7 **P**, **Q**, **R**, **S**, **T**, **U**, and **V** are the seven structural isomers with molecular formula $C_5H_{10}O$ that have a carbonyl group.

P $CH_3(CH_2)_3CHO$ **Q** $CH_3CH_2CH(CH_3)CHO$ **R** $(CH_3)_2CHCH_2CHO$

S $(CH_3)_3CCHO$ **T** $CH_3CH_2CH_2COCH_3$ **U** $CH_3CH_2COCH_2CH_3$

V $(CH_3)_2CHCOCH_3$

(a) Only one of these seven compounds has stereoisomers.

Draw three-dimensional diagrams of the **two** stereoisomers of this compound.

[2]

(b) **P**, **Q**, **R**, **S**, **T**, **U**, and **V** are treated separately with alkaline I_2(aq) and the product mixture is acidified.

(i) Identify the **two** compounds that give a positive result with alkaline I_2(aq).

..... and ..... [1]

(ii) Describe the observations when **one** of the compounds you have identified in **(b)(i)** is treated with alkaline I_2(aq) and give the structural formulae of the **two** carbon-containing products of this reaction.

observations .....

two carbon-containing products .....

and .....

[2]

P $CH_3(CH_2)_3CHO$ **Q** $CH_3CH_2CH(CH_3)CHO$ **R** $(CH_3)_2CHCH_2CHO$

S $(CH_3)_3CCHO$ **T** $CH_3CH_2CH_2COCH_3$ **U** $CH_3CH_2COCH_2CH_3$

V $(CH_3)_2CHCOCH_3$

(c) The proton (^{1}H) NMR spectra of **P**, **Q**, **R**, **S**, **T**, **U**, and **V** are compared.

(i) Identify the only compound that gives a spectrum with two singlets and no other peaks.

..... [1]

Fig. 7.1 shows the spectrum obtained from one of the compounds.

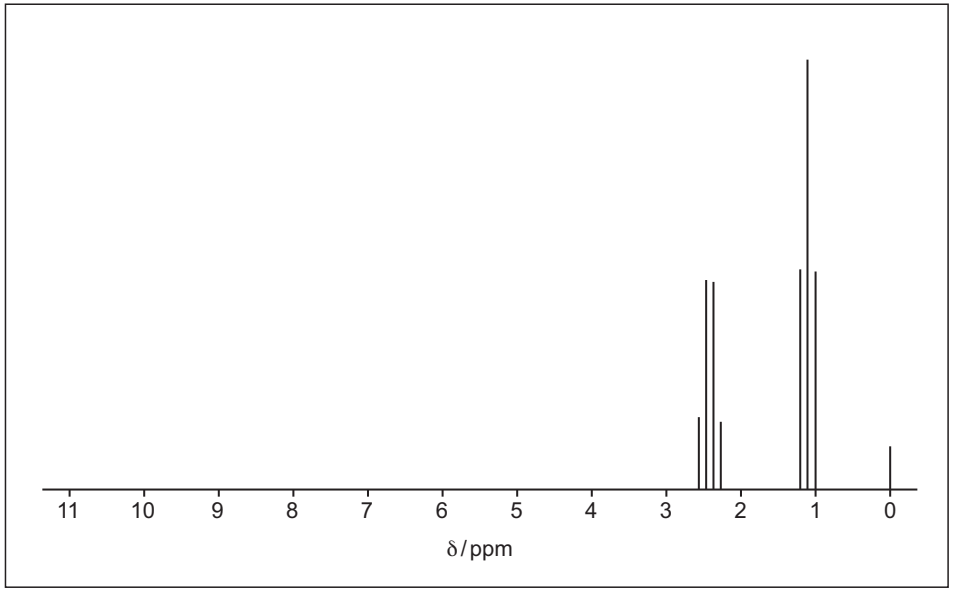


Fig. 7.1

(ii) Identify the compound that gives this spectrum.

..... [1]

(iii) Name the splitting pattern of the peak at δ = 1.1 in Fig. 7.1.

Give the reason for this splitting.

name .....

reason .....

[1]

(iv) Identify the substance that gives the small peak at δ = 0 in Fig. 7.1.

..... [1]

(d) The carbon-13 NMR spectra of **R**, **S**, **T** and **U** are compared.

Complete Table 7.1 to state the number of peaks in the spectrum of each compound.

Table 7.1

compound		number of peaks
R	$(CH_3)_2CHCH_2CHO$	
S	$(CH_3)_3CCHO$	
T	$CH_3CH_2CH_2COCH_3$	
U	$CH_3CH_2COCH_2CH_3$	

[2]

[Total: 11]

6 **(a)** Thin-layer and gas/liquid chromatography can be used to separate mixtures into their individual components.

(i) Define the following terms used in chromatography.

R_f value .....

.....

retention time .....

.....

[2]

(ii) Each type of chromatography makes use of a stationary phase and a mobile phase.

Complete Table 6.1 with a description of each of these.

Table 6.1

	stationary phase	mobile phase
thin-layer chromatography		
gas/liquid chromatography		

[1]

(b) A mixture of two substances **A** and **B** is analysed by thin-layer chromatography.

The R_f value of substance **A** is larger than that of substance **B**.

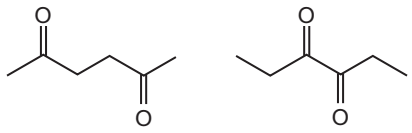
Suggest why substance **A** has a larger R_f value.

.....

..... [1]

(c) The two isomeric compounds **Y** and **Z** are analysed by proton (^{1}H) NMR spectroscopy.

Y **Z**



(i) Complete Table 6.2 to predict the number of peaks observed in the proton (^{1}H) NMR spectra for **Y** and **Z**.

Table 6.2

compound	number of peaks observed
Y	
Z	

[1]

(ii) Name **all** the different splitting patterns observed in the proton (^{1}H) NMR spectra for **Y** and **Z**.

Y .....

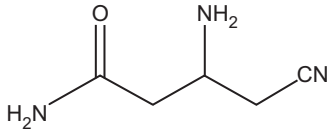
Z .....

[2]

[Total: 7]

6 **(a)** Compound **Z** is used in organic synthesis.

Z



Complete Table 6.1 to show the number of sp, sp^2 and sp^3 hybridised carbon atoms present in one molecule of **Z**.

Table 6.1

type of hybridisation	sp	sp^2	sp^3
number of carbon atoms			

[1]

(b) **Z** can undergo different reactions, as shown in Fig. 6.1.

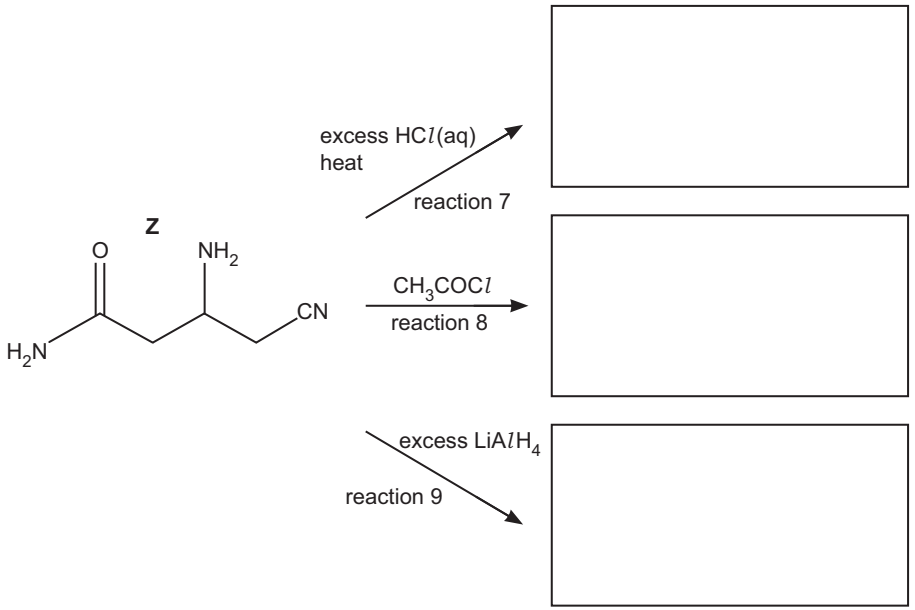


Fig. 6.1

(i) Name the **two** types of reaction occurring in reaction 7 in Fig. 6.1.

..... and ..... [1]

(ii) Draw the structures of the organic products of reactions 7, 8 and 9 in Fig. 6.1. [4]

(c) Compound **Z** is dissolved in D_2O and analysed by carbon-13 NMR and proton (^1H) NMR spectroscopy.

(i) Predict the number of peaks in the carbon-13 NMR spectrum of **Z**.

..... [1]

(ii) The proton (^1H) NMR spectrum of **Z** in D_2O gives three peaks for the proton environments, labelled **a**, **b** and **c**, as shown on Fig. 6.2.

Z

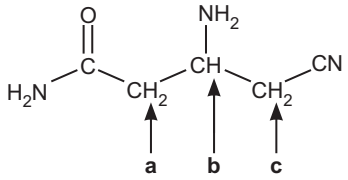


Fig. 6.2

Complete Table 6.2 for the proton (^1H) NMR spectrum of **Z** in D_2O.

Table 6.2

proton environment	**a**	**b**	**c**
name of splitting pattern			
chemical shift range, δ / ppm			

[2]

Table 6.3

environment of proton	example	chemical shift range, δ / ppm
alkane	–C**H**$_3$, –C**H**$_2$–, >C**H**–	0.9–1.7
alkyl next to C=O	C**H**$_3$–C=O, –C**H**$_2$–C=O, >C**H**–C=O	2.2–3.0
alkyl next to nitrile	–C**H**$_2$–CN	2.0–3.0
alkyl next to electronegative atom	C**H**$_3$–O, –C**H**$_2$–O, –C**H**$_2$–N	3.2–4.0
attached to alkene	=C**H**R	4.5–6.0
alkyl amine	R–N**H**–	1.0–5.0
amide	RCON**H**R	5.0–12.0

[Total: 9]

8 **(a)** Describe the difference in reactivity between ethanoyl chloride and chlorobenzene with water.

Explain your answer.

.....

.....

.....

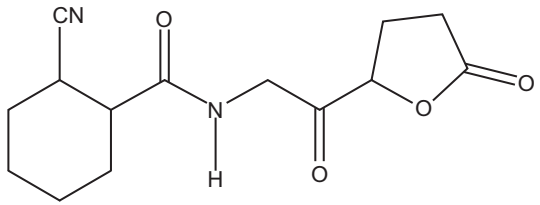
.....

.....

..... [2]

(b) The structure of compound **V** is shown.

V



(i) Name all the functional groups in **V**.

.....

.....

..... [2]

(ii) Deduce the number of possible optical isomers for **V**.

..... [1]

(iii) Suggest **one** reason, other than better biological activity and lower dosage required, why it is beneficial to synthesise a single optical isomer of **V** for use as a drug.

.....

.....

..... [1]

(c) A sample of **V** is hydrolysed with an excess of hot aqueous alkali.

The products are isolated from the reaction mixture at pH 12.

Draw the structures of the **two** organic products of the **complete** alkaline hydrolysis of **V** in Fig. 8.1.

Fig. 8.1

[3]

(d) A polypeptide formed from four amino acids, **A**, **B**, **C** and **D**, is completely hydrolysed and then analysed by gas–liquid chromatography.

The chromatogram produced is shown in Fig. 8.2.

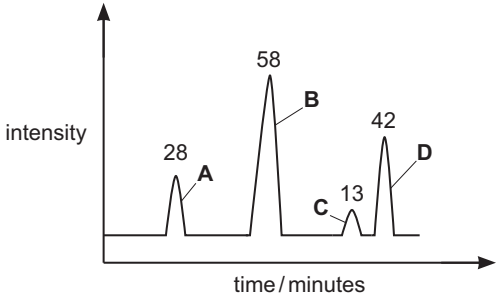


Fig. 8.2

The number above each peak represents the area under the peak.

The area under each peak is proportional to the mass of the respective amino acid in the mixture.

(i) Calculate the percentage by mass of amino acid **A** in the original mixture.

percentage by mass of amino acid **A** = ... [1]

(ii) The retention time for amino acid **D** is the longest.

Explain why **D** has a longer retention time than the **other** amino acids **A**, **B** and **C**.

.....

.....

.....

..... [1]

[Total: 11]

Important values, constants and standards

molar gas constant	$R = 8.31\,\text{J K}^{-1}\,\text{mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^{4}\,\text{C mol}^{-1}$
Avogadro constant	$L = 6.02 \times 10^{23}\,\text{mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19}\,\text{C}$
molar volume of gas	$V_m = 22.4\,\text{dm}^3\,\text{mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0\,\text{dm}^3\,\text{mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14}\,\text{mol}^2\,\text{dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18\,\text{kJ kg}^{-1}\,\text{K}^{-1}$ ($4.18\,\text{J g}^{-1}\,\text{K}^{-1}$)

The Periodic Table of Elements

Group 1	2												13	14	15	16	17	18
								1 H hydrogen 1.0										2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0												5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3												13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –	113 Nh nihonium –	114 Fl flerovium –	115 Mc moscovium –	116 Lv livermorium –	117 Ts tennessine –	118 Og oganesson –

Key

atomic number
atomic symbol
name
relative atomic mass

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –