# 7.13 $\alpha,\beta$ -UNSATURATED ALDEHYDES, ACIDS, AND ESTERS

 $\alpha,\beta$ -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  $\alpha,\beta$ -unsaturated acids and esters that are similar to those for enones (Table 7.9).

Consider 2-cyclohexenoic and 2-cycloheptenoic acids as examples:

COOH

$$\alpha, \beta$$
-dialkyl

Double bond is in a six-membered ring, adds nothing

 $\alpha, \beta$ -dialkyl

Double bond is in a seven-membered ring

 $\alpha, \beta$ -dialkyl

Double bond is in a seven-membered ring

 $\alpha, \beta$ -dialkyl

 $\alpha, \beta$ -dialkyl

# 

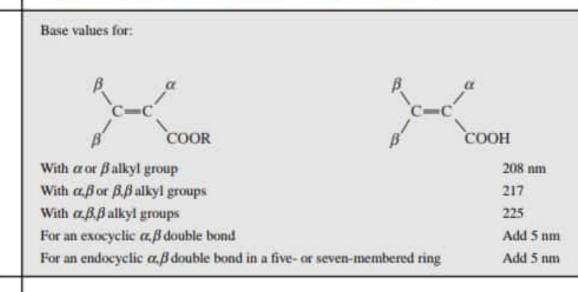
200	100
Parent	208 nm
With $\alpha$ or $\beta$ alkyl groups	220
With $\alpha, \beta$ or $\beta, \beta$ alkyl groups	230
With $\alpha, \beta, \beta$ alkyl groups	242

#### 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  $\pi \to \pi^+$  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



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

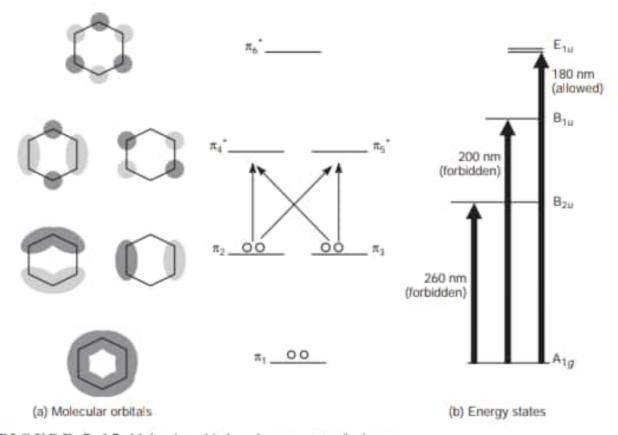


FIGURE 7.17 Molecular orbitals and energy states for benzene.

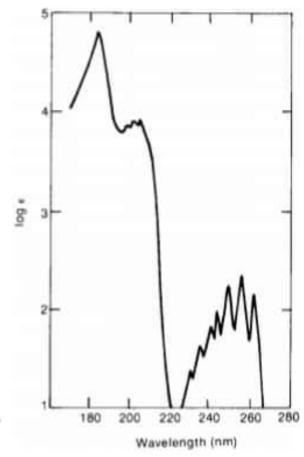


FIGURE 7.18 Ultraviolet spectrum of benzene.
(From Petruska, J., Journal of Chemical Physics, 34
(1961): 1121. Reprinted by permission.)

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  $\pi$  system through resonance.

The more available these n electrons are for interaction with the  $\pi$  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  $\pi$  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  $n \to \pi^*$  transitions. If an n electron is excited into the extended  $\pi^*$  chromophore, the atom from which it was removed becomes electron deficient, while the  $\pi$  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  $\pi^*$  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

	Prin	Primary		Secondary	
Substituent	λ (nm)		λ (nm)	E	
—Н	203.5	7,400	254	204	
-он	210.5	6,200	270	1,450	
-0-	235	9,400	287	2,600	
-NH <sub>2</sub>	230	8,600	280	1,430	
-NH <sub>1</sub> *	203	7,500	254	165	
-соон	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  $\pi$  system. Consequently, the spectrum of anilinium ion is almost identical to that of benzene.

## B. Substituents Capable of $\pi$ -Conjugation

Substituents that are themselves chromophores usually contain  $\pi$  electrons. Just as in the case of n electrons, interaction of the benzene-ring electrons and the  $\pi$  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

		Prim	iary	Second	dary
Substituent		λ (nm)	e	λ (nm)	ε
	-Н	203.5	7,400	254	204
_	-CH <sub>3</sub>	206.5	7,000	261	225
***	-C1	209.5	7,400	263.5	190
Electron- releasing	-Br	210	7,900	261	192
substituents	-OH	210.5	6,200	270	1,450
	-OCH <sub>3</sub>	217	6,400	269	1,480
	-NH <sub>2</sub>	230	8,600	280	1,430
Electron- withdrawing substituents	-CN	224	13,000	271	1,000
	-соон	230	11,600	273	970
	-COCH <sub>3</sub>	245.5	9,800		
	-СНО	249.5	11,400		
	$-NO_2$	268.5	7,800		

TABLE 7.11
ULTRAVIOLET MAXIMA FOR VARIOUS AROMATIC COMPOUNDS

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:

$$\begin{bmatrix} H_2 \ddot{N} & & & \\ & \ddots & & \\ & & & \\ & & & \\ \end{bmatrix} - \dot{N} & & & \\ & & & \\ O^- & & & \\ \end{bmatrix} - \dot{N} & & \\ O^- & & \\ \end{bmatrix}$$

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	
R = alkyl or ring residue		24
R = H		25
R = OH or Oalkyl		23
Increment for each substituent:		
-Alkyl or ring residue	o, m	
	p	1
—OH, —OCH <sub>3</sub> , or —Oalkyl	o, m	
	p	2
-0-	0	1
	m	2
	p	7
—CI	o, m	
	p	1
—Br	o, m	
	р	1
-NH <sub>2</sub>	o, m	- 1
	p	5
-NHCOCH <sub>3</sub>	o, m	2
	р	-4
—NHCH <sub>3</sub>	p	7
-N(CH <sub>3</sub> ) <sub>2</sub>	o, m	2
	p	8

Following are two sample applications of these rules:

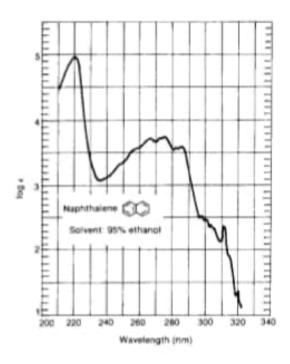
Parent chromophore: 246 nm 
$$o$$
-Ring residue: 3  $m$ -OH:  $2 \times 7 = 14$   $p$ -OH:  $\frac{2}{25}$   $\frac{2}{251 \text{ nm}}$  Observed: 253 nm Observed: 270 nm

## 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.



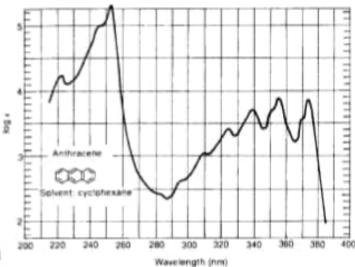


FIGURE 7.19 Ultraviolet spectra of naphthalene and anthracene. (From Friedel, R. A., and M. Orchin, *Ultraviolet* Spectra of Aromatic Compounds, John Wiley and Sons, New York, 1951. Reprinted by permission.)

Heterocyclic molecules have electronic transitions that include combinations of  $\pi \to \pi^*$  and  $n \to \pi^*$  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).

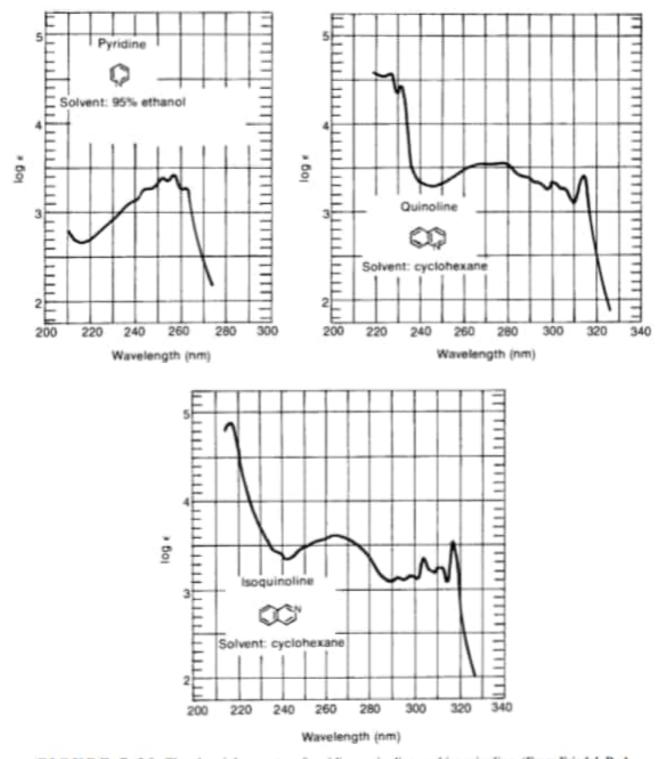


FIGURE 7.20 The ultraviolet spectra of pyridine, quinoline, and isoquinoline, (From Friedel, R. A., and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, New York, 1951.
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#### 7.15 MODEL COMPOUND STUDIES

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  $\pi$  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<sub>15</sub>H<sub>12</sub>. 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.

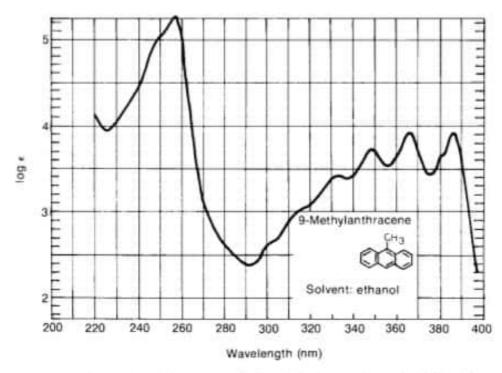


FIGURE 7.21 The ultraviolet spectrum of 9-methylanthracene. (From Friedel, R. A., and M. Orchin, Ultraviolet Spectra of Aromatic Compounds, John Wiley and Sons, New York, 1951. Reprinted by permission.)

#### 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.

TABLE 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
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):  $λ_{max} = 452 \text{ nm}$ , orange Cyanidin (blue pigment of cornflower):  $λ_{max} = 545 \text{ nm}$ , blue Malachite green (a triphenylmethane dye):  $λ_{max} = 617 \text{ nm}$ , green

β-Carotene (a carotenoid, which is a class of plant pigments)  $\lambda_{max} = 452 \text{ nm}$ 

Cyanidin chloride (an anthocyanin, another class of plant pigments)  $\lambda_{max} = 545 \text{ nm}$ 

Malachite green (a triphenylmethane dye)  $\lambda_{max} = 617 \text{ nm}$ 

## 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:

- A single band of low-to-medium intensity (ε = 100 to 10,000) at wavelengths less than 220 nm usually indicates an n → σ\* 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 → π\* transition of cyano groups (-C=N:) appears in this region. However, this is a weak transition (ε < 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.</li>
- 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→ π\* 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<sub>2</sub>, -COOR, -COOH, or -CONH<sub>2</sub>. 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<sub>max</sub> 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<sub>max</sub> 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 → π\* transition at longer wavelengths (>300 nm, low intensity) and a π → π\* transition at shorter wavelengths (<250 nm, high intensity). With conjugation (enones), the λ<sub>max</sub> of the π → π\* 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 → π\* transition.

For  $\alpha,\beta$ -unsaturated esters and acids, Nielsen's Rules (Section 7.13) may be used to predict the position of  $\lambda_{max}$  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.