)	∼1710
	and ∼5.88	(s)	∼1700
Imides, cyclic, α,β-unsaturated, 6-membered ring	∼5.78	(s)	∼1730
	and ∼5.99	(s)	∼1670
Imides, cyclic, 5-membered ring	∼5.65	(s)	∼1770
	and ∼5.88	(s)	∼1700
Imides, cyclic, α,β-unsaturated, 5-membered ring	∼5.59	(s)	∼1790
	and ∼5.85	(s)	∼1710
b. N—H Stretching vibrations			
Primary, free: two bands	∼2.86	(m)	∼3500
	and ∼2.94	(m)	∼3400
Primary, bonded: two bands	∼2.99	(m)	∼3350
	and ∼3.15	(m)	∼3180
Secondary, free: one band	∼2.92	(m)	∼3430
Secondary, bonded: one band	3.0–3.2	(m)	3320–3140
c. N—H Bending vibrations			
Primary amides, dilute solution	6.17–6.29	(s)	1620–1590
Secondary amides, dilute solution	6.45–6.62	(s)	1550–1510
C. Miscellaneous chromophoric groups			
1. ALCOHOLS AND PHENOLS			
a. O—H Stretching vibrations			
Free O—H	2.74–2.79	(v, sh)	3650–3590
Intermolecularly hydrogen bonded (change on dilution)			
single bridge compounds	2.82–2.90	(v, sh)	3550–3450
polymeric association	2.94–3.13	(s, b)	3400–3200
Intramolecularly hydrogen bonded (no change on dilution)			
single bridge compounds	2.80–2.90	(v, sh)	3570–3450
chelate compounds	3.1–4.0	(w, b)	3200–2500

---

† Abbreviations: s = strong, m = medium, w = weak, v = variable, b = broad, sh = sharp, ∼ = approximately

ARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS

5

Group	Range µ	Intensity	Range cm⁻¹
b. O—H Bending and C—O stretching vibrations			
Primary alcohols	~9.5	(s)	~1050
	and 7.4–7.3	(s)	1350–1260
Secondary alcohols	~9.1	(s)	~1100
	and 7.4–7.9	(s)	1350–1260
Tertiary alcohols	~8.7	(s)	~1150
	and 7.1–7.6	(s)	1410–1310
Phenols	~8.3	(s)	~1200
	and 7.1–7.6	(s)	1410–1310
2. AMINES			
a. N—H Stretching vibrations			
Primary, free; two bands	~2.86	(m)	~3500
	and ~2.94	(m)	~3400
Secondary, free; one band	2.86–3.02	(m)	3500–3310
Imines (=N—H); one band	2.94–3.03	(m)	3400–3300
Amine salts	3.2–3.3	(m)	3130–3030
b. N—H Bending vibrations			
Primary	6.06–6.29	(s-m)	1650–1590
Secondary	6.06–6.45	(w)	1650–1550
Amine salts	6.25–6.35	(s)	1600–1575
	and ~6.67	(s)	~1500
c. C—N Vibrations			
Aromatic, primary	7.46–8.00	(s)	1340–1250
Aromatic, secondary	7.41–7.81	(s)	1350–1280
Aromatic, tertiary	7.36–7.64	(s)	1360–1310
Aliphatic	8.2–9.8	(w)	1220–1020
	and ~7.1	(w)	~1410
3. UNSATURATED NITROGEN COMPOUNDS			
a. C≡N Stretching vibrations			
Alkyl nitriles	4.42–4.45	(m)	2260–2240
α,β-Unsaturated alkyl nitriles	4.47–4.51	(m)	2235–2215
Aryl nitriles	4.46–4.50	(m)	2240–2220
Isocyanates	4.40–4.46	(m)	2275–2240
Isocyanides	4.50–4.83	(m)	2220–2070
b. >C=N— Stretching vibrations (imines, oximes)			
Alkyl compounds	5.92–6.10	(v)	1690–1640
α,β-Unsaturated compounds	6.02–6.14	(v)	1660–1630
c. —N=N— Stretching vibrations, azo compounds	6.14–6.35	(v)	1630–1575
d. —N=C=N— Stretching vibrations, diimides	4.64–4.70	(s)	2155–2130
e. —N_3 Stretching vibrations, azides	4.63–4.72	(s)	2160–2120
	and 7.46–8.48	(w)	1340–1180

CHARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS†

6

Group	Range µ	Intensity	Range cm⁻¹
f. C—NO_2, Nitro compounds:			
aromatic	6.37–6.67	(s)	1570–1500
	and 7.30–7.70	(s)	1370–1300
aliphatic	6.37–6.45	(s)	1570–1550
	and 7.25–7.30	(s)	1380–1370
g. O—NO_2, Nitrates	6.06–6.25	(s)	1650–1600
	and 7.70–8.00	(s)	1300–1250
h. C—NO, Nitroso compounds	6.25–6.67	(s)	1600–1500
i. O—NO, Nitrites	5.95–6.06	(s)	1680–1650
	and 6.15–6.21	(s)	1625–1610
4. HALOGEN COMPOUNDS, C—X STRETCHING VIBRATIONS			
a. C—F	7.1–10.0	(s)	1400–1000
b. C—Cl	12.5–16.6	(s)	800–600
c. C—Br	16.6–20.0	(s)	600–500
d. C—I	~20	(s)	~500
5. SULFUR COMPOUNDS			
a. S—H Stretching vibrations	3.85–3.92	(w)	2600–2550
b. C=S Stretching vibrations	8.33–9.52	(s)	1200–1050
c. S=O Stretching vibrations:			
sulfoxides	9.35–9.71	(s)	1070–1030
sulfones	8.62–8.77	(s)	1160–1140
	and 7.41–7.69	(s)	1350–1300
sulfites	8.13–8.70	(s)	1230–1150
	and 7.00–7.41	(s)	1430–1350
sulfonyl chlorides	8.44–8.59	(s)	1185–1165
	and 7.30–7.46	(s)	1370–1340
sulfonamides	8.48–8.77	(s)	1180–1140
	and 7.41–7.69	(s)	1350–1300
sulfonic acids.	8.27–8.70	(s)	1210–1150
	9.43–9.71	(s)	1060–1030
	and ~15.4	(s)	~650

---

† Abbreviations: s = strong, m = medium, w = weak, v = variable, b = broad, sh = sharp, ~ = approximately

TURN OVER

Proton Chemical Shifts (Values are given on the officially approved δ scale; τ = 10.00 − δ.) 1

Substituent Group	Methyl Protons	Methylene Protons	Methine Proton
HC—C—CH$_3$	0.95	1.20	1.55
HC—C—NR$_2$	1.05	1.45	1.70
HC—C—C=C	1.00	1.35	1.70
HC—C—C=O	1.05	1.55	1.95
HC—C—NRAr	1.10	1.50	1.80
HC—C—NH(C=O)R	1.10	1.50	1.90
HC—C—(C=O)NR$_2$	1.10	1.50	1.80
HC—C—(C=O)Ar	1.15	1.55	1.90
HC—C—(C=O)OR	1.15	1.70	1.90
HC—C—Ar	1.15	1.55	1.80
HC—C—OH (and OR)	1.20	1.50	1.75
HC—C—C≡CR	1.20	1.50	1.80
HC—C—C≡N	1.25	1.65	2.00
HC—C—SR	1.25	1.60	1.90
HC—C—OAr	1.30	1.55	2.00
HC—C—O(C=O)R	1.30	1.60	1.80
HC—C—SH	1.30	1.60	1.65
HC—C—(S=O)R and —SO$_2$R	1.35	1.70	
HC—C—NR$_3^+$	1.40	1.75	2.05
HC—C—O(C=O)CF$_3$	1.40	1.65	
HC—C—Cl	1.55	1.80	1.95
HC—C—O(C=O)Ar	1.65	1.75	1.85
HC—C—Br	1.80	1.85	1.90
HC—CH$_3$	0.90	1.30	1.50
HC—C=C	1.60	2.05	
HC—C≡C	1.70	2.20	2.80
HC—(C=O)OR (and NR$_2$)	2.00	2.25	2.50
HC—SR	2.05	2.55	3.00
HC—O—O	2.10	2.30	2.55
HC—(C=O)R	2.10	2.35	2.65
HC—C≡N	2.15	2.45	2.90
~~HC—~~CHO	2.20	2.40	
HC—Ar (and NR$_2$)	2.25	2.45	2.85
HC—SSR	2.35	2.70	
HC—(C=O)Ar	2.40	2.70	3.40
HC—SAr	2.40		
HC—NRAr	2.60	3.10	3.60
HC—SO$_2$R and —(SO)R	2.60	3.05	
HC—Br	2.70	3.40	4.10
HC—NR$_3^+$	2.95	3.10	3.60
HC—NH(C=O)R	2.95	3.35	3.85
HC—Cl	3.05	3.45	4.05
HC—OH and —OR	3.20	3.40	3.60
HC—NH$_2$	3.50	3.75	4.05
HC—O(C=O)R	3.65	4.10	4.95
HC—OAr	3.80	4.00	4.60
HC—O(C=O)Ar	3.80	4.20	5.05

Substituent Group	Methyl Protons	Methylene Protons	Methine Proton
HC—F	4.25	4.50	4.80
HC—NO$_2$	4.30	4.35	4.60
Cyclopropane		0.20	0.40
Cyclobutane		2.45	
Cyclopentane		1.65	
Cyclohexane		1.50	1.80
Cycloheptane		1.25	

Substituent Group	Proton Shift	Substituent Group	Proton Shift
HC≡CH	2.35	HO—C=O	10–12
HC≡CAr	2.90	HO—SO$_2$	11–12
HC≡C—C=C	2.75	HO—Ar	4.5–6.5
HAr	7.20	HO—R	0.5–4.5
HCO—O	8.1	HS—Ar	2.8–3.6
HCO—R	9.4–10.0	HS—R	1–2
HCO—Ar	9.7–10.5	HN—Ar	3–6
HO—N=C(oxime)	9–12	HN—R	0.5–5

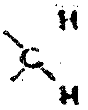
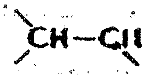
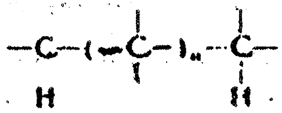
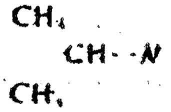
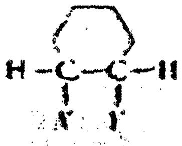
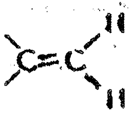
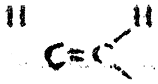
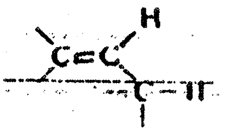
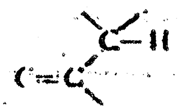
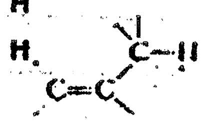
^{13}C Chemical Shifts (Values given on the δ scale, relative to TMS.)

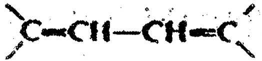
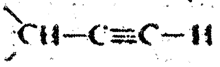
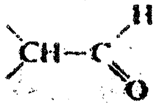
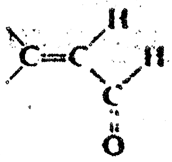
Substituent Group	Primary Carbon	Secondary Carbon	Tertiary Carbon	Quaternary Carbon
Alkanes				
C—C$\lessgtr$	−20 to 30	25 to 45	30 to 60	35 to 70
C—O	40 to 60	40 to 70	60 to 75	70 to 85
C—N	20 to 45	40 to 60	50 to 70	65 to 75
C—S	10 to 30	25 to 45	40 to 55	55 to 70
C—Halide	−37 to 35 (I) (Cl)	−10 to 45 (I) (Cl)	30 to 65 (I) (Cl)	35 to 75 (I) (Cl)

Alkynes	70 to 100	Isocyanides	130 to 150
Alkenes	110 to 150	Carbonates	150 to 160
Aromatics	110 to 135	Oximes	155 to 165
C-substituted	125 to 145	Ureas	150 to 170
Heteroaromatics	115 to 140	Thioureas	165 to 185
C-α	135 to 155	Esters, Anhydrides	150 to 175
Cyanates	105 to 120	Amides	160 to 180
Isocyanates	115 to 135	Acids, Acyl chlorides	160 to 185
Thiocyanates	110 to 120	Aldehydes	175 to 205
Isothiocyanates	120 to 140	Ketones	175 to 225
Cyanides	110 to 130		

TURN OVER

SPIN-SPIN COUPLING CONSTANTS

Type	J, cps
H_2†	280
CH_4†	12.4
	12-15
	2-9
	~0
CH_3-CH_2-X	6.5-7.5
 $(CH_3)_2CH-X$	5.5-7.0
	a,a 5-10 a,e 2-4 e,e 2-4
	0.5-3
	7-12
	13-18
	4-10
	[illegible] 0.5-2.5
	~0

Type	J, cps
	9-13
$H-C\equiv C-H$†	9.1
	2-3
	1-3
	6-8
	o- 6-9 m- 1-3 p- 0-1
	αβ 1.6-2.0 αβ' 0.6-1.0 αα' 1.3-1.8 ββ' 3.2-3.8
	αβ 2.0-2.6 αβ' 1.5-2.2 αα' 1.8-2.3 ββ' 2.8-4.0
	αβ 4.6-5.8 αβ' 1.0-1.8 αα' 2.1-3.3 ββ' 3.0-4.2
	αβ 4.9-5.7 αγ 1.6-2.6 αβ' 0.7-1.1 αα' 0.2-0.5 βγ 7.2-8.5 ββ' 1.4-1.9

Conjugated dienes & Trienes, Solvent: Ethanol

Parent value for Butadiene system or acyclic conjugated diene	217 nm
Acyclic triene	245 nm
Homoannular conjugated diene	253 nm
Hetroannular conjugated diene	215 nm
Increment for each substituents	
Alkyl substituents or ring residue	5 nm
Exocyclic double bond	5 nm
Double bond extending conjugation	30 nm
Auxochrome	
-OR	+6 nm
-SR	+30 nm
-Cl, -Br	+5 nm
NR_2	+60 nm
$-OCOCH_3$	0

Woodward Fieser rules for αβ-unsaturated carbonyl compounds:-

a) Parent values	
αβ-unsaturated acyclic or six membered ketone	215 nm
αβ-unsaturated five membered ring ketone	202 nm
αβ-unsaturated aldehyde	207 nm
b)Increments	
i) Each alkyl substituents or ring residue	
At α position	10 nm
At β position	12 nm
At gamma and higher position	18 nm
ii) Each exocyclic double bond	5 nm
iii) Double bond extending conjugation	30 nm
iv) Homoannular conjugated diene	39 nm

Auxochromes	**Positions**		
	α	β	**gamma**
-OH	35	30	50
-OR	35	30	17
-SR	-	85	-
$-OCOCH_3$	6	6	6
-Cl	15	12	-
-Br	25	30	-
$-NR_2$	-	95	-