C H A P T E R   7

ULTRAVIOLET SPECTROSCOPY

Most organic molecules and functional groups are transparent in the portions of the electromagnetic spectrum that we call the **ultraviolet** (**UV**) and **visible** (**VIS**) regions—that is, the regions where wavelengths range from 190 nm to 800 nm. Consequently, absorption spectroscopy is of limited utility in this range of wavelengths. However, in some cases we can derive useful information from these regions of the spectrum. That information, when combined with the detail provided by infrared and nuclear magnetic resonance (NMR) spectra, can lead to valuable structural proposals.

7.1 THE NATURE OF ELECTRONIC EXCITATIONS

When continuous radiation passes through a transparent material, a portion of the radiation may be absorbed. If that occurs, the residual radiation, when it is passed through a prism, yields a spectrum with gaps in it, called an **absorption spectrum.** As a result of energy absorption, atoms or molecules pass from a state of low energy (the initial, or **ground state**) to a state of higher energy (the **excited state**). Figure 7.1 depicts this excitation process, which is quantized. The electromagnetic radiation that is absorbed has energy exactly equal to the energy *difference* between the excited and ground states.

In the case of ultraviolet and visible spectroscopy, the transitions that result in the absorption of electromagnetic radiation in this region of the spectrum are transitions between **electronic** energy levels. As a molecule absorbs energy, an electron is promoted from an occupied orbital to an unoccupied orbital of greater potential energy. Generally, the most probable transition is from the **highest occupied molecular orbital** (**HOMO**) to the **lowest unoccupied molecular orbital** (**LUMO**). The energy differences between electronic levels in most molecules vary from 125 to 650 kJ/mole (kilojoules per mole).

For most molecules, the lowest-energy occupied molecular orbitals are the σ orbitals, which correspond to σ bonds. The π orbitals lie at somewhat higher energy levels, and orbitals that hold unshared pairs, the **nonbonding** (**n**) **orbitals**, lie at even higher energies. The unoccupied, or **antibonding orbitals** (π^* and σ^*), are the orbitals of highest energy. Figure 7.2a shows a typical progression of electronic energy levels.
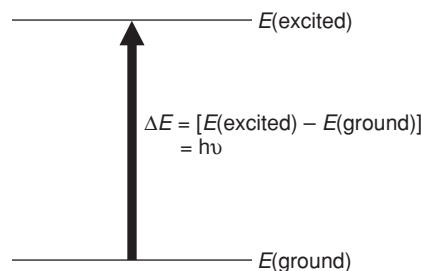
$$E(\text{excited})$$

$$\Delta E = [E(\text{excited}) - E(\text{ground})]$$
$$= h\upsilon$$

F I G U R E   7 . 1   The excitation process.
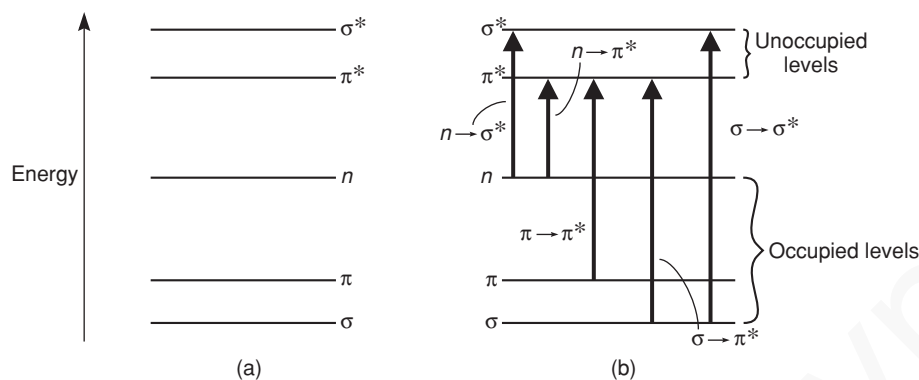
$$E(\text{ground})$$

381

F I G U R E   7 . 2   Electronic energy levels and transitions.

In all compounds other than alkanes, the electrons may undergo several possible transitions of different energies. Some of the most important transitions are

$\sigma \longrightarrow \sigma^*$	In alkanes	
$\sigma \longrightarrow \pi^*$	In carbonyl compounds	
$\pi \longrightarrow \pi^*$	In alkenes, carbonyl compounds, alkynes, azo compounds, and so on	
$n \longrightarrow \sigma^*$	In oxygen, nitrogen, sulfur, and halogen compounds	
$n \longrightarrow \pi^*$	In carbonyl compounds	

Increasing energy ↑

Figure 7.2b illustrates these transitions. Electronic energy levels in aromatic molecules are more complicated than the ones depicted here. Section 7.14 will describe the electronic transitions of aromatic compounds.

Clearly, the energy required to bring about transitions from the highest occupied energy level (HOMO) in the ground state to the lowest unoccupied energy level (LUMO) is less than the energy required to bring about a transition from a lower occupied energy level. Thus, in Figure 7.2b an $n \rightarrow \pi^*$ transition would have a lower energy than a $\pi \rightarrow \pi^*$ transition. For many purposes, the transition of lowest energy is the most important.

Not all of the transitions that at first sight appear possible are observed. Certain restrictions, called **selection rules,** must be considered. One important selection rule states that transitions that involve a change in the spin quantum number of an electron during the transition are not allowed to take place; they are called **"forbidden" transitions.** Other selection rules deal with the numbers of electrons that may be excited at one time, with symmetry properties of the molecule and of the electronic states, and with other factors that need not be discussed here. Transitions that are formally forbidden by the selection rules are often not observed. However, theoretical treatments are rather approximate, and in certain cases forbidden transitions *are* observed, although the intensity of the absorption tends to be much lower than for transitions that are **allowed** by the selection rules. The $n \rightarrow \pi^*$ transition is the most common type of forbidden transition.

7.2 THE ORIGIN OF UV BAND STRUCTURE

For an atom that absorbs in the ultraviolet, the absorption spectrum sometimes consists of very sharp lines, as would be expected for a quantized process occurring between two discrete energy levels. For molecules, however, the UV absorption usually occurs over a wide range of wavelengths because molecules (as opposed to atoms) normally have many excited modes of vibration and rotation at room temperature. In fact, the vibration of molecules cannot be completely "frozen out" even at absolute zero. Consequently, a collection of molecules generally has its members in many states of vibrational and rotational excitation. The energy levels for these states are quite closely spaced, corresponding to energy differences considerably smaller than those of electronic levels. The rotational and vibrational levels are thus "superimposed" on the electronic levels. A molecule may therefore undergo electronic and vibrational–rotational excitation simultaneously, as shown in Figure 7.3.

Because there are so many possible transitions, each differing from the others by only a slight amount, each electronic transition consists of a vast number of lines spaced so closely that the spectrophotometer cannot resolve them. Rather, the instrument traces an "envelope" over the entire pattern. What is observed from these types of combined transitions is that the UV spectrum of a molecule usually consists of a broad **band** of absorption centered near the wavelength of the major transition.

7.3 PRINCIPLES OF ABSORPTION SPECTROSCOPY

The greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption. Furthermore, the more effectively a molecule absorbs light of a given wavelength, the greater the extent of light absorption. From these guiding ideas, the following empirical expression, known as the **Beer–Lambert Law,** may be formulated.
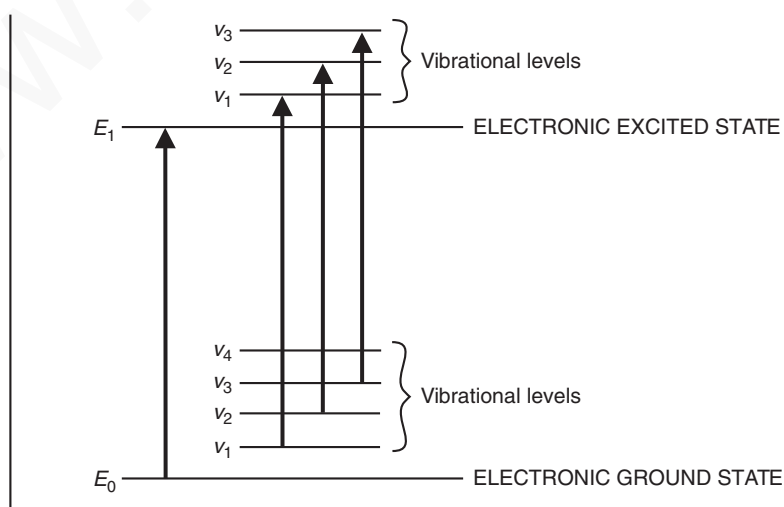

FIGURE 7.3 Electronic transitions with vibrational transitions superimposed. (Rotational levels, which are very closely spaced within the vibrational levels, are omitted for clarity.)

$$A = \log(I_0/I) = \varepsilon c l \text{ for a given wavelength} \qquad \textbf{Equation 7.1}$$

A = absorbance

I_0 = intensity of light incident upon sample cell

I = intensity of light leaving sample cell

c = molar concentration of solute

l = length of sample cell (cm)

ε = molar absorptivity

The term log (I_0/I) is also known as the **absorbance** (or the **optical density** in older literature) and may be represented by A. The **molar absorptivity** (formerly known as the **molar extinction coefficient**) is a property of the molecule undergoing an electronic transition and is not a function of the variable parameters involved in preparing a solution. The size of the absorbing system and the probability that the electronic transition will take place control the absorptivity, which ranges from 0 to 10^6. Values above 10^4 are termed **high-intensity absorptions,** while values below 10^3 are **low-intensity absorptions.** Forbidden transitions (see Section 7.1) have absorptivities in the range from 0 to 1000.

The Beer–Lambert Law is rigorously obeyed when a *single species* gives rise to the observed absorption. The law may not be obeyed, however, when different forms of the absorbing molecule are in equilibrium, when solute and solvent form complexes through some sort of association, when *thermal* equilibrium exists between the ground electronic state and a low-lying excited state, or when fluorescent compounds or compounds changed by irradiation are present.

7.4 INSTRUMENTATION

The typical ultraviolet–visible spectrophotometer consists of a **light source,** a **monochromator,** and a **detector.** The light source is usually a deuterium lamp, which emits electromagnetic radiation in the ultraviolet region of the spectrum. A second light source, a tungsten lamp, is used for wavelengths in the visible region of the spectrum. The monochromator is a diffraction grating; its role is to spread the beam of light into its component wavelengths. A system of slits focuses the desired wavelength on the sample cell. The light that passes through the sample cell reaches the detector, which records the intensity of the transmitted light I. The detector is generally a photomultiplier tube, although in modern instruments photodiodes are also used. In a typical double-beam instrument, the light emanating from the light source is split into two beams, the **sample beam** and the **reference beam.** When there is no sample cell in the reference beam, the detected light is taken to be equal to the intensity of light entering the sample I_0.

The sample cell must be constructed of a material that is transparent to the electromagnetic radiation being used in the experiment. For spectra in the visible range of the spectrum, cells composed of glass or plastic are generally suitable. For measurements in the ultraviolet region of the spectrum, however, glass and plastic cannot be used because they absorb ultraviolet radiation. Instead, cells made of quartz must be used since quartz does not absorb radiation in this region.

The instrument design just described is quite suitable for measurement at only one wavelength. If a complete spectrum is desired, this type of instrument has some deficiencies. A mechanical system is required to rotate the monochromator and provide a scan of all desired wavelengths. This type of system operates slowly, and therefore considerable time is required to record a spectrum.

A modern improvement on the traditional spectrophotometer is the **diode-array spectrophotometer.** A diode array consists of a series of photodiode detectors positioned side by side on a silicon crystal. Each diode is designed to record a narrow band of the spectrum. The diodes are connected so that the entire spectrum is recorded at once. This type of detector has no moving parts and

can record spectra very quickly. Furthermore, its output can be passed to a computer, which can process the information and provide a variety of useful output formats. Since the number of photodiodes is limited, the speed and convenience described here are obtained at some small cost in resolution. For many applications, however, the advantages of this type of instrument outweigh the loss of resolution.

7.5 PRESENTATION OF SPECTRA

The ultraviolet–visible spectrum is generally recorded as a plot of absorbance versus wavelength. It is customary to then replot the data with either ε or log ε plotted on the ordinate and wavelength plotted on the abscissa. Figure 7.4, the spectrum of benzoic acid, is typical of the manner in which spectra are displayed. However, very few electronic spectra are reproduced in the scientific literature; most are described by indications of the wavelength maxima and absorptivities of the principal absorption peaks. For benzoic acid, a typical description might be

$$\lambda_{max} = 230 \text{ nm} \qquad \log \varepsilon = 4.2$$
$$272 \qquad\qquad 3.1$$
$$282 \qquad\qquad 2.9$$

Figure 7.4 is the actual spectrum that corresponds to these data.
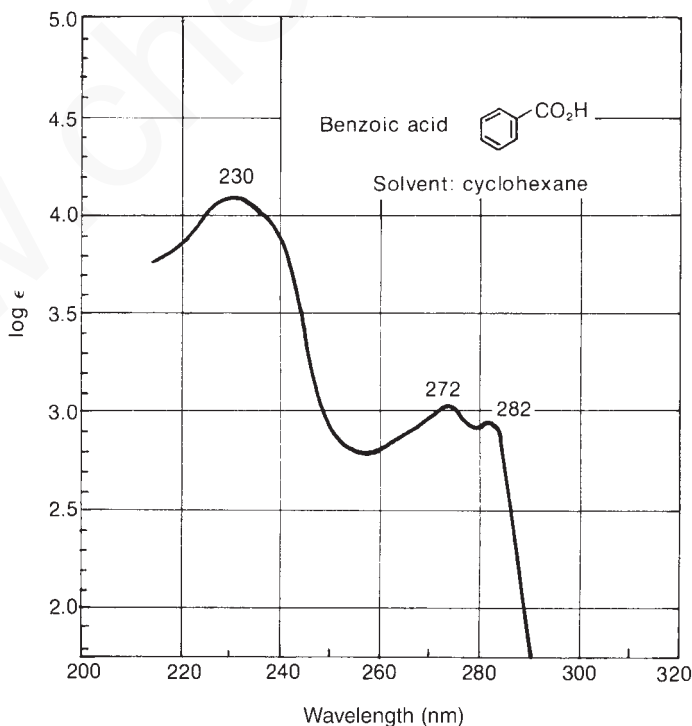
FIGURE 7.4 Ultraviolet spectrum of benzoic acid in cyclohexane. (From Friedel, R. A., and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, New York, 1951. Reprinted by permission.)

7.6 SOLVENTS

The choice of the solvent to be used in ultraviolet spectroscopy is quite important. The first criterion for a good solvent is that it should not absorb ultraviolet radiation in the same region as the substance whose spectrum is being determined. Usually solvents that do not contain conjugated systems are most suitable for this purpose, although they vary regarding the shortest wavelength at which they remain transparent to ultraviolet radiation. Table 7.1 lists some common ultraviolet spectroscopy solvents and their cutoff points or minimum regions of transparency.

Of the solvents listed in Table 7.1, water, 95% ethanol, and hexane are most commonly used. Each is transparent in the regions of the ultraviolet spectrum in which interesting absorption peaks from sample molecules are likely to occur.

A second criterion for a good solvent is its effect on the fine structure of an absorption band. Figure 7.5 illustrates the effects of polar and nonpolar solvents on an absorption band. A nonpolar solvent does not hydrogen bond with the solute, and the spectrum of the solute closely approximates the spectrum that would be produced in the gaseous state, in which fine structure is often observed. In a polar solvent, the hydrogen bonding forms a solute–solvent complex, and the fine structure may disappear.

TABLE 7.1
SOLVENT CUTOFFS

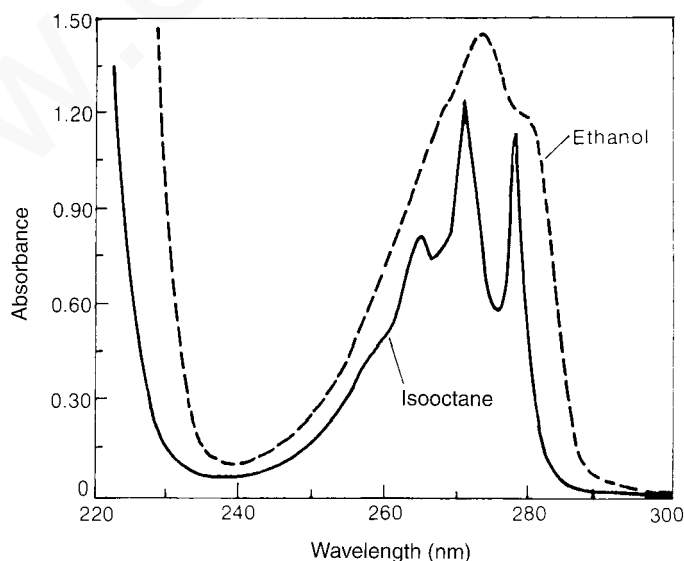| Acetonitrile	190 nm	n-Hexane	201 nm
Chloroform	240	Methanol	205
Cyclohexane	195	Isooctane	195
1,4-Dioxane	215	Water	190
95% Ethanol	205	Trimethyl phosphate	210

FIGURE 7.5 Ultraviolet spectra of phenol in ethanol and in isooctane. (From Coggeshall, N. D., and E. M. Lang, *Journal of the American Chemical Society, 70* (1948): 3288. Reprinted by permission.)

TABLE 7.2
SOLVENT SHIFTS ON THE $n \rightarrow \pi^*$ TRANSITION OF ACETONE

Solvent	H_2O	CH_3OH	C_2H_5OH	$CHCl_3$	C_6H_{14}
λ_{max} (nm)	264.5	270	272	277	279

A third criterion for a good solvent is its ability to influence the wavelength of ultraviolet light that will be absorbed via stabilization of either the ground or the excited state. Polar solvents do not form hydrogen bonds as readily with the excited states of polar molecules as with their ground states, and these polar solvents increase the energies of electronic transitions in the molecules. Polar solvents shift transitions of the $n \rightarrow \pi^*$ type to shorter wavelengths. On the other hand, in some cases the excited states may form stronger hydrogen bonds than the corresponding ground states. In such a case, a polar solvent shifts an absorption to longer wavelength since the energy of the electronic transition is decreased. Polar solvents shift transitions of the $\pi \rightarrow \pi^*$ type to longer wavelengths. Table 7.2 illustrates typical effects of a series of solvents on an electronic transition.

7.7 WHAT IS A CHROMOPHORE?

Although the absorption of ultraviolet radiation results from the excitation of electrons from ground to excited states, the nuclei that the electrons hold together in bonds play an important role in determining which wavelengths of radiation are absorbed. The nuclei determine the strength with which the electrons are bound and thus influence the energy spacing between ground and excited states. Hence, the characteristic energy of a transition and the wavelength of radiation absorbed are properties of a group of atoms rather than of electrons themselves. The group of atoms producing such an absorption is called a **chromophore.** As structural changes occur in a chromophore, the exact energy and intensity of the absorption are expected to change accordingly. Very often, it is extremely difficult to predict from theory how the absorption will change as the structure of the chromophore is modified, and it is necessary to apply empirical working guides to predict such relationships.

Alkanes. For molecules, such as alkanes, that contain nothing but single bonds and lack atoms with unshared electron pairs, the only electronic transitions possible are of the $\sigma \rightarrow \sigma^*$ type. These transitions are of such a high energy that they absorb ultraviolet energy at very short wavelengths—shorter than the wavelengths that are experimentally accessible using typical spectrophotometers. Figure 7.6 illustrates this type of transition. The excitation of the σ-bonding electron to the σ^*-antibonding orbital is depicted at the right.

Alcohols, Ethers, Amines, and Sulfur Compounds. In saturated molecules that contain atoms bearing nonbonding pairs of electrons, transitions of the $n \rightarrow \sigma^*$ type become important. They are also
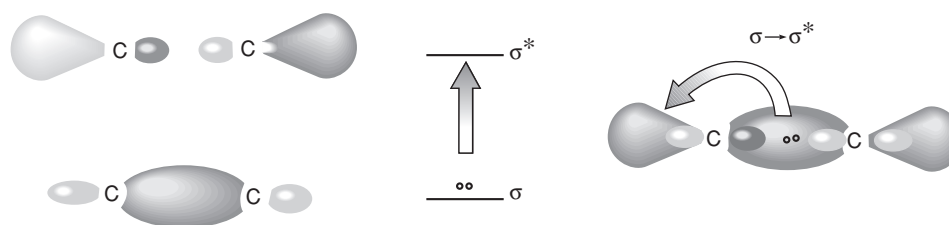

FIGURE 7.6 $\sigma \rightarrow \sigma^*$ transition.

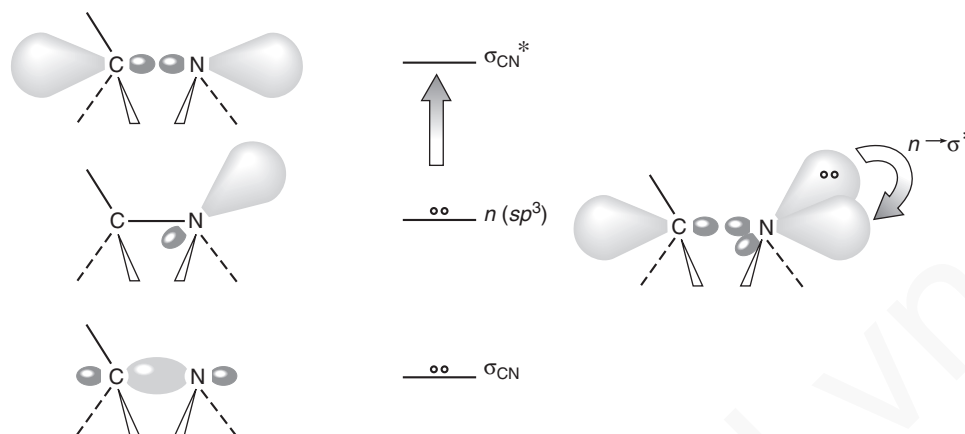**F I G U R E   7 . 7** $n \rightarrow \sigma^*$ transition.

rather high-energy transitions, but they do absorb radiation that lies within an experimentally accessible range. Alcohols and amines absorb in the range from 175 to 200 nm, while organic thiols and sulfides absorb between 200 and 220 nm. Most of the absorptions are below the cutoff points for the common solvents, so they are not observed in solution spectra. Figure 7.7 illustrates an $n \rightarrow \sigma^*$ transition for an amine. The excitation of the nonbonding electron to the antibonding orbital is shown at the right.

Alkenes and Alkynes. With unsaturated molecules, $\pi \rightarrow \pi^*$ transitions become possible. These transitions are of rather high energy as well, but their positions are sensitive to the presence of substitution, as will be clear later. Alkenes absorb around 175 nm, and alkynes absorb around 170 nm. Figure 7.8 shows this type of transition.

Carbonyl Compounds. Unsaturated molecules that contain atoms such as oxygen or nitrogen may also undergo $n \rightarrow \pi^*$ transitions. These are perhaps the most interesting and most studied transitions, particularly among carbonyl compounds. These transitions are also rather sensitive to substitution on the chromophoric structure. The typical carbonyl compound undergoes an $n \rightarrow \pi^*$ transition around 280 to 290 nm ($\varepsilon = 15$). Most $n \rightarrow \pi^*$ transitions are forbidden and hence are of low intensity. Carbonyl compounds also have a $\pi \rightarrow \pi^*$ transition at about 188 nm ($\varepsilon = 900$). Figure 7.9 shows the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the carbonyl group.[1]
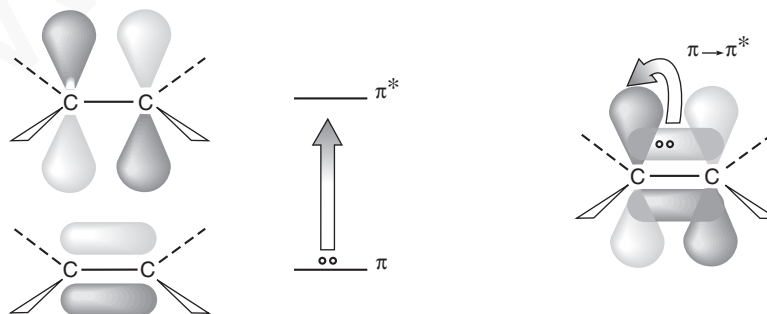
F I G U R E   7 . 8 $\pi \rightarrow \pi^*$ transition.

---

[1] Contrary to what you might expect from simple theory, the oxygen atom of the carbonyl group is *not* sp^2 hybridized. Spectroscopists have shown that although the carbon atom is sp^2 hybridized, the hybridization of the oxygen atom more closely approximates *sp*.
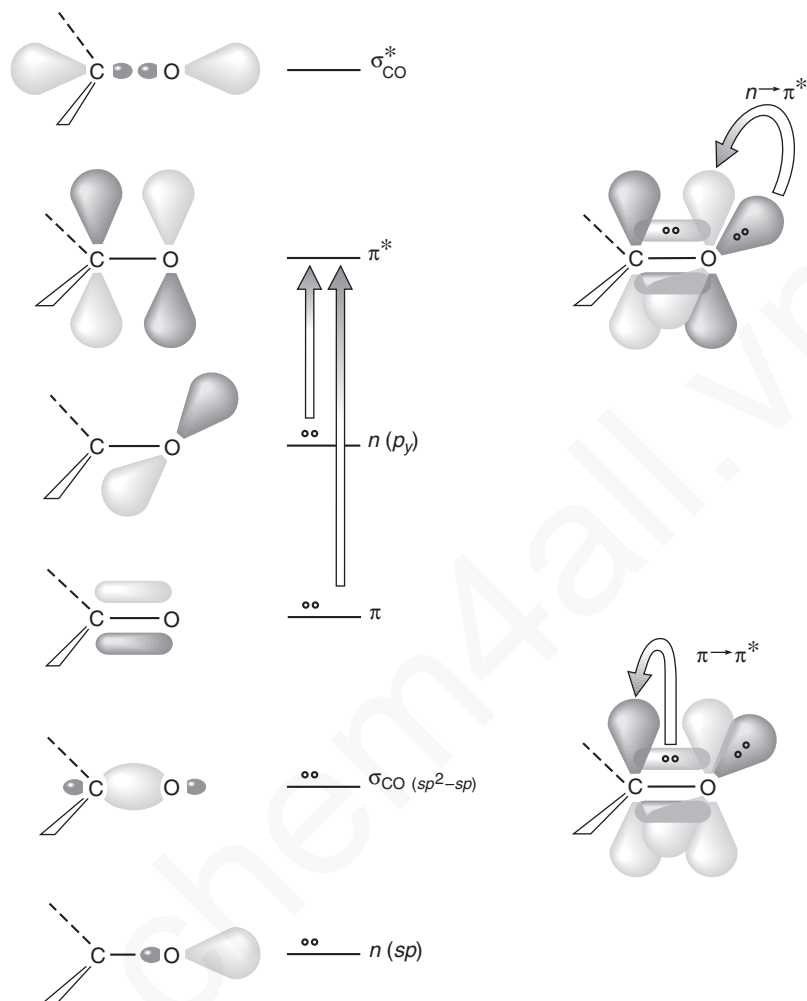
F I G U R E   7 . 9   Electronic transitions of the carbonyl group.

Table 7.3 lists typical absorptions of simple isolated chromophores. You may notice that these *simple* chromophores nearly all absorb at approximately the same wavelength (160 to 210 nm).

The attachment of substituent groups in place of hydrogen on a basic chromophore structure changes the position and intensity of an absorption band of the chromophore. The substituent groups may not give rise to the absorption of the ultraviolet radiation themselves, but their presence modifies the absorption of the principal chromophore. Substituents that increase the intensity of the absorption, and possibly the wavelength, are called **auxochromes.** Typical auxochromes include methyl, hydroxyl, alkoxy, halogen, and amino groups.

Other substituents may have any of four kinds of effects on the absorption:

1. **Bathochromic shift** (red shift)—a shift to lower energy or longer wavelength.

2. **Hypsochromic shift** (blue shift)—a shift to higher energy or shorter wavelength.

3. **Hyperchromic effect**—an increase in intensity.

4. **Hypochromic effect**—a decrease in intensity.

TABLE 7.3
TYPICAL ABSORPTIONS OF SIMPLE ISOLATED CHROMOPHORES

Class	Transition	λ_{max} (nm)	log ε	Class	Transition	λ_{max} (nm)	log ε
R—OH	$n \rightarrow \sigma^*$	180	2.5	R—NO$_2$	$n \rightarrow \pi^*$	271	<1.0
R—O—R	$n \rightarrow \sigma^*$	180	3.5	R—CHO	$\pi \rightarrow \pi^*$	190	2.0
R—NH$_2$	$n \rightarrow \sigma^*$	190	3.5		$n \rightarrow \pi^*$	290	1.0
R—SH	$n \rightarrow \sigma^*$	210	3.0	R$_2$CO	$\pi \rightarrow \pi^*$	180	3.0
R$_2$C=CR$_2$	$\pi \rightarrow \pi^*$	175	3.0		$n \rightarrow \pi^*$	280	1.5
R—C≡C—R	$\pi \rightarrow \pi^*$	170	3.0	RCOOH	$n \rightarrow \pi^*$	205	1.5
R—C≡N	$n \rightarrow \pi^*$	160	<1.0	RCOOR′	$n \rightarrow \pi^*$	205	1.5
R—N=N—R	$n \rightarrow \pi^*$	340	<1.0	RCONH$_2$	$n \rightarrow \pi^*$	210	1.5

7.8 THE EFFECT OF CONJUGATION

One of the best ways to bring about a bathochromic shift is to increase the extent of conjugation in a double-bonded system. In the presence of conjugated double bonds, the electronic energy levels of a chromophore move closer together. As a result, the energy required to produce a transition from an occupied electronic energy level to an unoccupied level decreases, and the wavelength of the light absorbed becomes longer. Figure 7.10 illustrates the bathochromic shift that is observed in a series of conjugated polyenes as the length of the conjugated chain is increased.

Conjugation of two chromophores not only results in a bathochromic shift but increases the intensity of the absorption. These two effects are of prime importance in the use and interpretation of electronic spectra of organic molecules because conjugation shifts the selective light absorption of isolated chromophores from a region of the spectrum that is not readily accessible to a region that
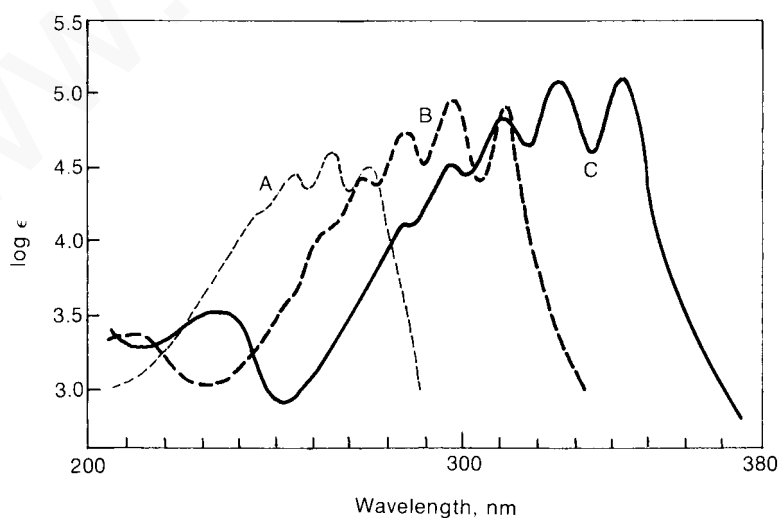
FIGURE 7.10 CH$_3$—(CH=CH)$_n$—CH$_3$ ultraviolet spectra of dimethylpolyenes. (a) $n = 3$; (b) $n = 4$; (c) $n = 5$. (From Nayler, P., and M. C. Whiting, *Journal of the Chemical Society* (1955): 3042.)

TABLE 7.4
EFFECT OF CONJUGATION ON ELECTRONIC TRANSITIONS

	λ_{max} (nm)	ε
Alkenes		
Ethylene	175	15,000
1,3-Butadiene	217	21,000
1,3,5-Hexatriene	258	35,000
β-Carotene (11 double bonds)	465	125,000
Ketones		
Acetone		
$\pi \rightarrow \pi^*$	189	900
$n \rightarrow \pi^*$	280	12
3-Buten-2-one		
$\pi \rightarrow \pi^*$	213	7,100
$n \rightarrow \pi^*$	320	27

is easily studied with commercially available spectrophotometers. The exact position and intensity of the absorption band of the conjugated system can be correlated with the extent of conjugation in the system. Table 7.4 illustrates the effect of conjugation on some typical electronic transitions.

7.9 THE EFFECT OF CONJUGATION ON ALKENES

The bathochromic shift that results from an increase in the length of a conjugated system implies that an increase in conjugation decreases the energy required for electronic excitation. This is true and can be explained most easily by the use of molecular orbital theory. According to molecular orbital (MO) theory, the atomic p orbitals on each of the carbon atoms combine to make π molecular orbitals. For instance, in the case of ethylene (ethene), we have two atomic p orbitals, ϕ_1 and ϕ_2. From these two p orbitals we form two π molecular orbitals, ψ_1 and ψ_2^*, by taking linear combinations. The bonding orbital ψ_1 results from the addition of the wave functions of the two p orbitals, and the antibonding orbital ψ_2^* results from the subtraction of these two wave functions. The new bonding orbital, a **molecular orbital,** has an energy lower than that of either of the original p orbitals; likewise, the antibonding orbital has an elevated energy. Figure 7.11 illustrates this diagrammatically.

Notice that *two* atomic orbitals were combined to build the molecular orbitals, and as a result, *two* molecular orbitals were formed. There were also two electrons, one in each of the atomic p orbitals. As a result of combination, the new π system contains *two* electrons. Because we fill the lower-energy orbitals first, these electrons end up in ψ_1, the bonding orbital, and they constitute a new π bond. Electronic transition in this system is a $\pi \rightarrow \pi^*$ transition from ψ_1 to ψ_2^*.

Now, moving from this simple two-orbital case, consider 1,3-butadiene, which has *four* atomic p orbitals that form its π system of two conjugated double bonds. Since we had four atomic orbitals with which to build, *four* molecular orbitals result. Figure 7.12 represents the orbitals of ethylene on the same energy scale as the new orbitals for the sake of comparison.

Notice that the transition of lowest energy in 1,3-butadiene, $\psi_2 \rightarrow \psi_3^*$, is a $\pi \rightarrow \pi^*$ transition and that it has a *lower energy* than the corresponding transition in ethylene, $\psi_1 \rightarrow \psi_2^*$. This result is general. As we increase the number of p orbitals making up the conjugated system, the transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) has
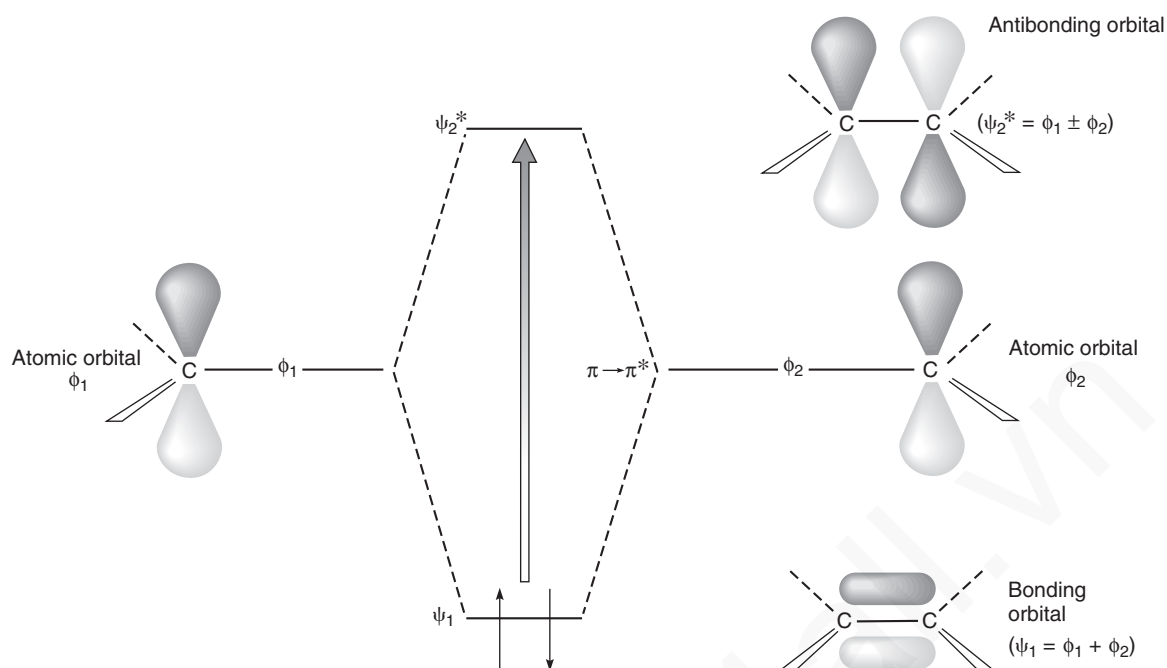
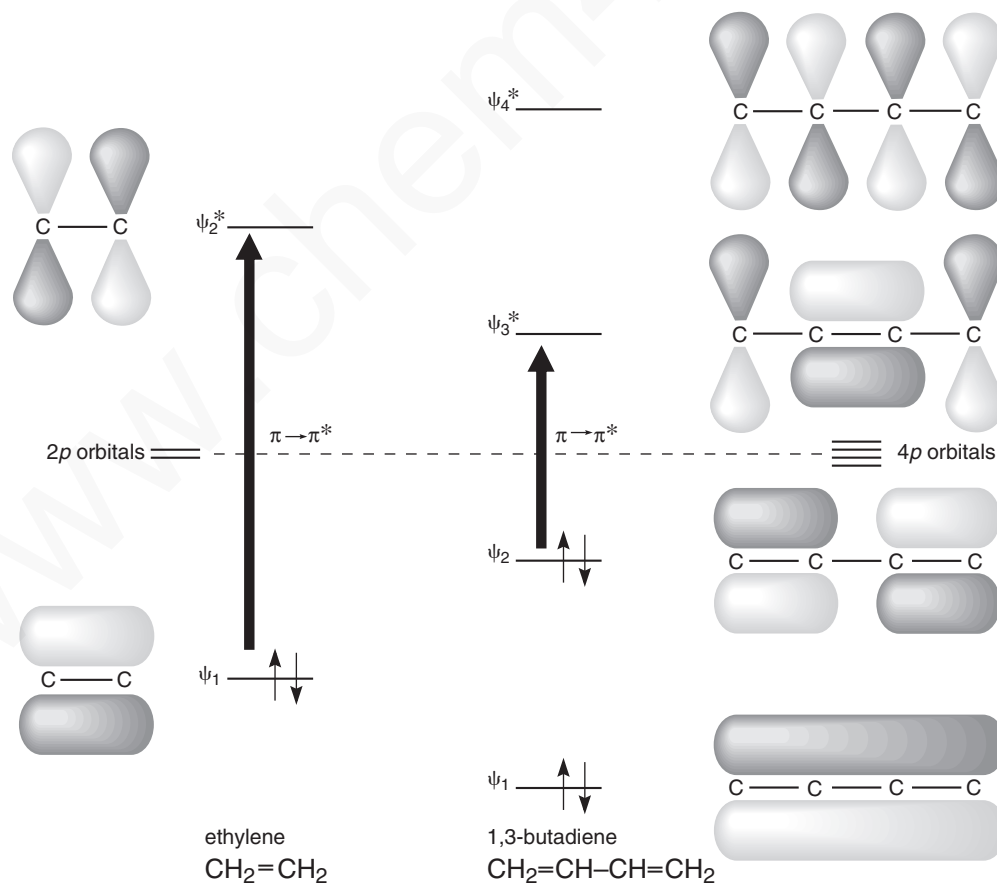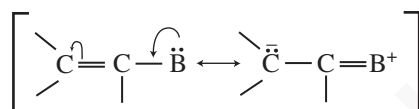**FIGURE 7.11** Formation of the molecular orbitals for ethylene.

FIGURE 7.12 A comparison of the molecular orbital energy levels and the energy of the $\pi \rightarrow \pi^*$ transitions in ethylene and 1,3-butadiene.

progressively lower energy. The energy gap dividing the bonding and antibonding orbitals becomes progressively smaller with increasing conjugation. Figure 7.13 plots the molecular orbital energy levels of several conjugated polyenes of increasing chain length on a common energy scale. Arrows indicate the HOMO–LUMO transitions. The increased conjugation shifts the observed wavelength of the absorption to higher values.

In a qualitatively similar fashion, many auxochromes exert their bathochromic shifts by means of an extension of the length of the conjugated system. The strongest auxochromes invariably possess a pair of unshared electrons on the atom attached to the double-bond system. Resonance interaction of this lone pair with the double bond(s) increases the length of the conjugated system.

$$
\left[\quad \overset{\diagdown}{\underset{\diagup}{C}} = C - \ddot{B} \quad \longleftrightarrow \quad \overset{\diagdown}{\underset{\diagup}{\ddot{C}}} - C = B^+ \quad \right]
$$

As a result of this interaction, as just shown, the nonbonded electrons become part of the π system of molecular orbitals, increasing its length by one extra orbital. Figure 7.14 depicts this interaction for ethylene and an unspecified atom, B, with an unshared electron pair. However, any of the typical auxochromic groups, $-OH$, $-OR$, $-X$, or $-NH_2$, could have been illustrated specifically.

In the new system, the transition from the highest occupied orbital ψ_2 to the antibonding orbital ψ_3^* always has lower energy than the $\pi \rightarrow \pi^*$ transition would have in the system without the interaction. Although MO theory can explain this general result, it is beyond the scope of this book.
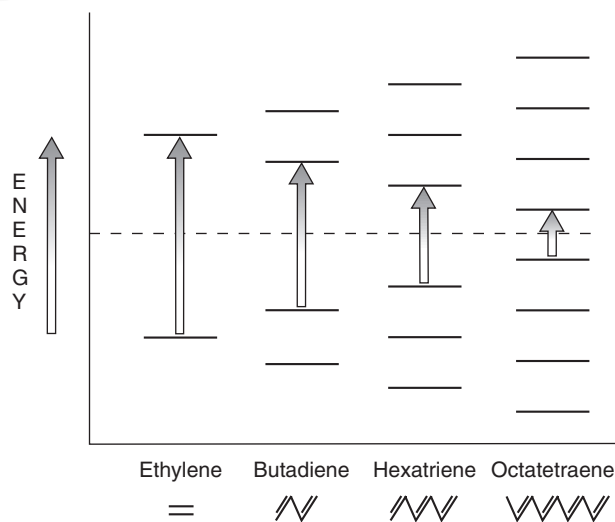
FIGURE 7.13 A comparison of the $\pi \rightarrow \pi^*$ energy gap in a series of polyenes of increasing chain length.
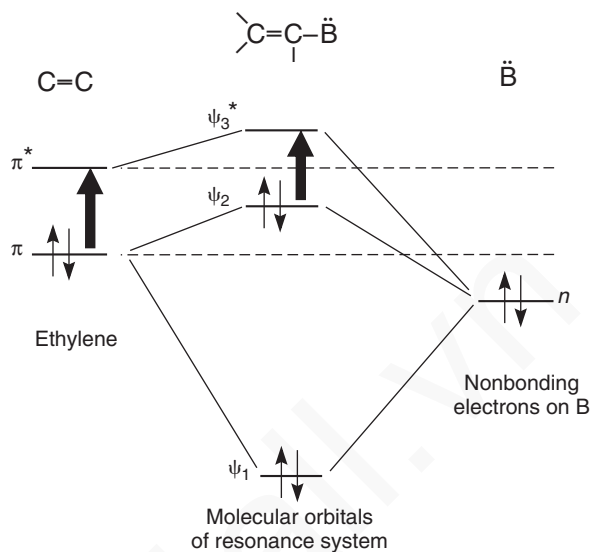
FIGURE 7.14 Energy relationships of the new molecular orbitals and the interacting π system and its auxochrome.

In similar fashion, methyl groups also produce a bathochromic shift. However, as methyl groups do not have unshared electrons, the interaction is thought to result from overlap of the C—H bonding orbitals with the π system as follows:
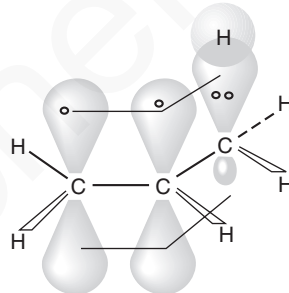
This type of interaction is often called **hyperconjugation.** Its net effect is an extension of the π system.

7.10 THE WOODWARD–FIESER RULES FOR DIENES

In butadiene, two possible $\pi \rightarrow \pi^*$ transitions can occur: $\psi_2 \rightarrow \psi_3^*$ and $\psi_2 \rightarrow \psi_4^*$. We have already discussed the easily observable $\psi_2 \rightarrow \psi_3^*$ transition (see Fig. 7.12). The $\psi_2 \rightarrow \psi_4^*$ transition is not often observed, for two reasons. First, it lies near 175 nm for butadiene; second, it is a forbidden transition for the *s-trans* conformation of double bonds in butadiene.
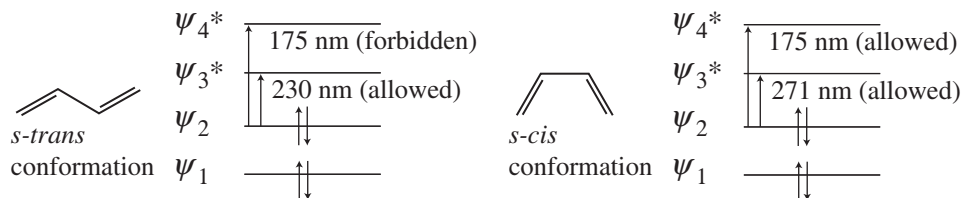
A transition at 175 nm lies below the cutoff points of the common solvents used to determine UV spectra (Table 7.1) and therefore is not easily detectable. Furthermore, the *s-trans* conformation is more favorable for butadiene than is the *s-cis* conformation. Therefore, the 175-nm band is not usually detected.

In general, conjugated dienes exhibit an intense band (ε = 20,000 to 26,000) in the region from 217 to 245 nm, owing to a $\pi \rightarrow \pi^*$ transition. The position of this band appears to be quite insensitive to the nature of the solvent.

Butadiene and many simple conjugated dienes exist in a planar *s-trans* conformation, as noted. Generally, alkyl substitution produces bathochromic shifts and hyperchromic effects. However, with certain patterns of alkyl substitution, the wavelength increases but the intensity decreases. The 1,3-dialkylbutadienes possess too much crowding between alkyl groups to permit them to exist in the *s-trans* conformation. They convert, by rotation around the single bond, to an *s-cis* conformation, which absorbs at longer wavelengths but with lower intensity than the corresponding *s-trans* conformation.

s-trans   *s-cis*
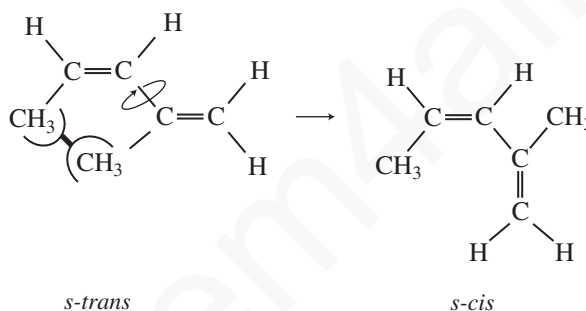
In cyclic dienes, where the central bond is a part of the ring system, the diene chromophore is usually held rigidly in either the *s-trans* (transoid) or the *s-cis* (cisoid) orientation. Typical absorption spectra follow the expected pattern:
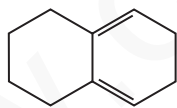
Homoannular diene (cisoid or *s-cis*)   Heteroannular diene (transoid or *s-trans*)
Less intense, ε = 5,000–15,000   More intense, ε = 12,000–28,000
λ longer (273 nm) λ shorter (234 nm)
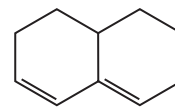
By studying a vast number of dienes of each type, Woodward and Fieser devised an empirical correlation of structural variations that enables us to predict the wavelength at which a conjugated diene will absorb. Table 7.5 summarizes the rules. Following are a few sample applications of these rules. Notice that the pertinent parts of the structures are shown in bold face.
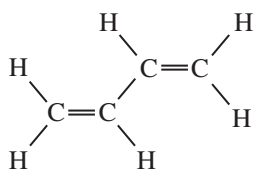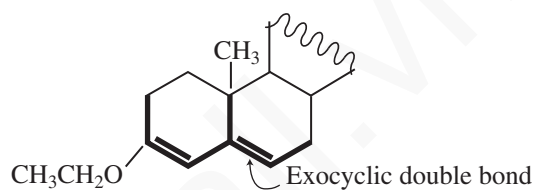
Transsoid: 214 nm
Observed: 217 nm
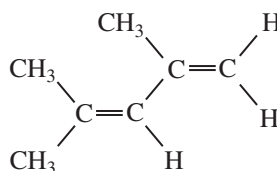
Transsoid: 214 nm
Alkyl groups: $3 \times 5 =$ 15
                              ———
                                229 nm

Observed: 228 nm

Exocyclic double bond
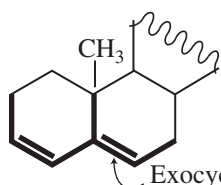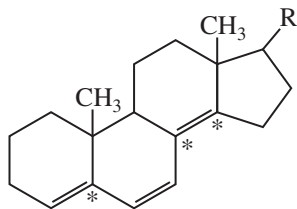
Transoid: 214 nm
Ring residues: $3 \times 5 =$ 15
Exocyclic double bond: 5
                                 ———
                                234 nm

Observed: 235 nm

CH_3CH_2O — Exocyclic double bond

Transoid: 214 nm
Ring residues: $3 \times 5 =$ 15
Exocyclic double bond: 5
—OR: 6
                                 ———
                                240 nm

Observed: 241 nm

TABLE 7.5
EMPIRICAL RULES FOR DIENES

	Homoannular (cisoid)	Heteroannular (transoid)
Parent	$\lambda = 253$ nm	$\lambda = 214$ nm
Increments for:		
Double-bond-extending conjugation	30	30
Alkyl substituent or ring residue	5	5
Exocyclic double bond	5	5
Polar groupings:		
$-OCOCH_3$	0	0
$-OR$	6	6
$-Cl, -Br$	5	5
$-NR_2$	60	60

In this context, an *exocyclic double bond* is a double bond that lies outside a given ring. Notice that the exocyclic bond may lie within one ring even though it is outside another ring. Often, an exocyclic double bond will be found at a junction point on rings. Here is an example of a compound with the exocyclic double bonds labeled with asterisks:

Three exocyclic double bonds = $3 \times 5 = 15$ nm
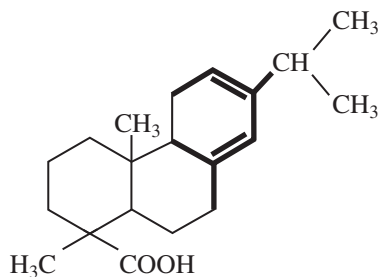
Cisoid:	253 nm
Alkyl substituent:	5
Ring residues: $3 \times 5 =$	15
Exocyclic double bond:	5
	278 nm
Observed:	275 nm
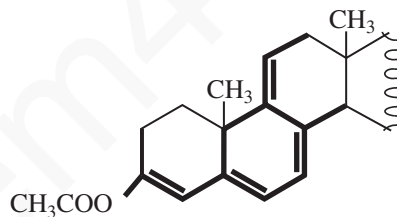
Cisoid:		253 nm
Ring residues: $5 \times 5 =$		25
Double-bond-extending conjugation: $2 \times 30 =$		60
Exocyclic double bond: $3 \times 5 =$		15
$CH_3COO—$:		0
		353 nm
Observed:		355 nm

7.11 CARBONYL COMPOUNDS; ENONES

As discussed in Section 7.7, carbonyl compounds have two principal UV transitions, the allowed $\pi \rightarrow \pi^*$ transition and the forbidden $n \rightarrow \pi^*$ transition.
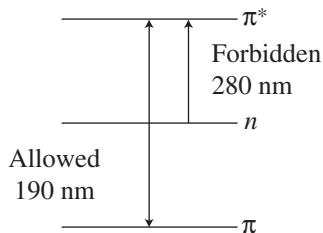
Of these, only the $n \rightarrow \pi^*$ transition, although it is weak (forbidden), is commonly observed above the usual cutoff points of solvents. Substitution on the carbonyl group by an auxochrome with a lone pair of electrons, such as $-NR_2$, $-OH$, $-OR$, $-NH_2$, or $-X$, as in amides, acids, esters, or acid chlorides, gives a pronounced hypsochromic effect on the $n \rightarrow \pi^*$ transition and a lesser, bathochromic effect on the $\pi \rightarrow \pi^*$ transition. Such bathochromic shifts are caused by resonance interaction similar to that discussed in Section 7.9. Seldom, however, are these effects large enough to bring the $\pi \rightarrow \pi^*$ band into the region above the solvent cutoff point. Table 7.6 lists the hypsochromic effects of an acetyl group on the $n \rightarrow \pi^*$ transition.

The hypsochromic shift of the $n \rightarrow \pi^*$ is due primarily to the inductive effect of the oxygen, nitrogen, or halogen atoms. They withdraw electrons from the carbonyl carbon, causing the lone pair of electrons on oxygen to be held more firmly than they would be in the absence of the inductive effect.

If the carbonyl group is part of a conjugated system of double bonds, both the $n \rightarrow \pi^*$ and the $\pi \rightarrow \pi^*$ bands are shifted to longer wavelengths. However, the energy of the $n \rightarrow \pi^*$ transition does not decrease as rapidly as that of the $\pi \rightarrow \pi^*$ band, which is more intense. If the conjugated chain becomes long enough, the $n \rightarrow \pi^*$ band is "buried" under the more intense $\pi \rightarrow \pi^*$ band. Figure 7.15 illustrates this effect for a series of polyene aldehydes.

Figure 7.16 shows the molecular orbitals of a simple enone system, along with those of the noninteracting double bond and the carbonyl group.

TABLE 7.6
HYPSOCHROMIC EFFECTS OF LONE-PAIR AUXOCHROMES
ON THE $n \rightarrow \pi^*$ TRANSITION OF A CARBONYL GROUP

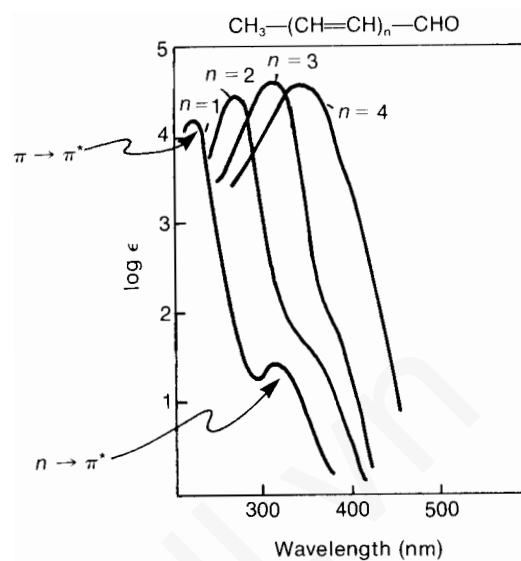|	λ_{max}	ε_{max}	Solvent
$CH_3-\overset{\overset{O}{\|\|}}{C}-H$	293 nm	12	Hexane
$CH_3-\overset{\overset{O}{\|\|}}{C}-CH_3$	279	15	Hexane
$CH_3-\overset{\overset{O}{\|\|}}{C}-Cl$	235	53	Hexane
$CH_3-\overset{\overset{O}{\|\|}}{C}-NH_2$	214	—	Water
$CH_3-\overset{\overset{O}{\|\|}}{C}-OCH_2CH_3$	204	60	Water
$CH_3-\overset{\overset{O}{\|\|}}{C}-OH$	204	41	Ethanol

F I G U R E 7 . 1 5 The spectra of a series of polyene aldehydes. (From Murrell, J. N., *The Theory of the Electronic Spectra of Organic Molecules*, Methuen and Co., Ltd., London, 1963. Reprinted by permission.)
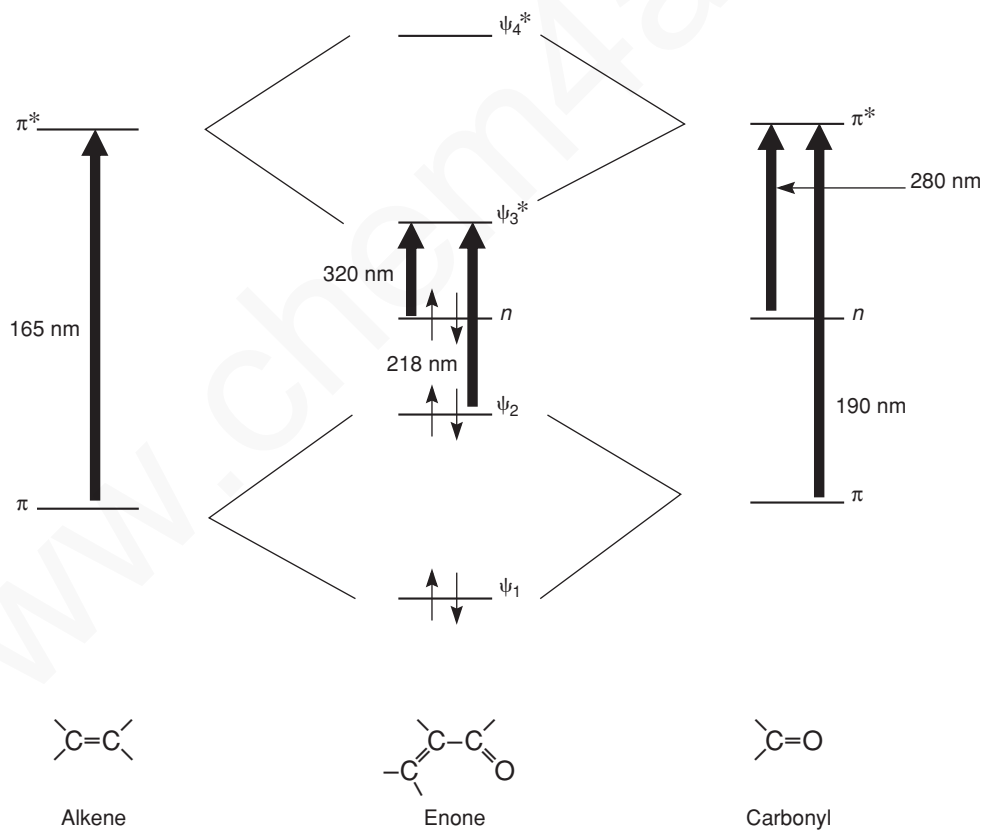

F I G U R E 7 . 1 6 The orbitals of an enone system compared to those of the noninteracting chromophores.

400   **Ultraviolet Spectroscopy**

☐ 7.12 WOODWARD'S RULES FOR ENONES

The conjugation of a double bond with a carbonyl group leads to intense absorption ($\varepsilon = 8{,}000$ to 20,000) corresponding to a $\pi \rightarrow \pi^*$ transition of the carbonyl group. The absorption is found between 220 and 250 nm in simple enones. The $n \rightarrow \pi^*$ transition is much less intense ($\varepsilon = 50$ to 100) and appears at 310 to 330 nm. Although the $\pi \rightarrow \pi^*$ transition is affected in predictable fashion by structural modifications of the chromophore, the $n \rightarrow \pi^*$ transition does not exhibit such predictable behavior.

Woodward examined the ultraviolet spectra of numerous enones and devised a set of empirical rules that enable us to predict the wavelength at which the $\pi \rightarrow \pi^*$ transition occurs in an unknown enone. Table 7.7 summarizes these rules.

T A B L E 7 . 7
EMPIRICAL RULES FOR ENONES

$$\overset{\beta}{\underset{|}{\text{C}}}\overset{\alpha}{\underset{|}{\text{C}}}$$
$$\beta-\text{C}=\text{C}-\text{C}=\text{O} \qquad\qquad \delta-\text{C}=\text{C}-\text{C}=\text{C}-\text{C}=$$

Base values:		
Six-membered ring or acyclic parent enone		= 215 nm
Five-membered ring parent enone		= 202 nm
Acyclic dienone		= 245 nm
Increments for:		
Double-bond-extending conjugation		30
Alkyl group or ring residue	α	10
	β	12
	γ and higher	18
Polar groupings:		
—OH	α	35
	β	30
	δ	50
—OCOCH$_3$	α,β,δ	6
—OCH$_3$	α	35
	β	30
	γ	17
	δ	31
—Cl	α	15
	β	12
—Br	α	25
	β	30
—NR$_2$	β	95
Exocyclic double bond		5
Homocyclic diene component		39
Solvent correction		Variable
	$\lambda_{\max}^{\text{EtOH}}(\text{calc}) = \text{Total}$	

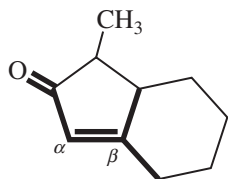Following are a few sample applications of these rules. The pertinent parts of the structures are shown in bold face.
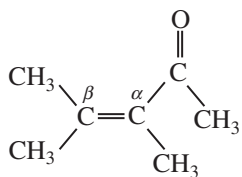
Acyclic enone:	215 nm
α-CH$_3$:	10
β-CH$_3$: 2 × 12 =	24
	249 nm
Observed:	249 nm
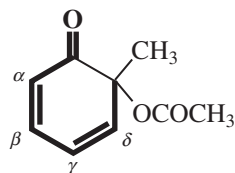
Six-membered enone:	215 nm
Double-bond-extending conjugation:	30
Homocyclic diene:	39
δ-Ring residue:	18
	302 nm
Observed:	300 nm

Five-membered enone:	202 nm
β-Ring residue: 2 × 12 =	24
Exocyclic double bond:	5
	231 nm
Observed:	226 nm
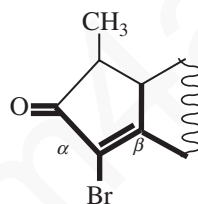
Five-membered enone:	202 nm
α-Br:	25
β-Ring residue: 2 × 12 =	24
Exocyclic double bond:	5
	256 nm
Observed:	251 nm
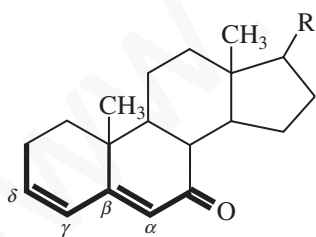
Six-membered enone:	215 nm
Double-bond-extending conjugation:	30
β-Ring residue:	12
δ-Ring residue:	18
Exocyclic double bond:	5
	280 nm
Observed:	280 nm

7.13 α,β-UNSATURATED ALDEHYDES, ACIDS, AND ESTERS

α,β-Unsaturated aldehydes generally follow the same rules as enones (see the preceding section) except that their absorptions are displaced by about 5 to 8 nm toward shorter wavelength than those of the corresponding ketones. Table 7.8 lists the empirical rules for unsaturated aldehydes.

Nielsen developed a set of rules for α,β-unsaturated acids and esters that are similar to those for enones (Table 7.9).

Consider 2-cyclohexenoic and 2-cycloheptenoic acids as examples:
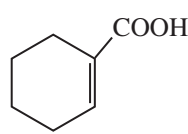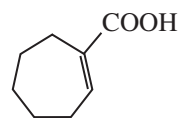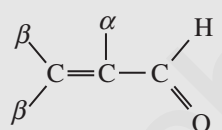
COOH	α,β-dialkyl	217 nm calc.
	Double bond is in a six-membered ring, adds nothing	217 nm obs.
COOH	α,β-dialkyl	217 nm
	Double bond is in a seven-membered ring	+ 5
		222 nm calc.
		222 nm obs.

TABLE 7.8
EMPIRICAL RULES FOR UNSATURATED ALDEHYDES

$$\beta\diagdown\underset{\beta}{\diagup}C=\overset{\alpha}{\underset{|}{C}}-C\overset{H}{\underset{O}{\diagup}}$$
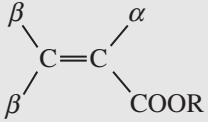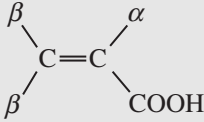
Parent	208 nm
With α or β alkyl groups	220
With α,β or β,β alkyl groups	230
With α,β,β alkyl groups	242

7.14 AROMATIC COMPOUNDS

The absorptions that result from transitions within the benzene chromophore can be quite complex. The ultraviolet spectrum contains three absorption bands, which sometimes contain a great deal of fine structure. The electronic transitions are basically of the $\pi \rightarrow \pi^*$ type, but their details are not as simple as in the cases of the classes of chromophores described in earlier sections of this chapter.

Figure 7.17a shows the molecular orbitals of benzene. If you were to attempt a simple explanation for the electronic transitions in benzene, you would conclude that there are four possible transitions, but each transition has the same energy. You would predict that the ultraviolet spectrum of benzene consists of one absorption peak. However, owing to electron–electron repulsions and symmetry considerations, the actual energy states from which electronic transitions occur are somewhat modified. Figure 7.17b shows the energy-state levels of benzene. Three electronic transitions take

TABLE 7.9
EMPIRICAL RULES FOR UNSATURATED ACIDS AND ESTERS

Base values for:

$$\beta\!-\!\!\underset{\beta}{C}\!=\!\underset{\text{COOR}}{C}\!-\!\alpha \qquad\qquad \beta\!-\!\!\underset{\beta}{C}\!=\!\underset{\text{COOH}}{C}\!-\!\alpha$$

With α or β alkyl group	208 nm
With α,β or β,β alkyl groups	217
With α,β,β alkyl groups	225
For an exocyclic α,β double bond	Add 5 nm
For an endocyclic α,β double bond in a five- or seven-membered ring	Add 5 nm

place to these excited states. Those transitions, which are indicated in Figure 7.17b, are the so-called **primary bands** at 184 and 202 nm and the **secondary** (fine-structure) **band** at 255 nm. Figure 7.18 is the spectrum of benzene. Of the primary bands, the 184-nm band (the **second primary band**) has a molar absorptivity of 47,000. It is an allowed transition. Nevertheless, this transition is not observed under usual experimental conditions because absorptions at this wavelength are in the vacuum ultraviolet region of the spectrum, beyond the range of most commercial instruments. In polycyclic aromatic compounds, the second primary band is often shifted to longer wavelengths, in which case

(a) Molecular orbitals
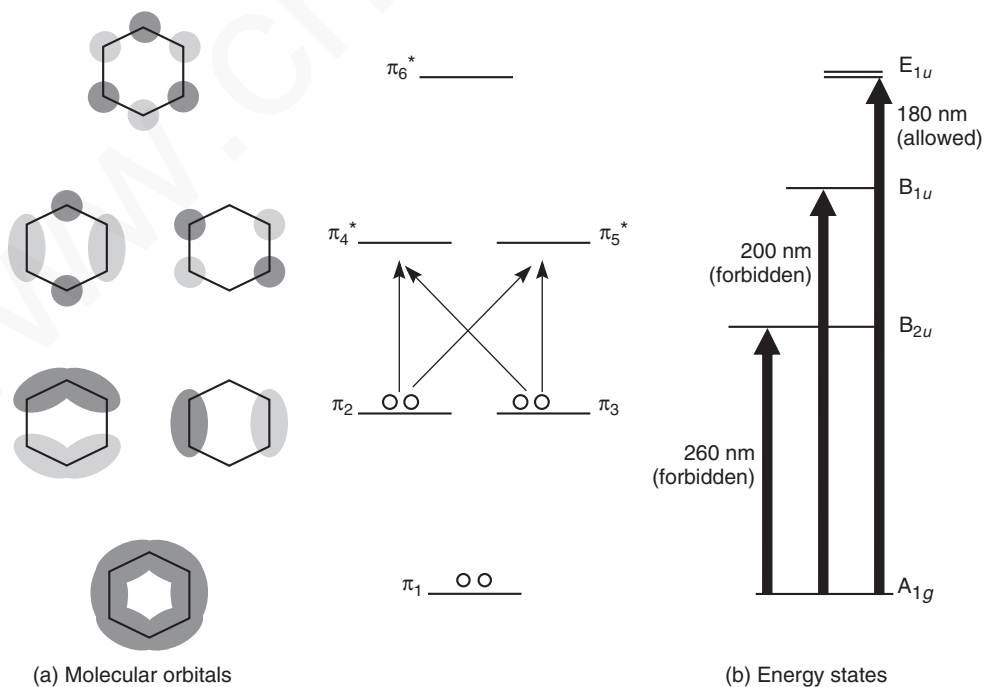
(b) Energy states

FIGURE 7.17 Molecular orbitals and energy states for benzene.
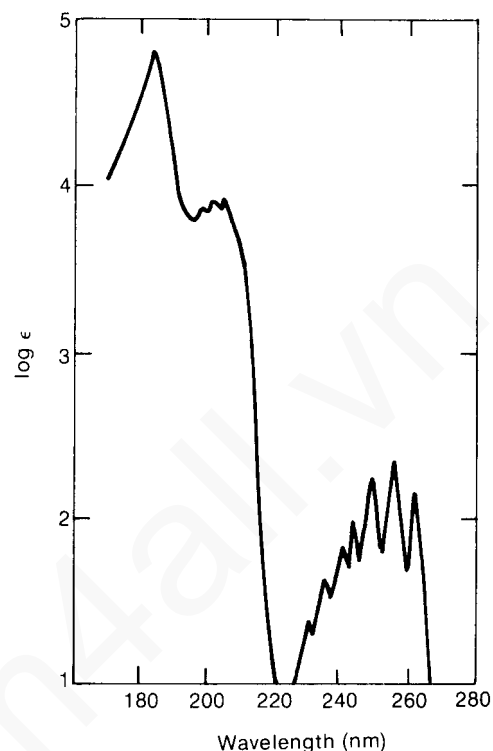
FIGURE 7.18 Ultraviolet spectrum of benzene. (From Petruska, J., *Journal of Chemical Physics, 34* (1961): 1121. Reprinted by permission.)

it can be observed under ordinary conditions. The 202-nm band is much less intense ($\varepsilon = 7400$), and it corresponds to a forbidden transition. The secondary band is the least intense of the benzene bands ($\varepsilon = 230$). It also corresponds to a symmetry-forbidden electronic transition. The secondary band, caused by interaction of the electronic energy levels with vibrational modes, appears with a great deal of fine structure. This fine structure is lost if the spectrum of benzene is determined in a polar solvent or if a single functional group is substituted onto the benzene ring. In such cases, the secondary band appears as a broad peak, lacking in any interesting detail.

Substitution on the benzene ring can cause bathochromic and hyperchromic shifts. Unfortunately, these shifts are difficult to predict. Consequently, it is impossible to formulate empirical rules to predict the spectra of aromatic substances as was done for dienes, enones, and the other classes of compounds discussed earlier in this chapter. You may gain a qualitative understanding of the effects of substitution by classifying substituents into groups.

A.   Substituents with Unshared Electrons

Substituents that carry nonbonding electrons (*n* electrons) can cause shifts in the primary and secondary absorption bands. The nonbonding electrons can increase the length of the π system through resonance.
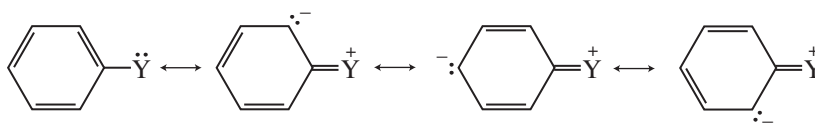
The more available these *n* electrons are for interaction with the π system of the aromatic ring, the greater the shifts will be. Examples of groups with *n* electrons are the amino, hydroxyl, and methoxy groups, as well as the halogens.

Interactions of this type between the *n* and π electrons usually cause shifts in the primary and secondary benzene absorption bands to longer wavelength (extended conjugation). In addition, the presence of *n* electrons in these compounds gives the possibility of $n \rightarrow \pi^*$ transitions. If an *n* electron is excited into the extended π^* chromophore, the atom from which it was removed becomes electron deficient, while the π system of the aromatic ring (which also includes atom Y) acquires an extra electron. This causes a separation of charge in the molecule and is generally represented as regular resonance, as was shown earlier. However, the extra electron in the ring is actually in a π^* orbital and would be better represented by structures of the following type, with the asterisk representing the excited electron:
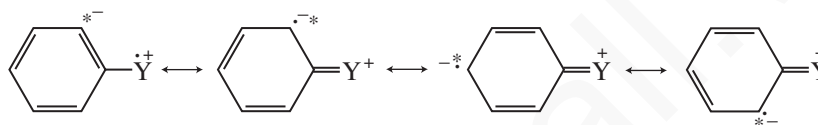
Such an excited state is often called a **charge-transfer** or an **electron-transfer** excited state.

In compounds that are acids or bases, pH changes can have very significant effects on the positions of the primary and secondary bands. Table 7.10 illustrates the effects of changing the pH of the solution on the absorption bands of various substituted benzenes. In going from benzene to phenol, notice the shift from 203.5 to 210.5 nm—a 7-nm shift—in the primary band. The secondary band shifts from 254 to 270 nm—a 16-nm shift. However, in phenoxide ion, the conjugate base of phenol, the primary band shifts from 203.5 to 235 nm (a 31.5-nm shift), and the secondary band shifts from 254 to 287 nm (a 33-nm shift). The intensity of the secondary band also increases. In phenoxide ion, there are more *n* electrons, and they are more available for interaction with the aromatic π system than in phenol.

TABLE 7.10
pH EFFECTS ON ABSORPTION BANDS

Substituent	Primary		Secondary	
	λ (nm)	ε	λ (nm)	ε
—H	203.5	7,400	254	204
—OH	210.5	6,200	270	1,450
—O⁻	235	9,400	287	2,600
—NH$_2$	230	8,600	280	1,430
—NH$_3^+$	203	7,500	254	169
—COOH	230	11,600	273	970
—COO⁻	224	8,700	268	560

The comparison of aniline and anilinium ion illustrates a reverse case. Aniline exhibits shifts similar to those of phenol. From benzene to aniline, the primary band shifts from 203.5 to 230 nm (a 26.5-nm shift), and the secondary band shifts from 254 to 280 nm (a 26-nm shift). However, these large shifts are not observed in the case of anilinium ion, the conjugate acid of aniline. For anilinium ion, the primary and secondary bands do not shift at all. The quaternary nitrogen of anilinium ion has no unshared pairs of electrons to interact with the benzene π system. Consequently, the spectrum of anilinium ion is almost identical to that of benzene.

B. Substituents Capable of π-Conjugation

Substituents that are themselves chromophores usually contain π electrons. Just as in the case of n electrons, interaction of the benzene-ring electrons and the π electrons of the substituent can produce a new electron transfer band. At times, this new band may be so intense as to obscure the secondary band of the benzene system. Notice that this interaction induces the opposite polarity; the ring becomes electron deficient.
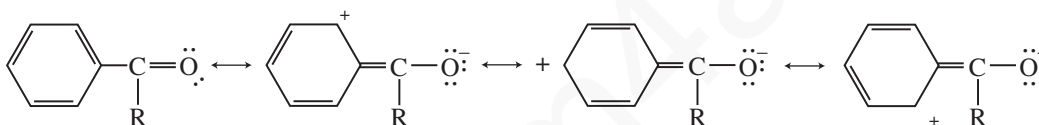
Table 7.10 demonstrates the effect of acidity or basicity of the solution on such a chromophoric substituent group. In the case of benzoic acid, the primary and secondary bands are shifted substantially from those noted for benzene. However, the magnitudes of the shifts are somewhat smaller in the case of benzoate ion, the conjugate base of benzoic acid. The intensities of the peaks are lower than for benzoic acid as well. We expect electron transfer of the sort just shown to be less likely when the functional group already bears a negative charge.
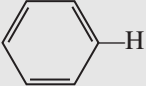
C. Electron-Releasing and Electron-Withdrawing Effects

Substituents may have differing effects on the positions of absorption maxima, depending on whether they are electron releasing or electron withdrawing. Any substituent, regardless of its influence on the electron distribution elsewhere in the aromatic molecule, shifts the primary absorption band to longer wavelength. Electron-withdrawing groups have essentially no effect on the position of the secondary absorption band unless, of course, the electron-withdrawing group is also capable of acting as a chromophore. However, electron-releasing groups increase both the wavelength and the intensity of the secondary absorption band. Table 7.11 summarizes these effects, with electron-releasing and electron-withdrawing substituents grouped together.
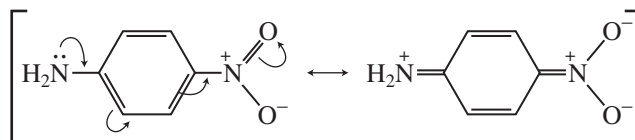
D. Disubstituted Benzene Derivatives

With disubstituted benzene derivatives, it is necessary to consider the effect of each of the two substituents. For *para*-disubstituted benzenes, two possibilities exist. If both groups are electron releasing or if they are both electron withdrawing, they exert effects similar to those observed with monosubstituted benzenes. The group with the stronger effect determines the extent of shifting of

TABLE 7.11
ULTRAVIOLET MAXIMA FOR VARIOUS AROMATIC COMPOUNDS

		Primary		Secondary	
Substituent		λ (nm)	ε	λ (nm)	ε
(benzene ring)—H		203.5	7,400	254	204
Electron-releasing substituents	—CH$_3$	206.5	7,000	261	225
	—Cl	209.5	7,400	263.5	190
	—Br	210	7,900	261	192
	—OH	210.5	6,200	270	1,450
	—OCH$_3$	217	6,400	269	1,480
	—NH$_2$	230	8,600	280	1,430
Electron-withdrawing substituents	—CN	224	13,000	271	1,000
	—COOH	230	11,600	273	970
	—COCH$_3$	245.5	9,800		
	—CHO	249.5	11,400		
	—NO$_2$	268.5	7,800		

the primary absorption band. If one of the groups is electron releasing while the other is electron withdrawing, the magnitude of the shift of the primary band is greater than the sum of the shifts due to the individual groups. The enhanced shifting is due to resonance interactions of the following type:
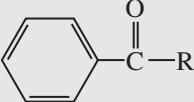
If the two groups of a disubstituted benzene derivative are either *ortho* or *meta* to each other, the magnitude of the observed shift is approximately equal to the sum of the shifts caused by the individual groups. With substitution of these types, there is no opportunity for the kind of direct resonance interaction between substituent groups that is observed with *para* substituents. In the case of *ortho* substituents, the steric inability of both groups to achieve coplanarity inhibits resonance.

For the special case of substituted benzoyl derivatives, an empirical correlation of structure with the observed position of the primary absorption band has been developed (Table 7.12). It provides a means of estimating the position of the primary band for benzoyl derivatives within about 5 nm.

TABLE 7.12
EMPIRICAL RULES FOR BENZOYL DERIVATIVES

Parent chromophore:

R = alkyl or ring residue		246
R = H		250
R = OH or Oalkyl		230

Increment for each substituent:

—Alkyl or ring residue	*o, m*	3
	p	10
—OH, —OCH$_3$, or —Oalkyl	*o, m*	7
	p	25
—O$^-$	*o*	11
	m	20
	p	78
—Cl	*o, m*	0
	p	10
—Br	*o, m*	2
	p	15
—NH$_2$	*o, m*	13
	p	58
—NHCOCH$_3$	*o, m*	20
	p	45
—NHCH$_3$	*p*	73
—N(CH$_3$)$_2$	*o, m*	20
	p	85

Following are two sample applications of these rules:
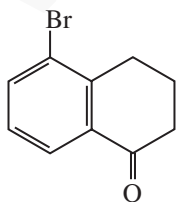
Parent chromophore:	246 nm
o-Ring residue:	3
m-Br:	2
	251 nm
Observed:	253 nm
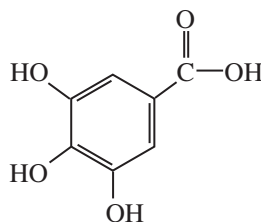
Parent chromophore:	230 nm
m-OH: 2 × 7 =	14
p-OH:	25
	269 nm
Observed:	270 nm

E.   Polynuclear Aromatic Hydrocarbons and Heterocyclic Compounds

Researchers have observed that the primary and secondary bands in the spectra of polynuclear aromatic hydrocarbons shift to longer wavelength. In fact, even the second primary band, which appears at 184 nm for benzene, is shifted to a wavelength within the range of most UV spectrophotometers. This band lies at 220 nm in the spectrum of naphthalene. As the extent of conjugation increases, the magnitude of the bathochromic shift also increases.

The ultraviolet spectra of the polynuclear aromatic hydrocarbons possess characteristic shapes and fine structure. In the study of spectra of substituted polynuclear aromatic derivatives, it is common practice to compare them with the spectrum of the unsubstituted hydrocarbon. The nature of the chromophore can be identified on the basis of similarity of peak shapes and fine structure. This technique involves the use of model compounds. Section 7.15 will discuss it further.

Figure 7.19 shows the ultraviolet spectra of naphthalene and anthracene. Notice the characteristic shape and fine structure of each spectrum, as well as the effect of increased conjugation on the positions of the absorption maxima.
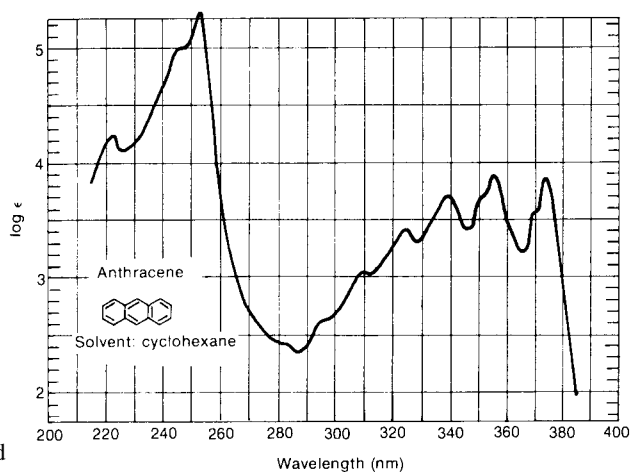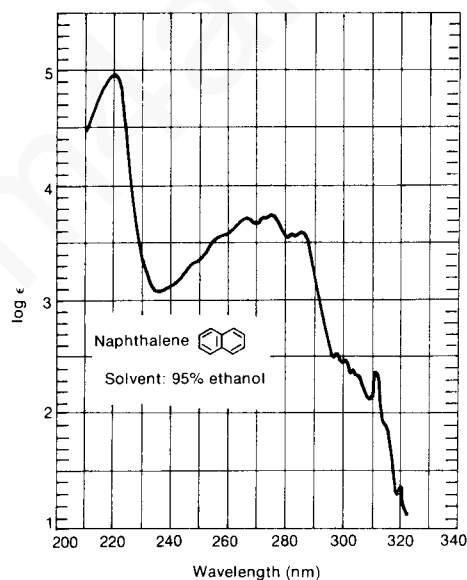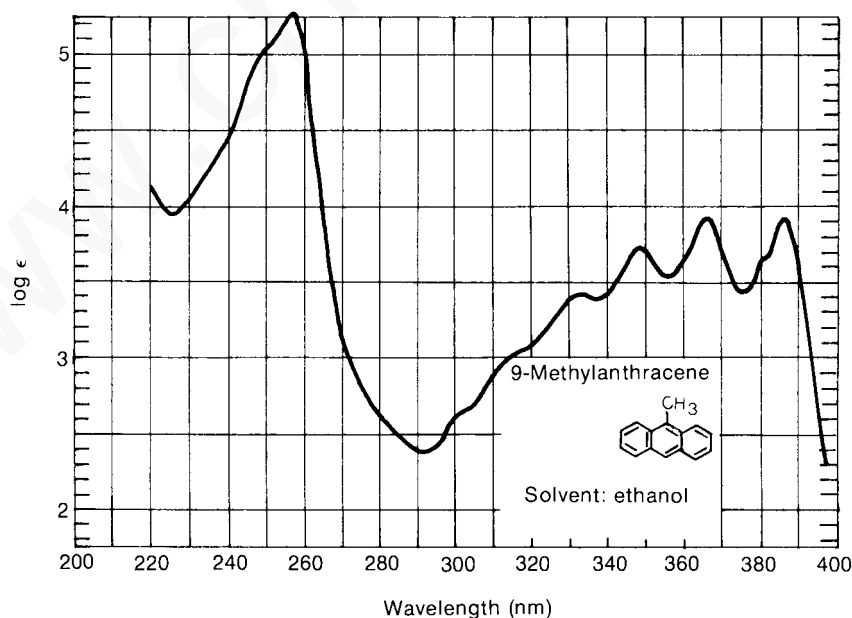

F I G U R E   7 . 1 9   Ultraviolet spectra of naphthalene and anthracene. (From Friedel, R. A., and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, New York, 1951. Reprinted by permission.)

Heterocyclic molecules have electronic transitions that include combinations of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The spectra can be rather complex, and analysis of the transitions involved will be left to more advanced treatments. The common method of studying derivatives of heterocyclic molecules is to compare them to the spectra of the parent heterocyclic systems. Section 7.15 will further describe the use of model compounds in this fashion.

Figure 7.20 includes the ultraviolet spectra of pyridine, quinoline, and isoquinoline. You may wish to compare the spectrum of pyridine with that of benzene (Fig. 7.18) and the spectra of quinoline and isoquinoline with the spectrum of naphthalene (Fig. 7.19).
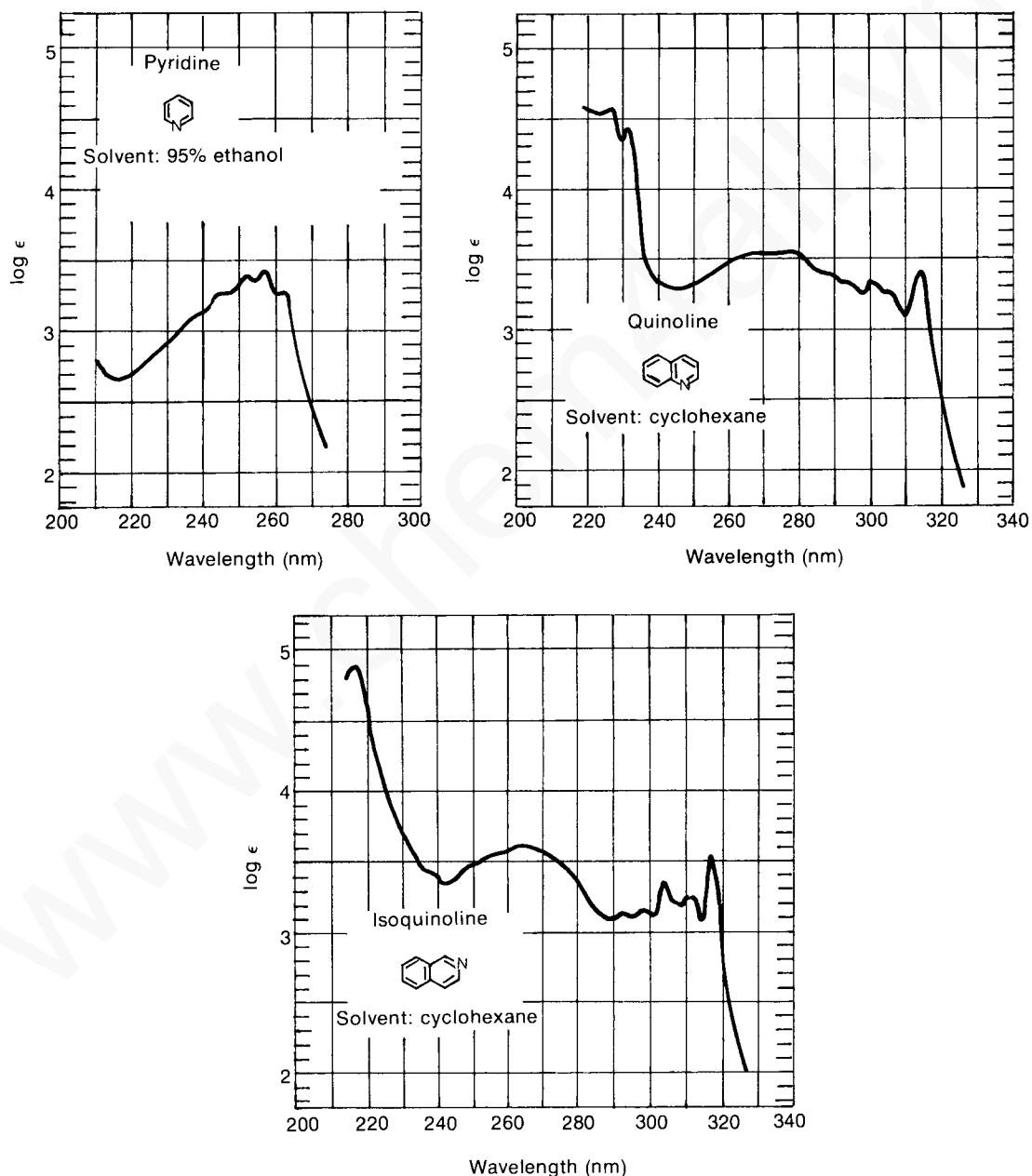
F I G U R E   7 . 2 0   The ultraviolet spectra of pyridine, quinoline, and isoquinoline. (From Friedel, R. A., and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, New York, 1951. Reprinted by permission.)

7.15 MODEL COMPOUND STUDIES

Very often, the ultraviolet spectra of several members of a particular class of compounds are very similar. Unless you are thoroughly familiar with the spectroscopic properties of each member of the class of compounds, it is very difficult to distinguish the substitution patterns of individual molecules by their ultraviolet spectra. You can, however, determine the gross nature of the chromophore of an unknown substance by this method. Then, based on knowledge of the chromophore, you can employ the other spectroscopic techniques described in this book to elucidate the precise structure and substitution of the molecule.

This approach—the use of model compounds—is one of the best ways to put the technique of ultraviolet spectroscopy to work. By comparing the UV spectrum of an unknown substance with that of a similar but less highly substituted compound, you can determine whether or not they contain the same chromophore. Many of the books listed in the references at the end of this chapter contain large collections of spectra of suitable model compounds, and with their help you can establish the general structure of the part of the molecule that contains the π electrons. You can then utilize infrared or NMR spectroscopy to determine the detailed structure.

As an example, consider an unknown substance that has the molecular formula $C_{15}H_{12}$. A comparison of its spectrum (Fig. 7.21) with that of anthracene (Fig. 7.19) shows that the two spectra are nearly identical. Disregarding minor bathochromic shifts, the same general peak shape and fine structure appear in the spectra of both the unknown and anthracene, the model compound. You may then conclude that the unknown is a substituted anthracene derivative. Further structure determination reveals that the unknown is 9-methylanthracene. The spectra of model compounds can be obtained from published catalogues of ultraviolet spectra. In cases in which a suitable model compound is not available, a model compound can be synthesized and its spectrum determined.

FIGURE 7.21 The ultraviolet spectrum of 9-methylanthracene. (From Friedel, R. A., and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, New York, 1951. Reprinted by permission.)

7.16 VISIBLE SPECTRA: COLOR IN COMPOUNDS

The portion of the electromagnetic spectrum lying between about 400 and 750 nm is the **visible** region. Light waves with wavelengths between these limits appear colored to the human eye. As anyone who has seen light diffracted by a prism or the diffraction effect of a rainbow knows, one end of the visible spectrum is violet, and the other is red. Light with wavelengths near 400 nm is violet, while that with wavelengths near 750 nm is red.

The phenomenon of color in compounds, however, is not as straightforward as the preceding discussion would suggest. If a substance absorbs visible light, it appears to have a color; if not, it appears white. However, compounds that absorb light in the visible region of the spectrum do not possess the color corresponding to the wavelength of the absorbed light. Rather, there is an inverse relationship between the observed color and the color absorbed.

When we observe light **emitted** from a source, as from a lamp or an emission spectrum, we observe the color corresponding to the wavelength of the light being emitted. A light source emitting violet light emits light at the high-energy end of the visible spectrum. A light source emitting red light emits light at the low-energy end of the spectrum.

However, when we observe the color of a particular object or substance, we do not observe that object or substance emitting light. (Certainly, the substance does not glow in the dark.) Rather, we observe the light that is being **reflected**. The color that our eye perceives is not the color corresponding to the wavelength of the light absorbed but its **complement**. When white light falls on an object, light of a particular wavelength is absorbed. The remainder of the light is reflected. The eye and brain register all of the reflected light as the color complementary to the color that was absorbed.

In the case of transparent objects or solutions, the eye receives the light that is **transmitted**. Again, light of a particular wavelength is absorbed, and the remaining light passes through to reach the eye. As before, the eye registers this transmitted light as the color complementary to the color that was absorbed. Table 7.13 illustrates the relationship between the wavelength of light absorbed by a substance and the color perceived by an observer.

Some familiar compounds may serve to underscore these relationships between the absorption spectrum and the observed color. The structural formulas of these examples are shown. Notice that each of these substances has a highly extended conjugated system of electrons. Such extensive conjugation shifts their electronic spectra to such long wavelengths that they absorb visible light and appear colored.

T A B L E   7.13
**RELATIONSHIP BETWEEN THE COLOR OF LIGHT ABSORBED BY A COMPOUND AND THE OBSERVED COLOR OF THE COMPOUND**

Color of Light Absorbed	Wavelength of Light Absorbed (nm)	Observed Color
Violet	400	Yellow
Blue	450	Orange
Blue-green	500	Red
Yellow-green	530	Red-violet
Yellow	550	Violet
Orange-red	600	Blue-green
Red	700	Green

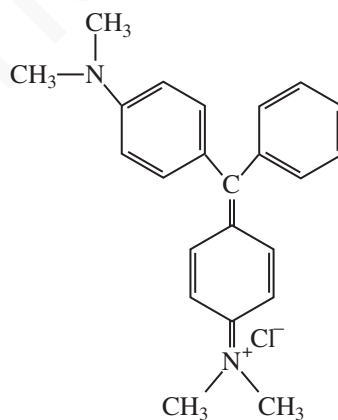β-Carotene (pigment from carrots): λ_{max} = 452 nm, **orange**
Cyanidin (blue pigment of cornflower): λ_{max} = 545 nm, **blue**
Malachite green (a triphenylmethane dye): λ_{max} = 617 nm, **green**
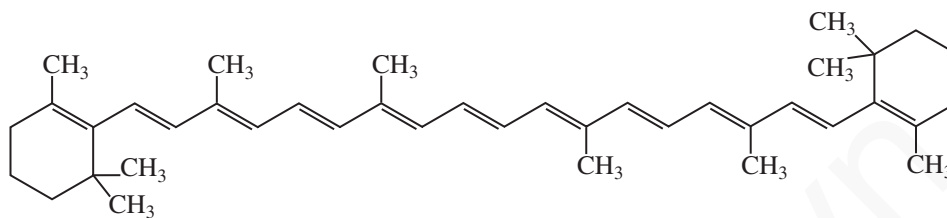
β-Carotene (a carotenoid, which is a class of plant pigments)
λ_{max} = 452 nm
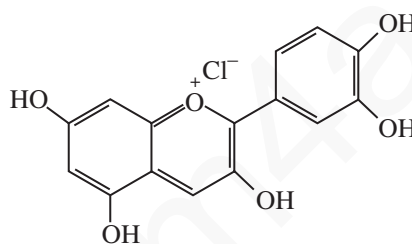
Cyanidin chloride (an anthocyanin, another class of plant pigments)
λ_{max} = 545 nm

Malachite green (a triphenylmethane dye)
λ_{max} = 617 nm

7.17 WHAT TO LOOK FOR IN AN ULTRAVIOLET SPECTRUM: A PRACTICAL GUIDE

It is often difficult to extract a great deal of information from a UV spectrum used by itself. It should be clear by now that a UV spectrum is most useful when at least a general idea of the structure is already known; in this way, the various empirical rules can be applied. Nevertheless, several generalizations can

serve to guide our use of UV data. These generalizations are a good deal more meaningful when combined with infrared and NMR data—which can, for instance, definitely identify carbonyl groups, double bonds, aromatic systems, nitro groups, nitriles, enones, and other important chromophores. In the absence of infrared or NMR data, the following observations should be taken only as guidelines:

1. *A single band of low-to-medium intensity (ε = 100 to 10,000) at wavelengths less than 220 nm* usually indicates an $n \rightarrow \sigma^*$ transition. Amines, alcohols, ethers, and thiols are possibilities, provided the nonbonded electrons are not included in a conjugated system. An exception to this generalization is that the $n \rightarrow \pi^*$ transition of cyano groups ($-C\equiv N :$) appears in this region. However, this is a weak transition ($\varepsilon < 100$), and the cyano group is easily identified in the infrared. Do not neglect to look for N$-$H, O$-$H, C$-$O, and S$-$H bands in the infrared spectrum.

2. *A single band of low intensity (ε = 10 to 100) in the region 250 to 360 nm, with no major absorption at shorter wavelengths (200 to 250 nm)*, usually indicates an $n \rightarrow \pi^*$ transition. Since the absorption does not occur at long wavelength, a simple, or unconjugated, chromophore is indicated, generally one that contains an O, N, or S atom. Examples of this may include C$=$O, C$=$N, N$=$N, $-NO_2$, $-COOR$, $-COOH$, or $-CONH_2$. Once again, infrared and NMR spectra should help a great deal.

3. *Two bands of medium intensity (ε = 1,000 to 10,000), both with λ_{max} above 200 nm*, generally indicate the presence of an aromatic system. If an aromatic system is present, there may be a good deal of fine structure in the longer-wavelength band (in nonpolar solvents only). Substitution on the aromatic rings increases the molar absorptivity above 10,000, particularly if the substituent increases the length of the conjugated system.

   In polynuclear aromatic substances, a third band appears near 200 nm, a band that in simpler aromatics occurs below 200 nm, where it cannot be observed. Most polynuclear aromatics (and heterocyclic compounds) have very characteristic intensity and band-shape (fine-structure) patterns, and they may often be identified via comparison to spectra that are available in the literature. The textbooks by Jaffé and Orchin and by Scott, which are listed in the references at the end of this chapter, are good sources of spectra.

4. *Bands of high intensity (ε = 10,000 to 20,000) that appear above 210 nm* generally represent either an α,β-unsaturated ketone (check the infrared spectrum), a diene, or a polyene. The greater the length of the conjugated system, the longer the observed wavelength. For dienes, the λ_{max} may be calculated using the Woodward–Fieser Rules (Section 7.10).

5. *Simple ketones, acids, esters, amides, and other compounds containing both π systems and unshared electron pairs show two absorptions:* an $n \rightarrow \pi^*$ transition at longer wavelengths (>300 nm, low intensity) and a $\pi \rightarrow \pi^*$ transition at shorter wavelengths (<250 nm, high intensity). With conjugation (enones), the λ_{max} of the $\pi \rightarrow \pi^*$ band moves to longer wavelengths and can be predicted by Woodward's Rules (Section 7.12). The ε value usually rises above 10,000 with conjugation, and as it is very intense, it may obscure or bury the weaker $n \rightarrow \pi^*$ transition.

   For α,β-unsaturated esters and acids, Nielsen's Rules (Section 7.13) may be used to predict the position of λ_{max} with increasing conjugation and substitution.

6. *Compounds that are highly colored* (have absorption in the visible region) are likely to contain a long-chain conjugated system or a polycyclic aromatic chromophore. Benzenoid compounds may be colored if they have enough conjugating substituents. For nonaromatic systems, usually a minimum of four to five conjugated chromophores are required to produce absorption in the visible region. However, some simple nitro, azo, nitroso, α-diketo, polybromo, and polyiodo compounds may also exhibit color, as may many compounds with quinoid structures.
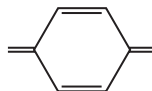
## PROBLEMS

***1.** The ultraviolet spectrum of benzonitrile shows a primary absorption band at 224 nm and a secondary band at 271 nm.

(a) If a solution of benzonitrile in water, with a concentration of 1×10^{-4} molar, is examined at a wavelength of 224 nm, the absorbance is determined to be 1.30. The cell length is 1 cm. What is the molar absorptivity of this absorption band?

(b) If the same solution is examined at 271 nm, what will be the absorbance reading ($\varepsilon = 1000$)? What will be the intensity ratio, I_0/I?

*2. Draw structural formulas that are consistent with the following observations:

(a) An acid $C_7H_4O_2Cl_2$ shows a UV maximum at 242 nm.

(b) A ketone $C_8H_{14}O$ shows a UV maximum at 248 nm.

(c) An aldehyde $C_8H_{12}O$ absorbs in the UV with $\lambda_{max} = 244$ nm.

***3.** Predict the UV maximum for each of the following substances:

(a)

$$CH_2=CH-\overset{\overset{\textstyle O}{\|}}{C}-CH_3$$

(b)

(c)

(d)

(e)

(f)

(g)

(h)

(i)

(j)
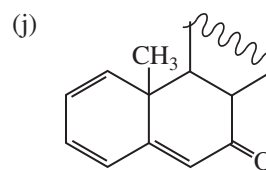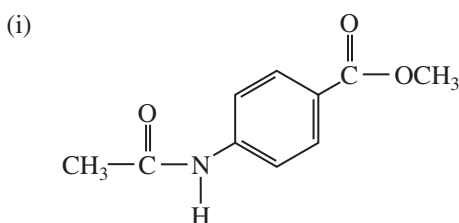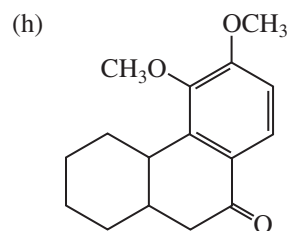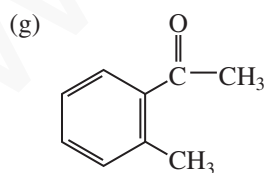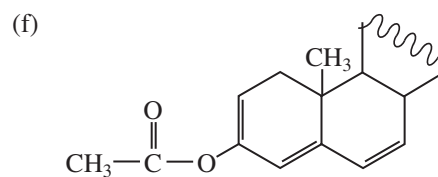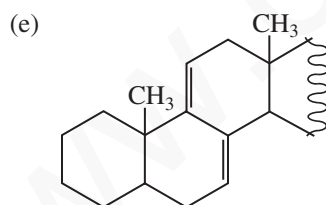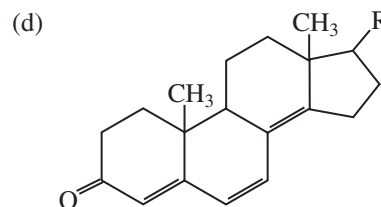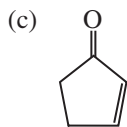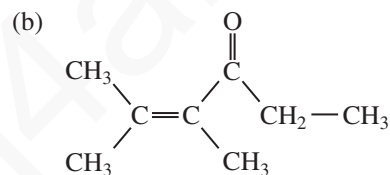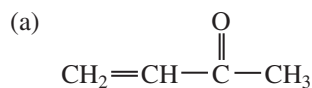
*4. The UV spectrum of acetone shows absorption maxima at 166, 189, and 279 nm. What type of transition is responsible for each of these bands?

*5. Chloromethane has an absorption maximum at 172 nm, bromomethane shows an absorption at 204 nm, and iodomethane shows a band at 258 nm. What type of transition is responsible for each band? How can the trend of absorptions be explained?

*6. What types of electronic transitions are possible for each of the following compounds?
   (a) Cyclopentene
   (b) Acetaldehyde
   (c) Dimethyl ether
   (d) Methyl vinyl ether
   (e) Triethylamine
   (f) Cyclohexane

7. Predict and explain whether UV/visible spectroscopy can be used to distinguish between the following pairs of compounds. If possible, support your answers with calculations.
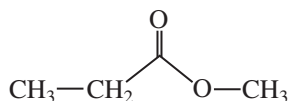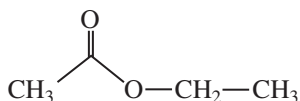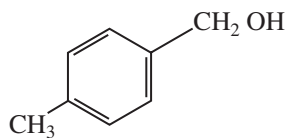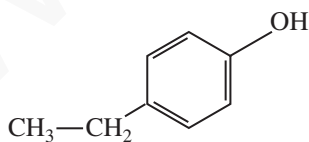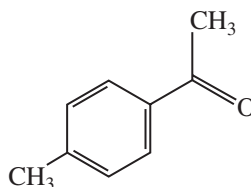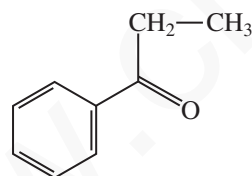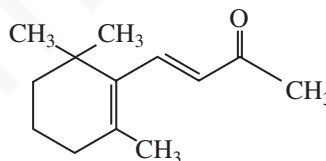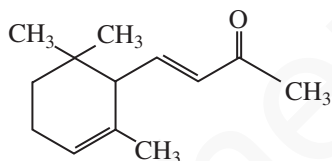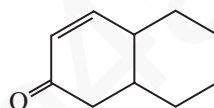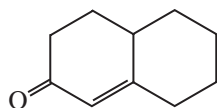
8. (a) Predict the UV maximum for the reactant and product of the following photochemical reaction:
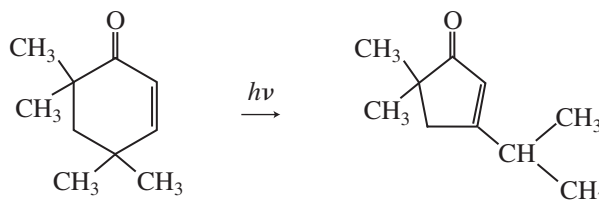
(b) Is UV spectroscopy a good way to distinguish the reactant from the product?

(c) How would you use infrared spectroscopy to distinguish between the reactant and the product?

(d) How would you use proton NMR to distinguish between the reactant and the product (two ways)?

(e) How could you distinguish between the reactant and the product by using DEPT NMR (see Chapter 10)?

REFERENCES

American Petroleum Institute Research Project 44, *Selected Ultraviolet Spectral Data*, Vols. I–IV, Thermodynamics Research Center, Texas A&M University, College Station, Texas, 1945–1977.

Friedel, R. A., and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, New York, 1951.

Graselli, J. G., and W. M. Ritchey, eds., *Atlas of Spectral Data and Physical Constants*, CRC Press, Cleveland, OH, 1975.

Hershenson, H. M., *Ultraviolet Absorption Spectra: Index for 1954–1957*, Academic Press, New York, 1959.

Jaffé, H. H., and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, John Wiley and Sons, New York, 1964.

Parikh, V. M., *Absorption Spectroscopy of Organic Molecules*, Addison–Wesley Publishing Co., Reading, MA, 1974, Chapter 2.

Scott, A. I., *Interpretation of the Ultraviolet Spectra of Natural Products*, Pergamon Press, New York, 1964.

Silverstein, R. M., F. X. Webster, and D. J. Kiemle *Spectrometric Identification of Organic Compounds*, 7th ed., John Wiley and Sons, New York, 2005.

Stern, E. S., and T. C. J. Timmons, *Electronic Absorption Spectroscopy in Organic Chemistry*, St. Martin's Press, New York, 1971.

Website

http://webbook.nist.gov/chemistry/
The National Institute of Standards and Technology (NIST) has developed the WebBook. This site includes UV/visible spectra, gas phase infrared spectra, and mass spectral data for compounds.