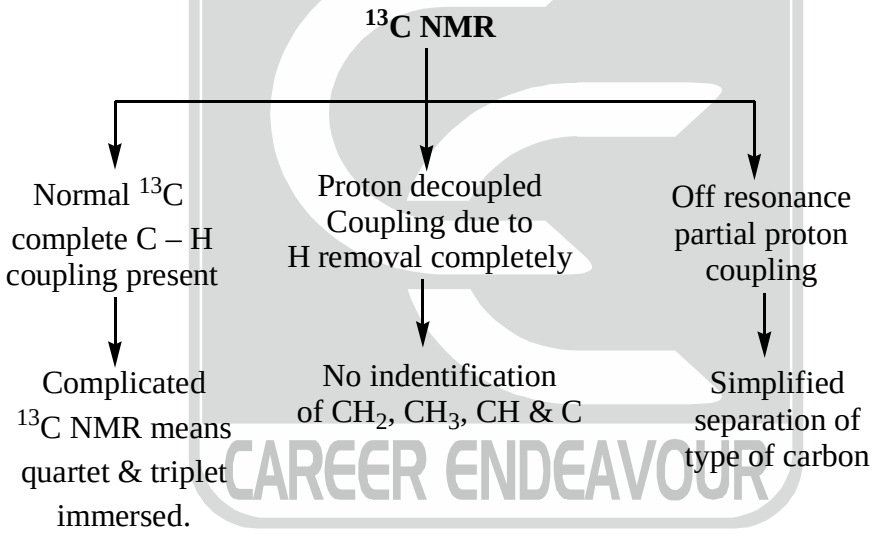
^{13}C NMR

Important points :

1. ^{13}C nucleus is around 400 times less sensitive than the proton.
2. Due to the low abundance of ^{13}C coupling b/w $^{13}C - ^{13}C$ can not be observed.
3. Multiplicity of the signals in ^{13}C NMR arises due to the proton or magnetic nuclei present on the same carbon and no. of signals will be equal to the set of equivalent carbons in the molecule.
4. Due to the long relaxation time of ^{13}C. Compare to proton. there is no meaning of integration of signal to find out the no. of carbon atoms.
5. Information from carbon NMR spectrum

   * Number of signals: equivalent carbons and molecular symmetry
   * Chemical shift: presence of high electronnegative atoms or π-electron clouds
   * Integration: ratios of equivalent carbons
   * Coupling: number of neighbors

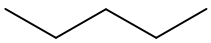
Number of Signals : Chemically equivalent carbon will appear as same signal.
Enantiotopic carbon will be chemically equivalent (So, it will also give same signal).
Diastereotopic carbon will be chemically non equivalent (So, it will give different signals).



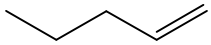
Chemical Shift :

Alkyl Carbon	10 – 40 ppm.
OCH_3, OCH_2] sp^3 carbon attached electronegative atom	40 – 80 ppm.
$C\equiv C-H$ Acetylenic	80 – 100 ppm.
Aklene and aromatic	110 – 140 ppm.
$>C=O$	160 – 220 ppm.
Aldehyde ketone	190 – 220 ppm.

Examples(Chemical shifts in ppm from TMS):

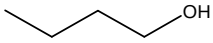


23

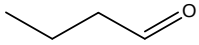


138

sp^3 hybridized carbon is more shielded than sp^2.

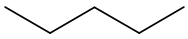


61



202

sp^3 hybridized carbon is more shielded than sp^2.



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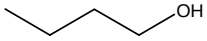
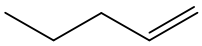
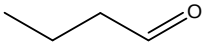


61

An electronegative atom deshields the carbon to which it is attached.

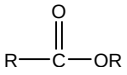
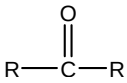


138



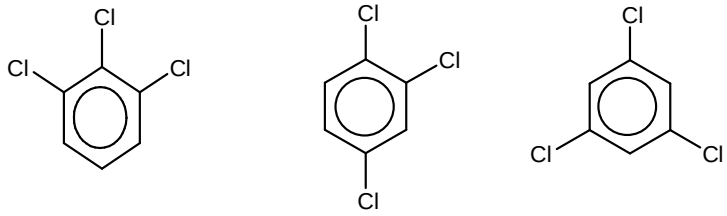
202

An electronegative atom deshields the carbon to which it is attached.

Type of carbon	**Chemical shift(δ), ppm**
RCH_3	0–35
R_2CH_2	15–40
R_3CH	25–50
R_4C	30–40
$CR{\equiv}CR$	65–90
$R_2C{=}CR_2$	100–150
	110–175
RCH_2Br	20–40
RCH_2Cl	25–50
RCH_2NH_2	35–50
RCH_2OH	50–65
RCH_2OR	50-65
	160-165
	190–220

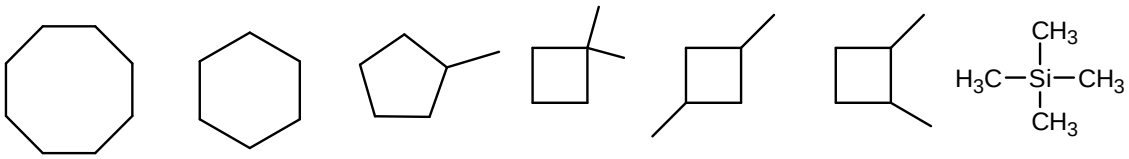
SOLVED PROBLEMS

1. How can you differentiate the following compounds on the basis of ^{13}C NMR spectroscopy.



Soln. ^{13}C NMR signals = 4 ^{13}C NMR signals = 6 ^{13}CNMR signal = 2

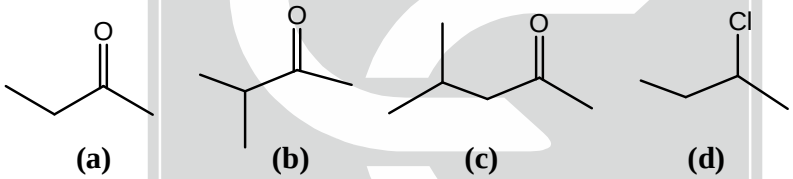
2. For each of the following compounds predict the expected number of signals in its ^{13}C NMR spectra.



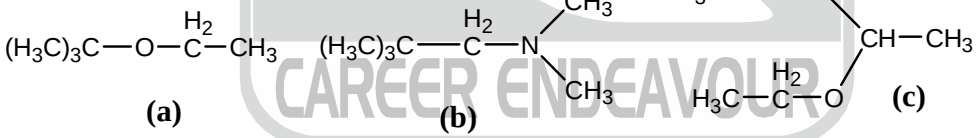
(a) **(b)** **(c)** **(d)** **(e)** **(f)** **(g)**

3. Draw the splitting pattern and predict the expected number of signals of the compounds in ^{1}H NMR spectra.

$(H_3C)_3C-O-CH_3$, $Br-\overset{H_2}{C}-\overset{H_2}{C}-Br$, $Br-\overset{H_2}{C}-\overset{H_2}{C}-CH_2-Br$, $(H_3C)_2HC-O-CH_3$



(a) **(b)** **(c)** **(d)**



(a) **(b)** **(c)**

4. C_4H_6O. Find the structure of organic compound with the help of given data.

DBE = C_n(number of carbon) $-\frac{H\text{ (number of hydrogen)}}{2} + \frac{N\text{(number of nitrogen)}}{2} + 1$

δ 28 quartet δ 138 doublet

δ 130 triplet δ 188 singlet

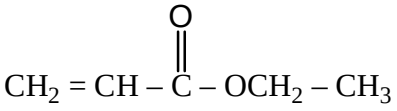
Soln. DBE = 4 – 3 + 1= 0

$$CH_2 = CH - \overset{\overset{O}{\|}}{C} - CH_3$$

5. $C_5H_8O_{2..}$ Find the structure of organic compound with the help of given data.

δ 128 d δ 60 t
δ 132 t δ 35 q
δ 170 S

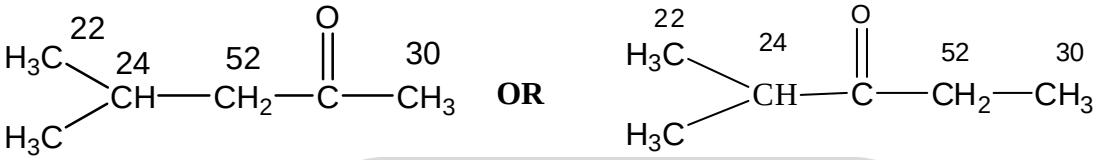
Soln. DBE = 5 – 4 + 1 = 0



6. $C_6H_{12}O$: Find the structure of organic compound with the help of given data.

δ 22	q	δ 52	t
δ 24	d	δ 208	s
δ 30	q		

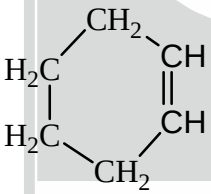
Soln. DBE = 6 + 1 – 6 = 1



7. C_6H_{10}. Find the structure of organic compound with the help of given data.

δ	23	t
δ	26	t
δ	128	d

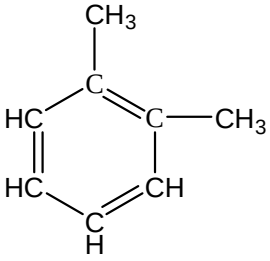
Soln. DBE = 6 + 1 – 5 = 2



8. C_8H_{10}. Find the structure of organic compound with the help of given data.

δ 20	q	δ 130	d
δ 125	d	δ 137	s

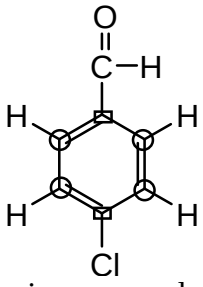
Soln. DBE = 8 + 1 – 5 = 4



9. C_7H_5ClO. Find the structure of organic compound with the help of given data.

δ 130	d	δ 141	s
δ 132	d	δ 180	d
δ 135	s		

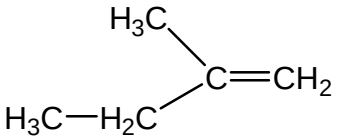
Soln. DBE = 7 + 1 – 3 = 5



10. $C_5H_{10.}$ Find the structure of organic compound with the help of given data.

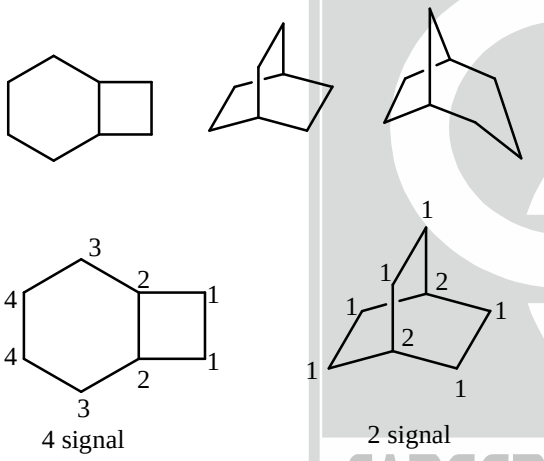
δ 12 q δ 110 t
δ 22 q δ 150 s
δ 30 t

Soln. **DBE = 5 + 1 – 5 = 1**



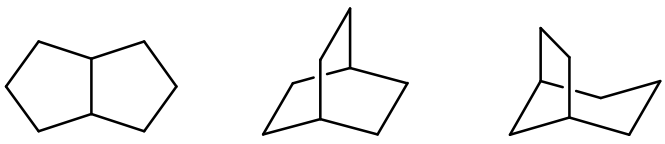
11. How many number of signals will appear in ^{13}C NMR.

Soln.



^{1}H and ^{13}C NMR compared: Both give us information about the number of chemically nonequivalent nuclei (nonequivalent hydrogens or nonequivalent carbons) both give us information about the environment of the nuclei (hybridization state, attached atoms, etc.). the signal for the NMR of a ^{13}C nucleus is 10^{-4} times weaker than the signal for a hydrogen nucleus a signal for a ^{13}C nucleus is only about 1% as intense as that for ^1H because of the magnetic properties of the nuclei, and at the "natural abundance" level only 1.1% of all the C atoms in a sample are ^{13}C (most are ^{12}C). 13C signals are spread over a much wider range than 1H signals making it easier to identify and count individual nuclei.

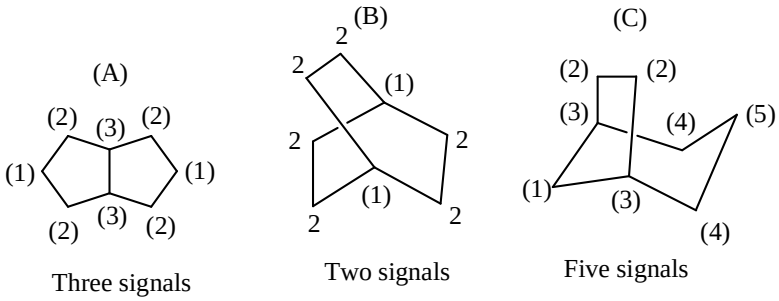
12. In the broad band decoupled ^{13}C NMR spectrum, the number of signals appearing for the bicyclooctane A–C, respectively, are



(A) **(B)** **(C)**

(a) Five, four and eight
(b) Three, two and five
(c) Five, four and five
(d) Three, two and eight

Soln.



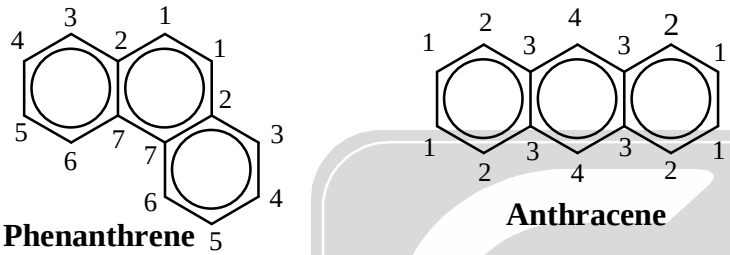
Three signals Two signals Five signals

Correct answer: (b)

13. The number of signals that appear in the broadband decoupled ^{13}C NMR spectrum of phenanthrene and anthracene, respectively are

(a) ten and four (b) ten and ten (c) seven and four (d) seven and seven.

Soln.



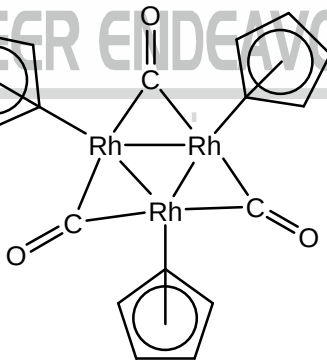
Phenanthrene **Anthracene**

Correct answer is (c).

14. The carbonyl resonance in ^{13}C NMR spectrum of $\left[\left(\eta^5-C_5H_5\right)Rh(CO)\right]_3$ (^{103}Rh, nuclear spin, I=1/2, 100%) shows a triplet at –65° C owing to the presence of

(a) Terminal CO (b) μ_2-CO (c) μ_3-CO (d) $\eta^5-C_5H_5$

Soln. Doublet of carbonyl carbon indicates the each CO is attached with chemically equivalent two Rh atoms, that means μ^2-CO complex. The actual structure is:



15. Match the following

Compound	**^{13}C NMR chemical shift** $(\delta$ ppm$)$
(A) Acetic acid	(i) 95
(B) Acetonitrile	(ii) 115
(C) Acetone	(iii) 175
(D) Carbon tetrachloride	(iv) 205

(a) (A)-(iii), (B)-(ii), (C)-(iv), (D)-(i) (b) (A)-(iii), (B)-(iv), (C)-(i), (D)-(ii)
(c) (A)-(i), (B)-(ii), (C)-(iv), (D)-(ii) (d) (A)-(iii), (B)-(i), (C)-(iii), (D)-(iv)

Soln. (i) Acetic acid = 175 ppm
(ii) Acetonitrile = 115 ppm
(iii) Acetone = 205 ppm
(iv) CCl_4 = 95 ppm
Correct answer is (a).

16. 4-Hydroxybenzoic acid exhibited signals at δ 171, 162, 133, 122 and 116 ppm in its broadband decoupled ^{13}C NMR spectrum. The correct assignment of the signals is

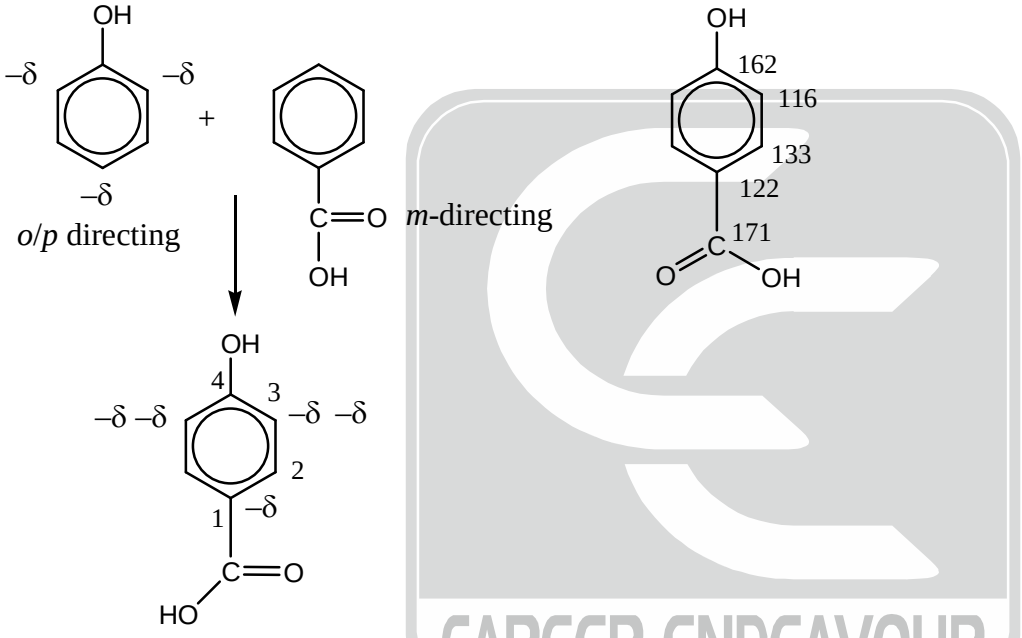
(a) $\delta\ 171(C-4), 162(COOH), 133(C-3\ \&\ 5), 122(C-1)$ and $116(C-2\ \&\ 6)$

(b) $\delta 171(COOH), 162(C-4), 133(C-2\ \&\ 6), 122(C-1)$ and $116(C-3\ \&\ 5)$

(c) $\delta 171(C-4), 162(COOH), 133(C-2\ \&\ 6), 122(C-1)$ and $116(C-3\ \&\ 5)$

(d) $\delta 171(COOH), 162(C-4), 133(C-3\ \&\ 5), 122(C-1)$ and $116(C-2\ \&\ 6)$

Soln.



• Positions-3 is most shielded because of ortho-to OH and meta to COOH. So, it will appear at 116 ppm.
• Position-1 is shielded because it is para-to OH. It will appear at 122 ppm.
If we compare position 2 and 4, position 4 is deshielded due to directly attached OH and it will appear at 162 ppm.
• Position is normal and apparent at 133 ppm.
Correct answer is (b)

17. The structure of the compound having the following characteristics spectral data, is IR : 1690 cm^{-1}. ^1H-NMR : 1.30 (3H, t, J = 7.2 Hz); 2.41 (2H, q, J = 7.2 Hz); 2.32 (3H, s); 7.44 (1H, t, J = 7.0 Hz); 7.57 (1H, dt, J = 7.0, 3.0 Hz); 7.77 (1H, t, J = 3.0 Hz); 7.90 (1H, dt, J = 7.0, 3.0 Hz); EI mass : m/z 119 (100%); 57 (80%)