You might start this exercise by drawing all of the isomers of C\textsubscript{7}H\textsubscript{16} of which there are nine:

![Isomers of C\textsubscript{7}H\textsubscript{16}]

Pick one with both secondary and tertiary carbon atoms and simply add an OH group to these atoms.

![OH-Modified Isomers]

Through this exercise you will hopefully equate light with energy. Here we need light of wavelength that corresponds to the strength of the Cl—Cl bond (58 kcal/mole). The relationship between wavelength and energy is:

\[ \lambda = \frac{28,600}{E} \]

and thus in this case, \( \lambda = \frac{28,600}{58} = 493 \) nm. The book is wrong is assigning this to the ultraviolet/visible range---it is well into the visible which starts at about 390 and spans to 750 nm for the typical human eye.

It is useful to store the correspondence of 71.5 kcal/mole with 400 nm. Simple math can then be used to determine the energy of other wavelengths (e.g., 800 nm corresponds to 35.75 kcal/mole, twice the wavelength half the energy).

We determine \( \delta \) by dividing the observed frequency by the frequency of the machine, as done in the answer in the book to this exercise.

The primary factor in the frequency for protons is electron density. The presence of nearby more electronegative atoms reduces electron density and shifts the signal to lower field. There are two different types of hydrogens in chloromethyl methyl ether (ClCH\textsubscript{2}OCH\textsubscript{3}) as it is normally called, those on the methyl carbon where the carbon is attached to an oxygen and those on the other carbon which has both an oxygen and a chlorine attached. The latter are observed at lower field.

This is an interesting molecule to pick as an example. Bis-chloromethyl methyl ether (ClCH\textsubscript{2}OCH\textsubscript{2}Cl) is always a contaminant in chloromethyl methyl ether. The former is a very highly carcinogenic compound. It is presumed that each of the carbons bearing chlorine can undergo substitution and in living systems, these substitutions can result in cross linking between strands of double helix DNA.
10-5 You were not expected to come up with exact numbers, as indicated in the back of the book, but just ranges. It would be worthwhile for you to look, for example, at all of the methyl groups in the (a)-(c) and see how they vary depending on to what the carbon is attached.

10-6 Worked out in the textbook.

10-7 Both of these molecules are symmetrical and thus have only one type of hydrogen. Each would result in a spectrum with a single signal.

10-8 The answer in the back of the book is adequate.

10-9 This exercise is worked out on page 403 as "Working with Concepts".

10-10 Every carbon atom is unique and therefore, every set of hydrogen atoms on the carbon atoms is also unique.

10-11 Two chlorine atoms on a cyclopropane ring can either be on the same or adjacent carbon atoms. In the later case, they can be cis or trans to each other, thus there are three dichlorocyclopropanes.

For 1,1-dichlorocyclopropane, all of the hydrogen atoms are identical and so we predict a single signal. The 1,2-isomers can be distinguished from the 1,2-isomer because each has two different types of hydrogens, those on carbon bearing chlorine and the two of the methylene group. The cis isomer can be distinguished from the trans as the two hydrogen atoms of the methylene group are identical in the trans isomer but not in the cis (in the cis, one hydrogen atom is on the same side and thus cis to the chlorine atoms whereas the other is trans to the chlorines.

10-12 (a) Diethylether has two identical ethyl groups with the methylene group of each shifted downfield by the oxygen. The methyl groups appear as a triplet as a result of the adjacent two hydrogens and the methylene groups are split into identical quartets by the methyl groups. (b) Here we can see the downfield shift effect of bromine. The central methylene has four identical adjacent hydrogen atoms and thus appears as a quintet whereas the other two methylenes are split into triplets by the pair of hydrogens on the central carbon atom. (c) There are two identical methyl groups lacking adjacent hydrogens and thus appear as a singlet. There is an ethyl group with the expected quartet and triplet, and finally a hydrogen on oxygen. Should should be aware that the position of an OH hydrogen varies greatly with the solution pH.
(d) Here we see the effect of two chlorines versus one. Note that the effect is not additive and the second chlorine does not result in as much downfield shift as the first. (Ponder why this might be.)

10-13 This exercise is worked out on page 412 as "Working with Concepts".

10-14 For small molecules of this size, we generally see unique signals for each set of hydrogen atoms. Thus, while it is possible that a signal for 3 H might be the overlap of a CH and a CH₂ group, it is much more likely that it is the result of a CH₃ group. Two solve a problem of this type, we start by listing the groups that we deduce are present from the spectrum: CH₂  CH₃  CH₃  CH₃  OH (the broad singlet). We compare thus with the molecular formula and that we are missing a carbon atom and thus there must be one carbon present with no hydrogen atoms. Next we examine the splitting information and see that we have two methyl groups with no adjacent hydrogens and that the third methyl is adjacent to a methylene that in turn is split into a quartet by the methyl. Thus, we have four groups, two methyls, one ethyl, and one OH to attach to our quaternary carbon atom. Only one structure results from this analysis:

10-15 This exercise is worked out on page 420 as "Working with Concepts".

10-16 (a) There are a total of four adjacent hydrogen atoms but they are not identical. It is not possible to predict if the selected methylene group will appear as a triplet of triplets where each of the adjacent methylene groups have different splitting constants or as a quintet if the splitting constants are not sufficiently different to be resolved. The pattern on the left, below, results from two quite different splitting constants, that on the right from identical constants. Note that the constants on the left were selected so that none of the peaks would overlap. Increasing the lower splitting constant will result in overlap of some of the peaks. Beware---complex patterns do always lend themselves to a simple peak count.
10-17 It is best not to over analysis an exercise such as this. We could go through each structure and predict what we would expect in each case. However, the exercise asks simple if we can distinguish these structural isomers base upon splitting. We note that only two of the structures have methyl groups and one will be a doublet and the other a triplet. We really do not need splitting to distinguish the third but we can base on it is the only isomer with a methylene group bearing chlorine with two adjacent hydrogen atoms.

![Structures](image)

10-18 One of the benefits of C13 spectroscopy is how readily it reveals symmetry. In 1-bromopropane, we have three unique carbon atoms so we expect three signals with one significantly downfield as a result of the attached bromine atom.

10-19 (a) Three identical methyl groups, a quaternary carbon, and a methylene bearing oxygen. (b) There are eight methylene groups four that are identical to each other and directly connected to the bridgehead carbons and the other four which are identical to each other. The bridgehead atoms are unique from the methylene groups but identical to each other. Thus, we predict three signals. (c) This is a nasty question as the stereochemistry shown requires the central ring to be a boat. There is a mirror plane that divides the molecule left to right but otherwise there are seven unique carbon atoms.

![Structure](image)

(d) All of the six methylene groups are identical as are the two bridgehead carbons: two peaks.

10-20 This exercise is worked out on page 426 as "Working with Concepts".

10-21 The key here is that reduction of the aldehyde functional group makes the functional groups on the two ends of these molecules functionally identical. However, this a very complex stereochemical situation, best view in more typical representations that with Fischer projections. Below are the two products of reduction:

![Products](image)
Note that the product derived from A is a meso stereoisomer and is shown in the conformation that has a mirror plane. (The central carbon atom IS a center of chirality as it has two different groups attached by virtue of stereochemistry, $R$ on the left and $S$ on the right---$R$ has higher priority than does $S$). The diastereomer on the right has no such mirror symmetry and the two $R$ centers of chirality are different. Note that here the central carbon is not a center of chirality---if you switch the OH and H, you can rotate 180 degrees left to right to return to where you started.

**10-22** Because DEPT spectra specifically identify carbons as primary, secondary and tertiary, it would be trivial to differentiate these two isomers as only A has methyl groups and only B has methylene groups.