



CHAPTER 19

SPECTROSCOPY

Until the second half of the twentieth century, the structure of a substance—a newly discovered natural product, for example—was determined using information obtained from chemical reactions. This information included the identification of functional groups by chemical tests, along with the results of experiments in which the substance was broken down into smaller, more readily identifiable fragments. After considering all the available chemical evidence, the chemist proposed a candidate structure (or structures) consistent with the observations. Proof of structure was provided either by converting the substance to some already known compound or by an independent synthesis.

Qualitative tests and chemical degradation have been supplemented and to a large degree replaced by instrumental methods of structure determination. The following are the most prominent methods and the structural clues they provide:

- **Nuclear magnetic resonance (NMR) spectroscopy** tells us about the carbon skeleton and the environments of the hydrogens attached to it.
- **Infrared (IR) spectroscopy** reveals the presence or absence of key functional groups.
- **Ultraviolet-visible (UV-Vis) spectroscopy** probes the electron distribution, especially in molecules that have conjugated π electron systems.
- **Mass spectrometry (MS)** gives the molecular weight and formula, both of the molecule itself and various structural units within it.

As diverse as these techniques are, all of them are based on the absorption of energy by a molecule, and all measure how a molecule responds to that absorption. In describing these techniques our emphasis will be on their application to structure determination.

CHAPTER OUTLINE

- 19.1 Principles of Molecular Spectroscopy
- 19.2 Nuclear Magnetic Resonance Spectroscopy
- 19.3 Nuclear Shielding and ^1H Chemical Shifts
- 19.4 Effects of Molecular Structure on ^1H Chemical Shifts
- 19.5 Interpreting Proton NMR Spectra
- 19.6 Spin-Spin Splitting in NMR Spectroscopy
- 19.7 Patterns of Spin-Spin Splitting
- 19.8 ^{13}C NMR Spectroscopy
- 19.9 ^{13}C Chemical Shifts
- 19.10 Infrared Spectroscopy
- Magnetic Resonance Imaging
- 19.11 Ultraviolet-Visible (UV-VIS) Spectroscopy
- 19.12 Connecting Spectroscopy and Structural Type
 - Alcohols
 - Aldehydes and Ketones
 - Carboxylic Acids
 - Carboxylic Acid Derivatives
 - Amines
- 19.13 Mass Spectrometry
 - Gas Chromatography, GC/MS, and MS/MS
- 19.14 Molecular Formula as a Clue to Structure
- Learning Objectives
- 19.15 Summary
- Additional Problems