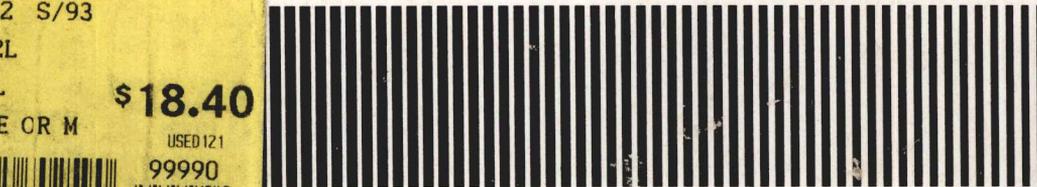
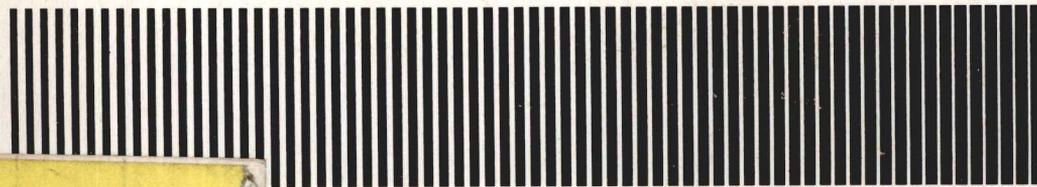
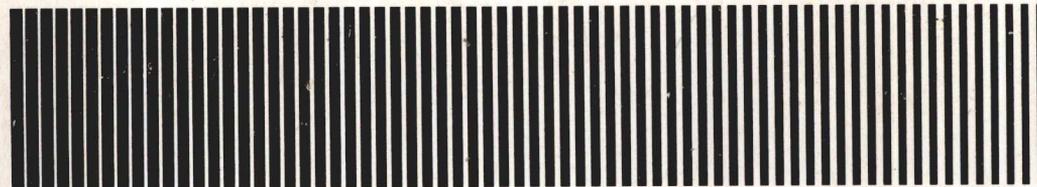
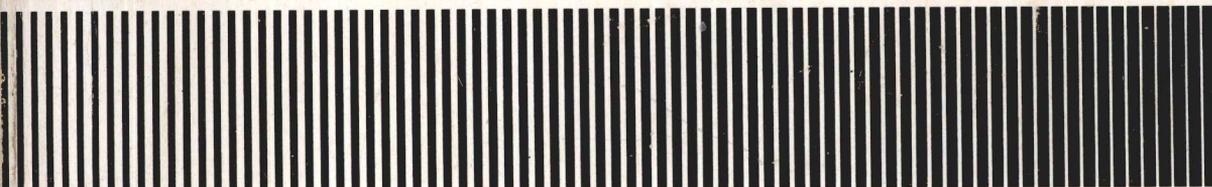
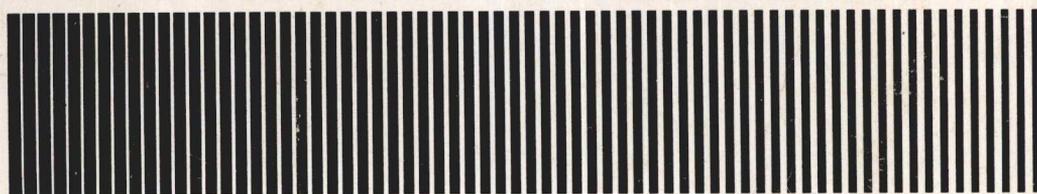


# Interpreting Spectra of Organic Molecules

THOMAS N. SORRELL



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# Interpreting Spectra of Organic Molecules

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**THOMAS N. SORRELL**

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## Preface

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Spectroscopy has become an integral part of organic chemistry, and most introductory organic chemistry textbooks present at least the fundamental aspects of this important subject. In addition, there are several texts on the market devoted specifically to correlating spectra and structure of organic molecules. In my own teaching, I have encountered two problems with the standard texts. First, they develop the subject of spectroscopy by introducing the data for each functional group separately. Anyone who has been involved with research knows that such an approach is limited, especially when working with unknown compounds. Second, many students taking chemistry have only a peripheral interest in the subject and do not want to be burdened with a lot of facts and information that will be of seemingly little use later in life.

At the University of North Carolina at Chapel Hill, we introduce students to the practice of interpreting IR, NMR,  $^{13}\text{C}$  NMR, and mass spectra in our second semester organic laboratory course in which they are working with unknown compounds (qualitative organic analysis). This is accomplished with interactive microcomputer software developed at UNC, with funding from the ACIS group at IBM. It was during the development of the software that I became aware of the need for an introductory-level text that emphasizes the strategies for interpreting spectra, and I began work on this book.

My aim has been to create a text to supplement either a lecture or laboratory course in organic chemistry. I have approached the subject by trying to outline general and useful approaches for interpreting spectra of simple compounds. The idea is to provide students who continue to study chemistry with a solid foundation for a more advanced course later. Therefore, I have touched only very lightly on some traditional topics like theory and instrumental design and operation. I have tried to keep the textual material to a minimum and have included as much data as possible in figures and tables so that they will be easily accessible for other courses or for research.

I have not included spectroscopy problems within the text since the aforementioned software is available. The software includes data (IR, NMR,  $^{13}\text{C}$  NMR, and mass spectra) for 20 compounds and questions (with answers) for 12 of those compounds. The questions focus the user's attention on the appropriate features of each spectrum that are necessary to deduce the structure for each unknown. Sufficient help screens in the form of tables and figures are included to assist learning the factual material that is included in this text.

Many people have contributed to help make this book a reality. I appreciate the many students at UNC who have given me useful comments about the software, many of which have helped me focus on what I needed to include in this text. I especially thank Martha Garrity for recording many of the spectra that appear in the book and for her valuable comments on the entire manuscript; and Professors Bob Bergman at UC Berkeley and Bob Hanson at St. Olaf's College, who offered many helpful suggestions and good critical reviews during the draft stages of the manuscript. Finally, I thank my wife Liz for her encouragement during the entire project.

*Thomas N. Sorrell*  
*Chapel Hill, 1988*

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Appendix A, page 153: Adapted from *Spectrometric Identification of Organic Compounds*, third edition, by R. N. Silverstein, G. C. Bassler, and T. C. Morrill; Appendix A of Chapter 2 ("Masses and Isotopic Abundance Ratios for Various Combinations of Carbon, Hydrogen, Nitrogen, and Oxygen"), pages 41–67. Copyright © 1974 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

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## Note to the Instructor

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*Interpreting Spectra of Organic Molecules* was written to be used in several different ways. For an introductory or short course on spectroscopic methods in organic chemistry, the text may be supplemented with problems from other sources, including spectra that students have recorded in a laboratory course. Second, this book may be used in conjunction with standard organic chemistry textbooks, most of which contain spectroscopy problems within each chapter. For both of these applications, this book provides the important concepts and strategies needed for a basic understanding of spectroscopic techniques in modern organic chemistry.

For a self-study module, this text is to be used in conjunction with the computer software *Spectroscopic Identification of Organic Compounds*. The software teaches students how to interpret spectra by presenting questions (and answers) that show what features of each type of spectrum are important and what information can be deduced. This book supplements the data presented in the software and also covers the underlying strategies that are necessary to interpret spectra. At the University of North Carolina, we use the book and software in conjunction with our second semester (sophomore) organic chemistry laboratory. At the beginning of the semester, teaching assistants cover the fundamentals of this text in two, one-hour lectures. The students then work with the software over the next several weeks (0 to 20 hours, depending on their interest) to reinforce their knowledge of the concepts and to learn how to interpret spectra. Toward the end of the course, each student identifies two unknown compounds based on their IR, NMR, and mass spectra.

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# Strategies for Interpreting Spectra of Organic Molecules

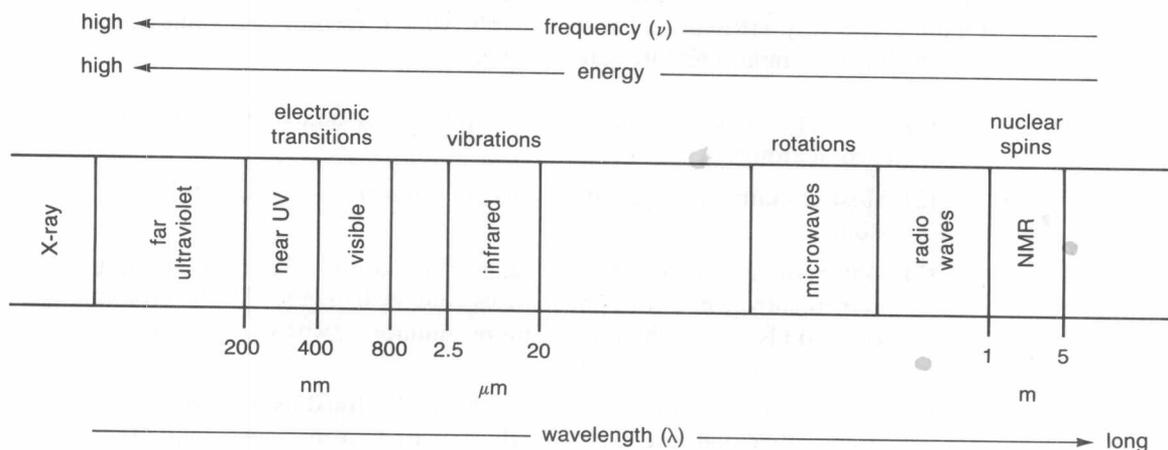
Radiation of different wavelengths can cause changes in the electronic or molecular structures of organic compounds. The study that deals with the theory and interpretation of such interactions between molecules and radiant energy is called *spectroscopy*.

Figure 1.1 shows some of the different characteristics of electromagnetic radiation. Equations 1.1 to 1.3 summarize the relationships between energy ( $E$ ), frequency ( $\nu$ ), and wavelength ( $\lambda$ ).

$$E = h\nu \quad (h = 6.63 \times 10^{-27} \text{ erg sec}) \quad (1.1)$$

$$\nu = c/\lambda \quad (c = 2.998 \times 10^{10} \text{ cm sec}^{-1}) \quad (1.2)$$

$$E = hc/\lambda \quad (1.3)$$



**Figure 1.1**

The electromagnetic spectrum. The three scales show the relative energies, frequencies, and wavelengths of radiation.

A spectroscopic analysis of a molecule requires at least one *spectrum*, which is a record of the changes that occur as you scan over the desired energy range. The most familiar type of spectrum results from plotting the change in the absorption of energy versus the wavelength of the energy being used. Other formats are sometimes more useful and will be described later. Rarely are you able to identify an organic compound from one spectrum. In practice, you will need several spectra, covering different energy ranges, to define a structure unambiguously.

A detailed presentation about each type of spectrum will be more informative if we first consider a general strategy for identifying organic molecules from spectroscopic data. Then each method can be viewed in relationship to the others, and you will be less tempted to overinterpret each spectrum. This chapter serves as the cornerstone for the book; please read it several times during the course of study to see how the overall strategy for spectral interpretation complements the information obtained from the individual spectra.

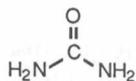
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## I. ORGANIC MOLECULES

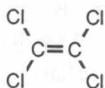
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Before we look at the different types of spectra to see what kind of information is available from each, we will consider briefly the substances that we wish to identify, namely, the organic compounds themselves. Although you are undoubtedly familiar with these from your study of organic chemistry, you may never have stopped to consider what individual structural features actually constitute an organic molecule. Figure 1.2 presents structures of several diverse yet representative organic compounds for which four common features are notable:

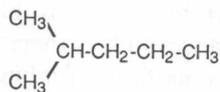
- (1) They all contain carbon, and there are usually bonds between two or more carbon atoms.
- (2) Most contain hydrogen atoms, usually, but not always, bonded to carbon atoms.
- (3) Many contain other elements, called heteroatoms, the most common being oxygen, nitrogen, sulfur, phosphorus, and the halogens. The heteroatoms can form bonds with each other or, more commonly, with carbon; and the bonds may be either single or multiple.
- (4) Most contain a functional group, which is defined as any group of bonded atoms other than the carbon-carbon or carbon-hydrogen single bond. The functional groups range in complexity from the carbon-carbon double bond to multiply bonded heteroatoms.



urea



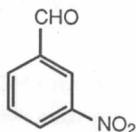
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2-methylpentane



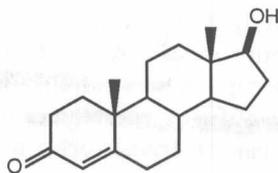
camphor



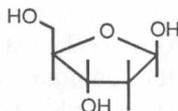
m-nitrobenzaldehyde



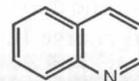
1,1,4-trichlorocyclohexane



testosterone



2-deoxyribose



quinoline

**Figure 1.2**

Representative structures of organic molecules.

## II. TYPES OF SPECTROSCOPY

Because organic compounds share the same few structural features, only a few spectroscopic techniques are needed to differentiate their structures. This book will be concerned with only the following four types of spectroscopy.

**a. Infrared (IR) spectra** result from absorption of energy that affects the vibrational modes of atoms that are bonded to one another. For a “typical” organic molecule, there should be many absorption bands, each produced by one of the many different groups of atoms. Since nearly all organic compounds contain C—C and

C—H bonds, many of the bands in an IR spectrum will be common to most substances and are therefore uninformative. As will be discussed later, IR spectroscopy is most useful for finding out what *functional groups* are present in a molecule.

**b. Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra** result from absorption of energy that affects the spins of the hydrogen nuclei. The near-ubiquity of hydrogen atoms in organic structures makes NMR spectroscopy especially useful. You can use the information about the local environment of each set of hydrogen atoms to find out which carbon atom each hydrogen atom is attached to, and what functional group or heteroatom is nearby.

**c. Carbon nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectra** are analogous to proton NMR spectra, except that you can observe the carbon atoms directly. Since every organic compound contains carbon, you can use the  $^{13}\text{C}$  NMR spectrum to study the backbone of a molecule.

**d. Mass spectra** result when a molecule is subjected to high-energy electron bombardment under vacuum and in a magnetic field. The molecule undergoes ionization, forming cation-radical species, followed by fragmentation of the molecular framework. The magnetic field is used to separate the different species based on their masses and charge (usually +1). As a result, mass spectroscopy is most useful for measuring the molecular weight of the compound and for identifying the presence of heteroatoms by their isotope patterns. In addition, certain carbon frameworks, for example, aromatic compounds, show characteristic fragmentation patterns.

In summary, these four kinds of spectroscopy give you the following information about a compound:

- (1) the number and types of atoms present;
- (2) the environments of the carbon and hydrogen atoms;
- (3) the functional groups present.

This information parallels the essential structural features for organic molecules outlined in Section I.

In learning more about each type of spectroscopy, try to develop a clear understanding of the advantages, disadvantages, and limitations of each method. Recognize, too, that you need not always use all four spectra to identify the structure of a molecule. In fact, you can often use either the IR and NMR or the NMR and  $^{13}\text{C}$  NMR spectra to deduce a compound's identity.

---

### III. GENERAL STRATEGIES FOR INTERPRETATION OF SPECTRA

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The following chapters will cover the strategies for interpreting each type of spectrum in detail. The purpose of this section is to outline ways to use the kinds of spectroscopy listed in the preceding section to arrive at the structure of the molecule under study.

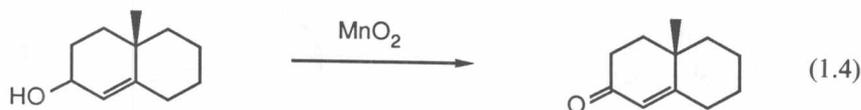
The first step in deducing the structure of an organic molecule is to consider the origin of the compound in question. Three typical situations are commonly encountered, and the strategy for applying the different spectroscopic methods to each one is presented in the following descriptions.

#### A. Identification of a Predicted Reaction Product

The simplest situation in which spectroscopic identification of an organic compound is necessary is when the chemist makes a predictable change to a well-characterized compound. In this situation, you will not necessarily record all four types of spectra, because you can *predict* the changes that you should observe.

Since in all but the rarest cases, chemical transformations will change at least one functional group, you might expect to use IR spectroscopy most often for making sure that a desired reaction has occurred. However, although IR spectroscopy, or any other spectroscopic method, might be useful to indicate the progress of a reaction, you must still record other spectra to confirm that no other changes have taken place. Thus, you will almost always have to record the NMR spectrum to confirm that the carbon-hydrogen framework has remained intact or has undergone the appropriate changes, something for which IR spectroscopy is less well-suited. Because changes in functional groups will often affect the hydrogen-atom environments in predictable ways, NMR spectroscopy has actually become the technique used most often to monitor organic reactions.

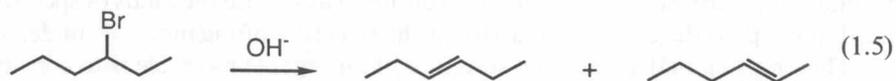
Consider, for example, the reaction shown in Equation 1.4, in which a secondary alcohol is oxidized to a ketone.



You could use *any* of the four types of spectra to confirm that the desired reaction occurred: the molecular weight has decreased; the functional group has been altered substantially; and the number and environments of the protons are different. But which method will give the answer with the least work and ambiguity? Since the functional group has been altered, the IR and  $^{13}\text{C}$  NMR spectra should show the most

easily recognized changes (the changes that are actually observed will be discussed later).  $^{13}\text{C}$  NMR spectroscopy would also allow you to be sure that the other carbon atoms within the molecule have *not* undergone a reaction.

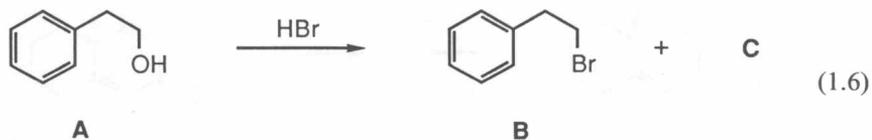
A second example illustrates what happens when a predictable reaction gives a product *mixture* as shown in Equation 1.5.



The first step in identifying the products here would be to isolate and purify the components. However, even when the two compounds have been isolated, spectroscopic identification is still necessary, not only to show that the desired reaction (i.e., functional-group change) has occurred, but also to distinguish between the two isomers. Again, as in the first example, any of the four spectroscopic methods will show that the reaction has occurred. The functional group has been changed from that of an alkyl bromide to that of an alkene (IR or  $^{13}\text{C}$  NMR spectra), the molecular weight has decreased by 80 mass units (mass spectra), and the number and type of protons have changed (NMR spectra). However, to distinguish between the two products, NMR spectroscopy would be the most useful, because the environments of the hydrogen atoms are quite different. For one isomer, the alkene carbon atoms are bonded to a methyl and a propyl group; in the other, the alkene carbon atoms are each bonded to an ethyl group. In contrast, the functional groups (*trans*-disubstituted double bond) and the molecular weights for the two isomers are the same; so the IR and mass spectra should be very similar.

## B. Identification of Reaction By-products

The second situation in which spectroscopic methods play an important role in organic chemistry involves the identification of an unexpected reaction product. Consider the reaction shown in Equation 1.6:

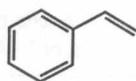


Here, you hope to carry out the substitution of the OH group in alcohol A to give bromide B, but find the additional product C. There are two options. The first is to treat product C as a complete unknown, and to follow the strategy outlined in the next

section. The second option, which is often more desirable, is to use other information to narrow the possibilities. This other information would include:

- (1) knowledge about the structure and reactivity of the starting material;
- (2) the reaction conditions;
- (3) the physical properties of the product.

For example, suppose you find that compound C is very nonpolar, and subsequently, from combustion analysis, that C contains only carbon and hydrogen. Since you know that alcohols tend to undergo an elimination reaction under acidic conditions, you might propose the following structure for C:



(1.7)

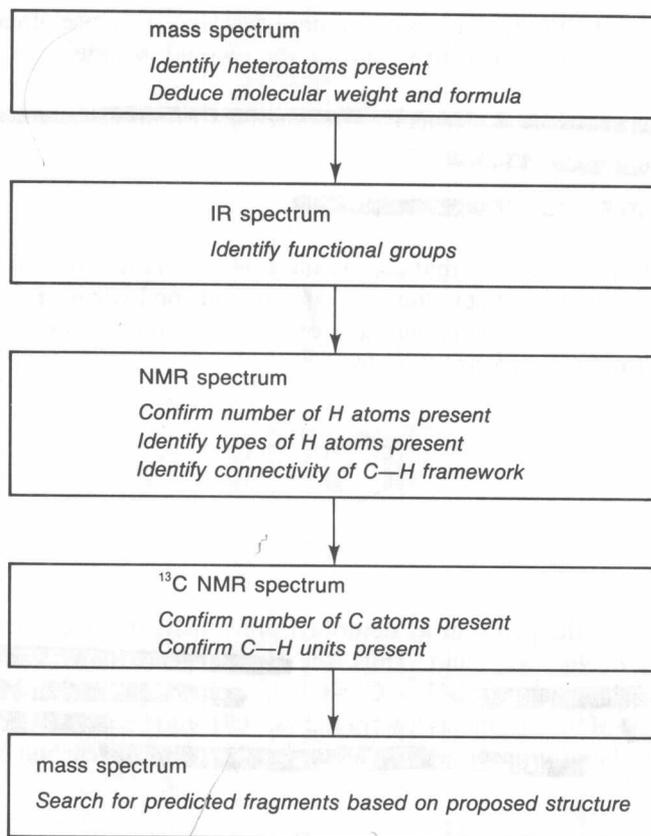
C

Now you can treat the problem as described previously, in which you confirm the structure of a known compound. Thus, the IR spectrum should indicate that the functional group has changed (OH vs. C=C); the mass spectrum should show that the molecular weight of the product is lower (122 vs. 104); and the NMR spectrum should show that all of the protons are bonded to  $sp^2$  rather than  $sp^3$  carbon atoms.

### C. Identification of an Unknown Compound

As shown by the last example, you can often use data on the physical properties and elemental composition of a compound to help identify its structure; but such information is not always available. For example, elemental analysis, which can confirm the presence of certain heteroatoms as well as the molecular formula, often requires large amounts of material in order to produce accurate results. If only a small amount of compound is available for identification, elemental analysis or wet chemical tests may waste valuable product. Using some combination of the four types of spectroscopy mentioned earlier will usually allow you to deduce the structure of an unknown compound without any additional information.

A strategy for identifying an organic molecule from its spectral data is outlined in Figure 1.3 (on page 8). The strategy is based on the premise that, at least for simple compounds, you can use proton NMR spectroscopy to establish the framework of a molecule, since most atoms in organic structures are either carbon or hydrogen. However, you need to know what heteroatoms and functional groups are present to make best use of the NMR spectrum.

**Figure 1.3**

A flow chart summarizing the strategy for interpreting spectra of organic compounds.

You can begin by consulting the mass spectrum in order to find the molecular weight and the molecular formula. Since mass spectrometers are not always routinely available, the first step may be by-passed, or other methods may be used to find the molecular weight. Nevertheless, if you know the molecular formula, you can calculate the number of sites of unsaturation (pi-bonds or rings) using the formula:

$$\text{sites of unsaturation} = \frac{(2n + 2) - m}{2}, \quad (1.8)$$

where  $n$  = number of carbon atoms in the molecule, and  $m$  = number of hydrogen atoms in the molecule (add 1 to  $m$  for each halogen atom; subtract 1 from  $m$  for each nitrogen or phosphorous atom).