Chapter 20: Identification of Compounds

Chemists are frequently faced with the problem of identifying unknown compounds. Environmental scientists may have to identify pollutants in soils and water, synthetic chemists may want to confirm that a reaction gives the desired product, and researchers will need to positively identify intermediates in the course of their projects. Frequently, the possibilities are narrowed down considerably due to knowledge of the compound's origin or synthesis. For our purposes, we will be concerned with identifying unknowns using three types of information: IR spectra, NMR spectra, and the molecular formula. In many of the problems you will be assigned, you will be given the molecular formula. The molecular formula in turn is determined from the elemental analysis data and molecular weight that is derived from mass spectroscopic data. IR, NMR, mass spectroscopy, and elemental analysis were covered in depth in previous chapters. The big question now is, how do you put all this information together to determine the molecular structure?

20.1 Degree of Unsaturation

The true molecular formula of a compound gives important structural information about the compound. Obviously, it gives the types of atoms present in a molecule. Also, from the number of atoms present, one can calculate the *degree of unsaturation* (often denoted as Ω). The degree of unsaturation presents useful information on how the atoms are put together in the molecule. It limits the structural units or functional groups consistent with a particular molecular formula.

The formula for a saturated hydrocarbon is C_nH_{2n+2}. A molecule with 10 carbon atoms will have 22 hydrogen atoms if it is fully saturated. Each pair of missing hydrogens is considered one degree of unsaturation. For instance, a molecule of formula $C_{10}H_{20}$ has one degree of unsaturation (in other words, $\Omega = 1$), a molecule of formula $C_{10}H_{16}$ has three degrees of unsaturation ($\Omega = 3$), and a molecule of formula $C_{10}H_{22}$ has zero degrees of unsaturation ($\Omega = 0$). The degrees of unsaturation in a hydrocarbon can be calculated in a single step by applying this formula, where C and H are the number of carbons and hydrogens in the molecule:

$$\Omega = \mathrm{C} - \frac{\mathrm{H}}{2} + 1$$

The degree of unsaturation is equal to the total number of rings and π bonds in a molecule. Some examples are shown in Figure 20-1. Once the degrees of unsaturation are known, the number of hydrogens can easily be determined without having to count all the hydrogen atoms individually. In the examples below, all of these molecules are hydrocarbons with ten carbons, so each degree of unsaturation will mean a pair of hydrogens missing from the formula $C_{10}H_{22}$. (In the last few examples, counting the number of rings may become a little complicated. It helps to visualize cutting the molecule apart – what is the maximum number of cuts you can make to the molecule and still have it stay in one piece? If the answer is two cuts, then there are two rings in the molecule.)

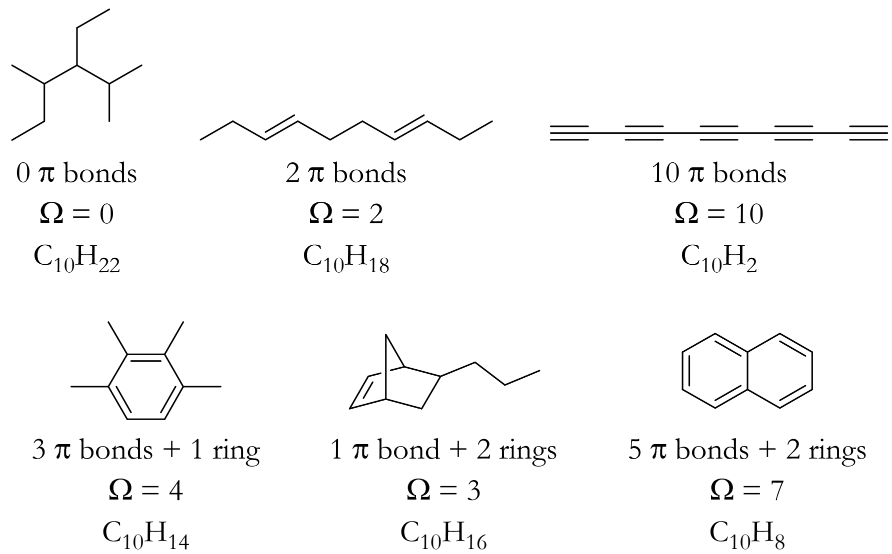


Figure 20-1: Some examples of how to find degreees of unsaturation from structure.

What if you are considering a molecule that is not a hydrocarbon (in other words, it has atoms other than carbon and hydrogen)? In this case, you will need to convert it into a "hydrocarbon equivalent formula", one with the same degree of unsaturation but with only carbon and hydrogen atoms. To do so, use the following rules:

1. Replace halogens with hydrogens.
2. Omit oxygens and sulfurs.
3. For each nitrogen, omit one nitrogen and one hydrogen.

Example Problem

Compound V has formula C_8H_8NOBr. What is its degree of unsaturation, and what are some possible structures that match its formula?

1. Replace halogens with hydrogens.

C_8H_8NOBr becomes C_8H_9NO.

2. Omit oxygens and sulfurs.

C_8H_9NO becomes C_8H_9N.

3. For each nitrogen, omit one nitrogen and one hydrogen.

C_8H_9N becomes C_8H_8.

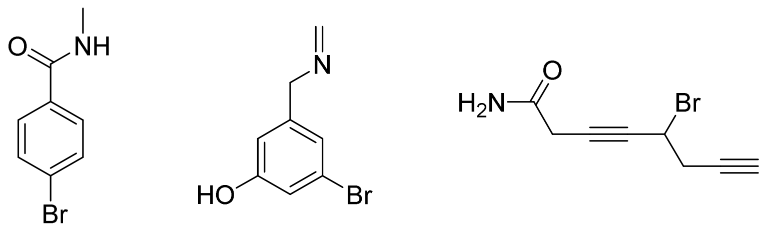
4. Calculate the degrees of unsaturation.

A compound with 8 carbons should have 18 hydrogens if it is fully saturated. This compound is missing 10 hydrogens, so it must have 5 degrees of unsaturation. Alternatively,

$$\Omega = 8 - \frac{8}{2} + 1 = 5$$

5. Draw some possible structures.

Anything with a total of 5 rings and/or π bonds will work. Some examples are shown below.



20.2 Structure Elucidation by Spectroscopic Methods

The previous chapters have explained how to look at an IR spectrum to determine the functional groups it contains, an NMR spectrum to determine the connectivity, and the mass spectral/elemental analysis data to determine the molecular formula. But, how does one actually put all this information together to determine the structure of a compound?

Given the IR, NMR, and molecular formula or mass spectral/elemental analysis data, follow steps 1–5 to determine the structure of the compound.

1. Find the molecular formula.

If you have already been given the molecular formula, proceed to step 2.

The problems assigned as homework and the problems on quizzes in the organic chemistry teaching labs at CU Boulder all provide the molecular formula, however, textbook problems and problem sets at other universities might give you the elemental analysis and mass spectral data instead. See Chapter 18 for how to use this information.

2. Find the degrees of unsaturation.

See section 20.1.

3. Study the IR spectrum and list possible functional groups.

Search the IR spectrum for functional groups (see Chapter 16). Be sure your findings are consistent with the degree of unsaturation. For instance, you cannot have a carbonyl in the molecule if there are zero degrees of unsaturation.

4. Study the NMR spectrum and determine the connectivity of the molecule.

Analyze the NMR spectrum to obtain evidence about the symmetry and connectivity of the carbon skeleton (Chapter 17), then determine a structure that fits the spectrum.

5. Check that your structure fits all the data.

Check your structure by assuring yourself it agrees with all of the above data. Label the protons on your structure with letters and then assign the peaks on the NMR spectrum using these letters.

Example Problem

Compound W has molecular formula C_2H_6O and the IR and NMR spectra in Figure 20-2 and Figure 20-3. Determine the structure of the compound.

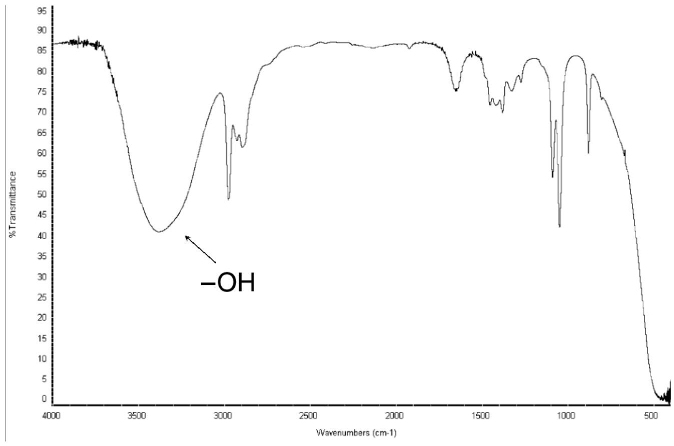


Figure 20-2: The IR spectrum of compound W.

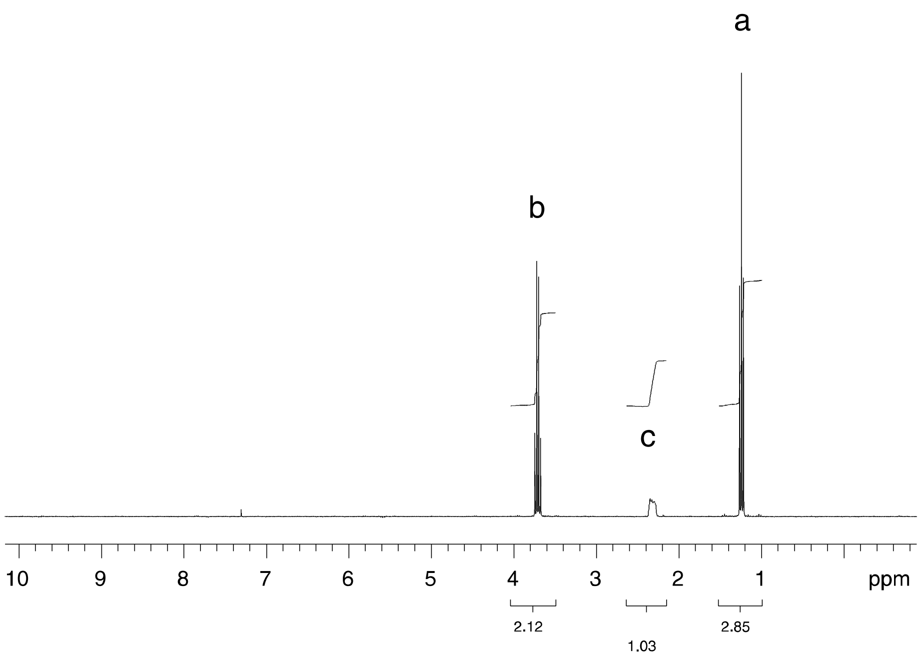


Figure 20-3: The NMR spectrum of compound W.

1. Find the molecular formula.

The molecular formula is already given as C_2H_6O.

2. Find the degrees of unsaturation.

Converting the formula to a hydrocarbon equivalent formula gives C_2H_6, which has $\Omega = 0$.

3. Study the IR spectrum and list possible functional groups.

There is a clear OH group in the IR spectrum with a peak at 3346 cm^{-1}.

4. Study the NMR spectrum and determine the connectivity of the molecule.

a: triplet at ~1.2 ppm, integral 3, this implies 3 protons split by 2 protons

b: quartet at ~3.7 ppm, integral 2, this implies 2 protons split by 3 protons

c: singlet at ~3.4 ppm, integral 1, this implies 1 proton split by 0 protons, possibly -OH

Groups **a** and **b** indicate an ethyl group, CH_3CH_2–, and taken together with the **c** probably representing –OH, the following structure is consistent with all data:

CH_3CH_2OH

5. Check that your structure fits all the data.

Look over the evidence supporting your structure assignment, label the important peaks on the IR spectrum, and label the protons (and the peaks on the spectrum) as follows: