

A more detailed discussion of hydrogen deficiency can be found in the May 1995 issue of the *Journal of Chemical Education*, pp. 245–248.

and one double bond and an index of hydrogen deficiency of 2. *Oxygen atoms have no effect on the index of hydrogen deficiency.*

A halogen substituent, like hydrogen, is monovalent and when present in a molecular formula is treated as if it were hydrogen for counting purposes.

How does one distinguish between rings and double bonds? This additional piece of information comes from catalytic hydrogenation experiments in which the amount of hydrogen consumed is measured exactly. Each of a molecule's double bonds consumes one molar equivalent of hydrogen, but rings are unaffected. For example, a substance with a hydrogen deficiency of 5 that takes up 3 mol of hydrogen must have two rings.

PROBLEM 13.27

How many rings are present in each of the following compounds? Each consumes 2 mol of hydrogen on catalytic hydrogenation.

- | | |
|--------------------|--------------------|
| (a) $C_{10}H_{18}$ | (d) C_8H_8O |
| (b) C_8H_8 | (e) $C_8H_{10}O_2$ |
| (c) $C_8H_8Cl_2$ | (f) C_8H_9ClO |

Sample Solution (a) The molecular formula $C_{10}H_{18}$ contains four fewer hydrogens than the alkane having the same number of carbon atoms ($C_{10}H_{22}$). Therefore, the index of hydrogen deficiency of this compound is 2. Because it consumes two molar equivalents of hydrogen on catalytic hydrogenation, it must have either a triple bond or two double bonds and no rings.

13.26 SUMMARY

Section 13.1 Structure determination in modern organic chemistry relies heavily on instrumental methods. Several of the most widely used ones depend on the absorption of electromagnetic radiation.

Section 13.2 Absorption of electromagnetic radiation causes a molecule to be excited from its most stable state (the *ground* state) to a higher energy state (an *excited* state).

Spectroscopic method

Nuclear magnetic resonance

Infrared

Ultraviolet-visible

Transitions between

Spin states of an atom's nucleus

Vibrational states

Electronic states

Mass spectrometry is not based on absorption of electromagnetic radiation, but monitors what happens when a substance is ionized by collision with a high-energy electron.

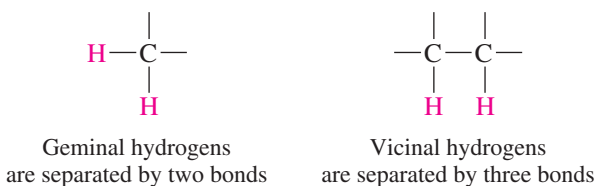
¹H Nuclear Magnetic Resonance Spectroscopy

Section 13.3 In the presence of an external magnetic field, the $+\frac{1}{2}$ and $-\frac{1}{2}$ nuclear spin states of a proton have slightly different energies.

Section 13.4 The energy required to “flip” the spin of a proton from the lower energy spin state to the higher state depends on the extent to which a nucleus is shielded from the external magnetic field by the molecule's electrons.

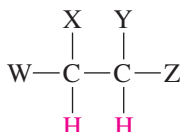
Section 13.5 Protons in different environments within a molecule have different **chemical shifts**; that is, they experience different degrees of shielding. Chemical shifts (δ) are reported in parts per million (ppm) from tetramethylsilane (TMS). Table 13.1 lists characteristic chemical shifts for various types of protons.

- Section 13.6 In addition to *chemical shift*, a ^1H NMR spectrum provides structural information based on:
- Number of signals*, which tells how many different kinds of protons there are
 - Integrated areas*, which tells the ratios of the various kinds of protons
 - Splitting pattern*, which gives information about the number of protons that are within two or three bonds of the one giving the signal
- Section 13.7 **Spin-spin splitting** of NMR signals results from coupling of the nuclear spins that are separated by two bonds (*geminal coupling*) or three bonds (*vicinal coupling*).



In the simplest cases, the number of peaks into which a signal is split is equal to $n + 1$, where n is the number of protons to which the proton in question is coupled. *Protons that have the same chemical shift do not split each other's signal.*

- Section 13.8 The methyl protons of an ethyl group appear as a *triplet* and the methylene protons as a *quartet* in compounds of the type $\text{CH}_3\text{CH}_2\text{X}$.
- Section 13.9 The methyl protons of an isopropyl group appear as a *doublet* and the methine proton as a *septet* in compounds of the type $(\text{CH}_3)_2\text{CHX}$.
- Section 13.10 A *doublet of doublets* characterizes the signals for the protons of the type shown (where W, X, Y, and Z are not H or atoms that split H themselves).

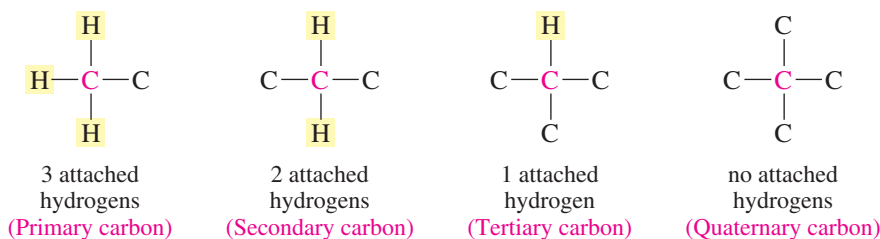


- Section 13.11 Complicated splitting patterns can result when a proton is unequally coupled to two or more protons that are different from one another.
- Section 13.12 Splitting resulting from coupling to the O—H proton of alcohols is not normally observed, because the hydroxyl proton undergoes rapid intermolecular exchange with other alcohol molecules, which “decouples” it from other protons in the molecule.
- Section 13.13 Many processes such as conformational changes take place faster than they can be detected by NMR. Consequently, NMR provides information about the *average* environment of a proton. For example, cyclohexane gives a single peak for its 12 protons even though, at any instant, 6 are axial and 6 are equatorial.

^{13}C Nuclear Magnetic Resonance Spectroscopy

- Section 13.14 ^{13}C has a nuclear spin of $\pm\frac{1}{2}$ but only about 1% of all the carbons in a sample are ^{13}C . Nevertheless, high-quality ^{13}C NMR spectra can be obtained by pulse FT techniques and are a useful complement to ^1H NMR spectra.
- Section 13.15 ^{13}C signals are more widely separated from one another than proton signals, and ^{13}C NMR spectra are relatively easy to interpret. Table 13.3 gives chemical shift values for carbon in various environments.
- Section 13.16 ^{13}C NMR spectra are rarely integrated because the pulse FT technique distorts the signal intensities.

Section 13.17 Carbon signals normally appear as singlets, but several techniques are available that allow one to distinguish among the various kinds of carbons shown.



Section 13.18 One of the special techniques for distinguishing carbons according to the number of their attached hydrogens is called **DEPT**. A series of NMR measurements using different pulse sequences gives normal, nulled, and inverted peaks that allow assignment of primary, secondary, tertiary, and quaternary carbons.

Section 13.19 2D NMR techniques are enhancements that are sometimes useful in gaining additional structural information. A ^1H - ^1H COSY spectrum reveals which protons are spin-coupled to other protons, which helps in determining connectivity. A HETCOR spectrum shows the C—H connections by correlating ^{13}C and ^1H chemical shifts.

Infrared Spectroscopy

Section 13.20 IR spectroscopy probes molecular structure by examining transitions between quantized vibrational energy levels using electromagnetic radiation in the $625\text{--}4000\text{-cm}^{-1}$ range, where cm^{-1} are units of **wavenumbers**, defined as λ^{-1} . Wavenumbers are proportional to frequency. The simplest vibration is the stretching of the bond between two atoms, but more complex vibrations can involve movement of many of a molecule's atoms.

Section 13.21 IR spectra are commonly regarded as consisting of a functional-group region ($1500\text{--}4000\text{ cm}^{-1}$) and a fingerprint region ($500\text{--}1500\text{ cm}^{-1}$). Included in the functional-group region are absorptions due to C—H stretching. In general, C—H stretching frequencies lie below 3000 cm^{-1} for sp^3 -hybridized carbon and above 3000 cm^{-1} for sp^2 . The fingerprint region is used less for determining structure than for verifying whether two compounds are identical or not.

Section 13.22 Functional-group identification is the main contribution of IR spectroscopy to organic chemistry. Various classes of compounds exhibit peaks at particular frequencies characteristic of the functional groups they contain. (Table 13.4).

Ultraviolet-Visible Spectroscopy

Section 13.23 Transitions between electronic energy levels involving electromagnetic radiation in the $200\text{--}800\text{-nm}$ range form the basis of UV-VIS spectroscopy. The absorption peaks tend to be broad but are often useful in indicating the presence of particular π electron systems within a molecule.

Mass Spectrometry

Section 13.24 Mass spectrometry exploits the information obtained when a molecule is ionized by electron impact and then dissociates to smaller fragments. Positive ions are separated and detected according to their mass-to-charge

(m/z) ratio. By examining the fragments and by knowing how classes of molecules dissociate on electron impact, one can deduce the structure of a compound. Mass spectrometry is quite sensitive; as little as 10^{-9} g of compound is sufficient for analysis.

Section 13.25 A compound's molecular formula gives information about the number of double bonds and rings it contains and is a useful complement to spectroscopic methods of structure determination.

PROBLEMS

13.28 Each of the following compounds is characterized by a ^1H NMR spectrum that consists of only a single peak having the chemical shift indicated. Identify each compound.

- | | |
|--|--|
| (a) C_8H_{18} ; δ 0.9 | (f) $\text{C}_2\text{H}_3\text{Cl}_3$; δ 2.7 |
| (b) C_5H_{10} ; δ 1.5 | (g) $\text{C}_5\text{H}_8\text{Cl}_4$; δ 3.7 |
| (c) C_8H_8 ; δ 5.8 | (h) $\text{C}_{12}\text{H}_{18}$; δ 2.2 |
| (d) $\text{C}_4\text{H}_9\text{Br}$; δ 1.8 | (i) $\text{C}_3\text{H}_6\text{Br}_2$; δ 2.6 |
| (e) $\text{C}_2\text{H}_4\text{Cl}_2$; δ 3.7 | |

13.29 Each of the following compounds is characterized by a ^1H NMR spectrum that consists of two peaks, both singlets, having the chemical shifts indicated. Identify each compound.

- (a) C_6H_8 ; δ 2.7 (4H) and 5.6 (4H)
 (b) $\text{C}_5\text{H}_{11}\text{Br}$; δ 1.1 (9H) and 3.3 (2H)
 (c) $\text{C}_6\text{H}_{12}\text{O}$; δ 1.1 (9H) and 2.1 (3H)
 (d) $\text{C}_6\text{H}_{10}\text{O}_2$; δ 2.2 (6H) and 2.7 (4H)

13.30 Deduce the structure of each of the following compounds on the basis of their ^1H NMR spectra and molecular formulas:

- | | | |
|---|--|--|
| (a) C_8H_{10} ; δ 1.2 (triplet, 3H)
δ 2.6 (quartet, 2H)
δ 7.1 (broad singlet, 5H) | (e) $\text{C}_4\text{H}_6\text{Cl}_4$; δ 3.9 (doublet, 4H)
δ 4.6 (triplet, 2H) | (f) $\text{C}_4\text{H}_6\text{Cl}_2$; δ 2.2 (singlet, 3H)
δ 4.1 (doublet, 2H)
δ 5.7 (triplet, 1H) |
| (b) $\text{C}_{10}\text{H}_{14}$; δ 1.3 (singlet, 9H)
δ 7.0 to 7.5 (multiplet, 5H) | (g) $\text{C}_3\text{H}_7\text{ClO}$; δ 2.0 (pentet, 2H)
δ 2.8 (singlet, 1H) | |
| (c) C_6H_{14} ; δ 0.8 (doublet, 12H)
δ 1.4 (septet, 2H) | (h) $\text{C}_{14}\text{H}_{14}$; δ 2.9 (singlet, 4H)
δ 7.1 (broad singlet, 10H) | |
| (d) C_6H_{12} ; δ 0.9 (triplet, 3H)
δ 1.6 (singlet, 3H)
δ 1.7 (singlet, 3H)
δ 2.0 (pentet, 2H)
δ 5.1 (triplet, 1H) | | |

13.31 From among the isomeric compounds of molecular formula $\text{C}_4\text{H}_9\text{Cl}$, choose the one having a ^1H NMR spectrum that

- (a) Contains only a single peak
 (b) Has several peaks including a doublet at δ 3.4
 (c) Has several peaks including a triplet at δ 3.5
 (d) Has several peaks including two distinct three-proton signals, one of them a triplet at δ 1.0 and the other a doublet at δ 1.5

13.32 Identify the $\text{C}_3\text{H}_5\text{Br}$ isomers on the basis of the following information:

- (a) Isomer A has the ^1H NMR spectrum shown in Figure 13.42.
 (b) Isomer B has three peaks in its ^{13}C NMR spectrum: δ 32.6 (CH_2); 118.8 (CH_2); and 134.2 (CH).
 (c) Isomer C has two peaks in its ^{13}C NMR spectrum: δ 12.0 (CH_2) and 16.8 (CH). The peak at lower field is only half as intense as the one at higher field.