37. Analytical techniques

37.3 Carbon-13 NMR spectroscopy

Paper 4

Question Paper

1 The amino acid serine, $HOCH_2CH(NH_2)COOH$, exists in two optically active forms. These optical isomers, isomer **P** and isomer **Q**, are shown in Fig. 8.1.

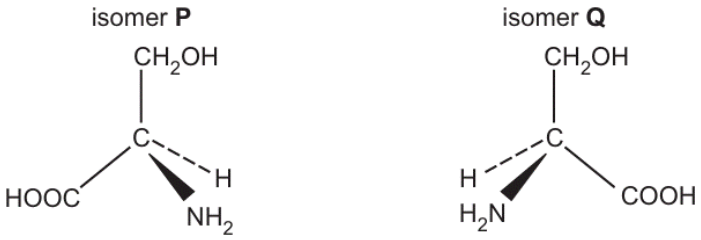
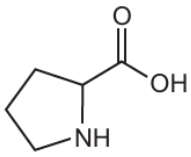


Fig. 8.1

(g) Proline is a naturally occurring amino acid. The skeletal formula of proline is shown.

proline



State the number of peaks in the carbon-13 (^{13}C) NMR spectrum of proline.

..... [1]

2 **(d)** Complete Table 4.1 to show the number of peaks observed in the carbon-13 NMR spectrum for **W** and **Z**.

Table 4.1

compound	number of peaks observed
W	
Z	

[1]

3 **(d)** Predict the number of peaks in the carbon-13 NMR spectrum of the Sunset Yellow anion.

..... [1]

4 Benzene can be used to make benzoic acid in the two-step process shown in Fig. 7.1.

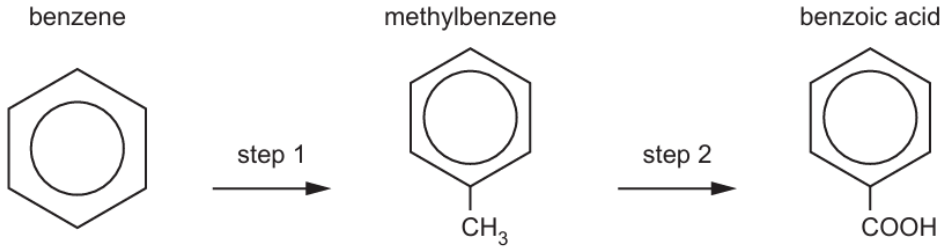


Fig. 7.1

(b) Methylbenzene and benzoic acid each have five different peaks in the carbon (^{13}C) NMR spectrum.

Table 7.1

hybridisation of the carbon atom	environment of carbon atom	example	chemical shift range / ppm
sp^3	alkyl	**C**H_3–, –**C**H_2–, –**C**H<, >**C**<	0–50
sp^3	next to alkene/arene	–**C**–C=C, –**C**–Ar	25–50
sp^3	next to carbonyl/carboxyl	**C**–COR, **C**–O_2R	30–65
sp^3	next to halogen	**C**–X	30–60
sp^3	next to oxygen	**C**–O	50–70
sp^2	alkene or arene	>**C**=**C**<, 	110–160
sp^2	carboxyl	R–**C**OOH, R–**C**OOR	160–185
sp^2	carbonyl	R–**C**HO, R–**C**O–R	190–220
sp	nitrile	R–**C**≡N	100–125

Use Table 7.1 to complete the two sentences to suggest descriptions of these two spectra.

The carbon (^{13}C) NMR spectrum of methylbenzene:

- has ..... peak(s) in the chemical shift range of ..... and
- has ..... peak(s) in the chemical shift range of ..... .

The carbon (^{13}C) NMR spectrum of benzoic acid:

- has ..... peak(s) in the chemical shift range of ..... and
- has ..... peak(s) in the chemical shift range of ..... .

[2]

5 **(b)** Complete Table 9.1 to give the number of peaks in the carbon-13 NMR spectrum of each of the five isomers of $C_5H_{10}O_2$ that has an ester group.

Table 9.1

structural formula	number of peaks
$CH_3CH_2CH_2CO_2CH_3$	
$CH_3CH_2CO_2CH_2CH_3$	
$CH_3CO_2CH_2CH_2CH_3$	
$(CH_3)_2CHCO_2CH_3$	
$CH_3CO_2CH(CH_3)_2$	

[2]

6 When answering this question it should be assumed that together all the hydrogen atoms in a benzene ring result in a single unsplit peak at $\delta = 7.2$ in a proton (^1H) NMR spectrum.
The structures of five isomeric ketones, **P**, **Q**, **R**, **S** and **T** are given.

P $C_6H_5COCH(CH_3)_2$

Q $C_6H_5COCH_2CH_2CH_3$

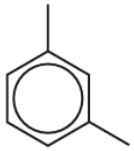
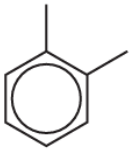
R $C_6H_5CH_2COCH_2CH_3$

S $C_6H_5CH_2CH_2COCH_3$

T $C_6H_5CH(CH_3)COCH_3$

(f) Complete Table 8.1 below to give the number of peaks in the carbon-13 NMR spectrum of each compound.

Table 8.1

compound	number of peaks	compound	number of peaks
			
			

[2]

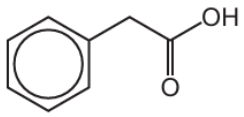
7 **(a)** There are four possible structural isomers of C_8H_{10} that contain a benzene ring.

Draw the **skeletal** formulae of the four structural isomers in the appropriate boxes. The number of peaks observed in the carbon-13 (^{13}C) NMR spectrum of each compound is given.

isomer 1 three peaks in ^{13}C NMR	isomer 2 four peaks in ^{13}C NMR
isomer 3 five peaks in ^{13}C NMR	isomer 4 six peaks in ^{13}C NMR

[4]

8 The structure of phenylethanoic acid is shown.

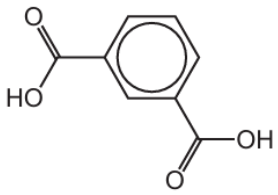


(a) Give the number of different peaks in the carbon-13 (^{13}C) NMR spectrum of phenylethanoic acid.

number of peaks = ... [1]

9 The structure of benzene-1,3-dicarboxylic acid is shown.

benzene-1,3-dicarboxylic acid



(b) Benzene-1,3-dicarboxylic acid is an isomer of benzene-1,4-dicarboxylic acid. These two isomers can be distinguished by carbon-13 (^{13}C) NMR spectroscopy.

State the number of peaks in the carbon-13 (^{13}C) NMR spectrum of each compound.

benzene-1,3-dicarboxylic acid	
benzene-1,4-dicarboxylic acid	

[2]

10 **(c)** **(i)** There are four different carbocations with the same formula, $C_4H_9^+$. One structure is given in the table.

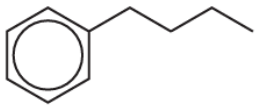
Suggest the structural formulae of the three other carbocations.

structure 1	structure 2	structure 3	structure 4
$CH_3CH_2CH_2CH_2^+$			

[3]

(ii) Benzene reacts with each of these carbocations in separate Friedel-Crafts alkylation reactions.
In each reaction an organic compound with formula $C_{10}H_{14}$ is formed. The number of peaks observed in the carbon-13 NMR spectrum of each compound is given.

Suggest the structures for the three other compounds.

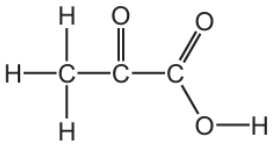
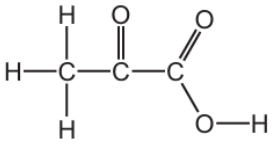
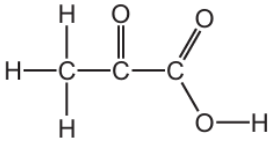
 number of peaks in carbon-13 NMR = 8	number of peaks in carbon-13 NMR = 6
number of peaks in carbon-13 NMR = 7	number of peaks in carbon-13 NMR = 8

[4]

11 **(d)** A sample of pyruvic acid, CH_3COCO_2H, is analysed by carbon-13 NMR spectroscopy. Three peaks are observed.

Complete the table by:

- circling the carbon atom responsible for the chemical shift
- stating the hybridisation of the circled carbon atom.

chemical shift (δ)	carbon atom responsible for chemical shift	hybridisation of the circled carbon atom
27		
163		
192		

[2]

12 **(e)** **(i)** Deduce the number of peaks that would be present in the carbon-13 NMR spectrum of benzophenone.

number of peaks ..... [1]

(ii) Identify **two** different environments of carbon atom that would result in different chemical shift ranges in this carbon-13 NMR spectrum of benzophenone.

environment of carbon atom	chemical shift range (δ)

[2]