Chapter 4: Nuclear magnetic resonance spectroscopy

4.1 Note first that in Figure 4.33 there are *four* different sets of peaks for the protons, with intensities in the ratio 1(δ 1.9), 2 (δ 3.6), 2 (δ 1.6), 3 (δ 0.9).

The resonance at δ 0.9 (integration 3) is a methyl group (CH_3), split into a triplet (1:2:1), evidently by an adjacent CH_2 group. The triplet at δ 3.6 (whose chemical shift suggests an adjacent oxygen atom) is also likely to be a methylene group (integration 2) split by another methylene group to give the triplet pattern. The part structure $-CH_2-CH_2-CH_3$ should be suggested, and confirmation is provided by the observation of a splitting pattern for the central $-CH_2-$ methylene group (δ 1.6) which has *five* CH neighbours, as confirmed by the pattern 1:5:10:10:5:1. A single hydrogen (at δ 1.9) is unsplit and broadened (typical of an OH signal).

Check with reference to the Table of Shifts (Table 4.2, page 75) and also Pascal's Pyramid (page 78) that this is consistent with the structure $HOCH_2CH_2CH_3$ (propan-1-ol,) and the formula given; note that further confirmation is provided by the ^{13}C spectrum (number of carbons: shifts, numbers of attached hydrogens).

4.2 Again, note first the fact that in Figure 4.34 there are *three* different environments for the protons, evidently in the intensity ratio 2 (δ 4.12), 3 (δ 2.05) and 3 (δ 1.25): i.e. we are dealing with a CH_2 group and 2 CH_3 groups (with a total of 8 protons (to match the formula). The absorption from the CH_2 group at δ 4.1 (whose shift is indicative of being next to an oxygen atom) is split into a 1:3:3:1 pattern, by an adjacent methyl group (whose absorption is recognized at δ 1.2, which is also split, into a triplet, as expected). This pair represents an ethyl group, giving the part structure $-OCH_2CH_3$.

The single methyl group resonance of δ 2.05 has no adjacent protons and may well be next to a carbonyl group, given the shift and the formula. This suggests the structure $CH_3C(O)OCH_2CH_3$, ethyl acetate.

Confirmation is provided by the ^{13}C spectrum which helps identify the number of carbon atoms and their environments. (Note, in particular the evidence for the carbonyl group at δ 170 as well as the numbers of attached protons).

4.3 The separation of the peaks (in δ units) is 0.015; since the spectrometer operates at 400 MHz, the value of Δv, given by $\nu.\Delta\delta/10^6$ (see page 79) is 400 x 0.015 = 6 Hz.

4.4 The ^{1}H NMR information indicates that the molecule possesses a mono-substituted benzene ring (C_6H_5), judging by the integration (5) and high chemical shift (in the aromatic region). It also possesses a CH_2 and a CH_3 group (not adjacent to each other), with chemical shifts which may indicate that these groups are adjacent to O and a carbonyl group, respectively. ^{13}C spectra should confirm the number of carbons (including the benzene ring), and attached protons, and also provide evidence for the carbonyl group via its characteristic shift of *ca*. 200 δ). We need further information on the formula, which should be provided by mass spectrometry before we can be confident of a structural assignment for this compound (see Answer to Exercise 5.4).

4.5 The ring will have two pairs of equivalent protons (the *ortho* and *meta* protons) and the single *para* proton. The *para* proton will have two nearest neighbours, and hence a 1:2:1 pattern, with overall intensity 1: this is the right-hand set of peaks with δ 7.12. The other two pairs will differ in that the *ortho*-protons (2,6) will have one neighbour each and hence become split into doublets (i.e. the peaks at δ 7.18). This leaves the triplet at 7.24 for the two *meta* protons (3,5) which will each have two neighbours and hence a splitting into a triplet pattern (1:2:1). The aromatic ring in phenylethene styrene (Figure 4.15) gives a similar pattern.

4.6 The cyclohexane ring exists in a chair *conformation* with different environments for the axial and equatorial protons (see structures 4.1 and 4.2 on page 82, section 4.4, and also Figure 6.26, page 149). When ring-flipping occurs (which interconverts the positions, and hence shifts of each of the protons) *averaging* takes place if and when the exchange is faster (i.e. at higher temperatures). For averaging to occur, the rate of flipping (ring-inversion) must be greater than $\Delta \nu$ for the two lines, i.e. > 500 x 0.48, i.e. 240 Hz.

4.7 The ^{31}P resonance will be split by interaction with three ^{19}F nuclei (for which $I = ½$), giving a 1:3:3:1 pattern (i.e. as with spin-spin splittings between a hydrogen atom and a neighbouring CH_3 group). The three (equivalent) fluorine atoms will each “see” a neighbouring spin-½ nucleus (^{31}P) and therefore appear as a 1:1 doublet.