Solutions to Exercises, Chapter 25

25.1 Use the eqn $E = hc/\lambda$ where $h = 6.626 \times 10^{-34}$ J s.
(a) 552 kJ mol^{-1} (b) 471 kJ mol^{-1} (c) 239 kJ mol^{-1}

25.2 Using the relationship $c_S = A/\varepsilon l$, the concentration is 4.72×10^{-6} mol dm^{-3}.

25.3 Spectrum (a) has a strong absorption in the region 1000–1100 cm^{-1} due to the C–O stretching vibration, but no absorption due to O–H stretching.   In spectrum (b), the distinctive broad absorption of an OH is observed in the region 3100–3600 cm^{-1} as well as the absorption at about 1000 cm^{-1} due to the C–O stretching.
(a) diethyl ether   (b) butan-1-ol

25.4 Spectrum (a) has a carbonyl absorption at about 1750 cm^{-1} and a C–O stretching absorption at about 1000 cm^{-1}, but no O–H stretching band (the weak absorption at about 3500 cm^{-1} is the carbonyl overtone band).   Spectrum (b) has a distinctive broad band over the wide range 2500–3300 cm^{-1} and a strong carbonyl absorption at about 1750 cm^{-1}.
(a) ethyl ethanoate   (b) butanoic acid

25.5 A carbonyl absorption at about 1700 cm^{-1} and the weak absorptions at 2700 and 2800 cm^{-1} are characteristic of an aldehyde.   Aromatic out-of-plane bending absorptions are also apparent around 700 cm^{-1} so the spectrum is assigned to benzaldehyde.

25.6
(a) 1   (b) 2   (c) 2   (d) 4   (e) 3

25.7 The isolated H in methyl methanoate is similar to an aldehydic H and the other Hs are in a methoxy group, so signals are expected at about 9–10 ppm and 3–4 ppm (they are actually observed at 9.42 and 3.69 ppm).

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25.8

(a) 3   (b) 4   (c) 2   (d) 3   (e) 1   (f) 2   (g) 2   (h) 7   (i) 2

25.9   Of the two singlets at 2.28 and 3.76 ppm, the former is due to the methyl group bonded to the benzene ring and the latter is due to the methoxy methyl which is deshielded by the O.   The combined electron-donating resonance and electron-withdrawing inductive effects of the methoxy group make its *ortho* positions more shielded than its *meta* positions.   Consequently, the higher field signal in the aromatic region (6.80 ppm) is assigned to the hydrogens *ortho* to the methoxy, and the lower field signal (7.07 ppm) to the hydrogens *ortho* to the methyl.

25.10   The doublet at 1.11 ppm is assigned to the methyl hydrogens of the isopropyl group which are coupled with the low-field methine proton; the methine H is a septet (the mutual coupling is confirmed by the separation of peaks in the doublet and the septet being the same).   The singlet at 2.15 ppm is due to a methyl which has no adjacent proton so is assigned to the methyl bonded to the carbonyl carbon; like the methine H (but not to the same extent), it is downfield due to the electron-withdrawing and diamagnetic effects of the carbonyl bond.   The integration of the three types of H (6:3:1 from the high field end) supports the assignment.

25.11

(a) CO_2H (b) H4   (c) H2   (d) H3

The triplets at 3.62 and 2.56 ppm are due to couplings of the two Hs at C4 and the two at C2 with the CH_2 between them; the Hs at C3 are a 5-peak multiplet because the coupling constants to the two flanking CH_2 groups are the same (or closely similar).   A broad signal at very low-field is typical of a carboxylic acid.

25.12   From the presence of N and the degree of unsaturation evident from the molecular formula, we deduce that both compounds are aromatic amines; signals around 7 ppm indicate benzene derivatives.

(a) A mutually coupled doublet and quartet at 1.35 ppm and 4.05 ppm, respectively, indicate >CH–CH$_3$, so the compound must be 1-phenylethanamine.
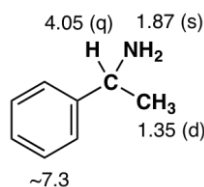
(b) A triplet at 1.17 ppm and a quartet at 2.51 ppm suggest an ethyl group and the ("roofed") pair of doublets in the aromatic region indicate a *p*-disubstituted benzene, so the compound is *p*-ethylaniline.
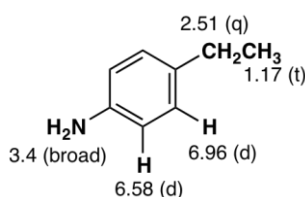

25.13

(a) The ^{13}C NMR signals at 26.0 and 124.5 ppm are of cyclohexa-1,4-diene; because of the symmetry of the time-averaged structure, there are only one kind of sp^2 C and one kind of sp^3 C.

(b) The ^{13}C NMR signals at 22.2, 124.4, and 126.2 ppm are of cyclohexa-1,3-diene; there are two kinds of sp^2 C but only one kind of sp^3 C.

25.14   The *o*-, *m*-, and *p*-dichlorobenzenes have 3, 4, and 2 kinds of sp^2 carbon atoms, respectively.   Consequently, signals are assigned as follows.

(a) 1,4-dichlorobenzene   (b) 1,2-dichlorobenzene   (c) 1,3-dichlorobenzene

25.15   The molecular ion could give secondary carbenium ions of comparable stability by loss of either an ethyl or a methyl radical.   As an ethyl radical is more stable than a methyl radical, the fragmentation shown will be the more favourable and the base peak will be *m/z* = 57.
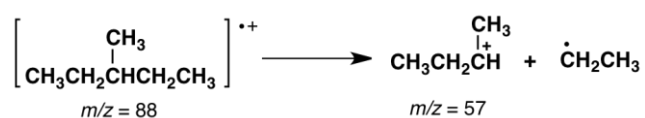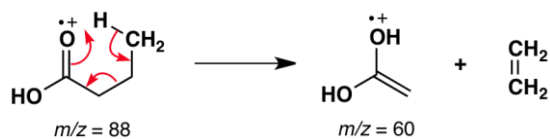
25.16   The base peak will be at $m/z = 91$ by the following fragmentation to give the (relatively) stable tropylium ion.
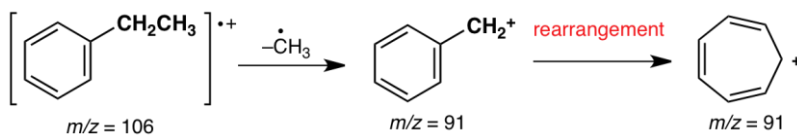
25.17   The base peak will be at $m/z = 45$ by the following favourable fragmentation to give protonated ethanal.
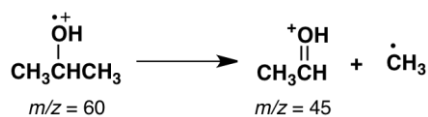
25.18   The base peak at $m/z = 60$ is due to a McLafferty rearrangement.

25.19

$C_{10}H_{17}N$, 151.1361; $C_9H_{13}NO$, 151.0997; $C_8H_9NO_2$, 151.0633; $C_7H_5NO_3$, 151.0270.