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 details provided by infrared and nuclear magnetic resonance (NMR) spectra, can lead to valuable structural proposals.

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 10.1 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.

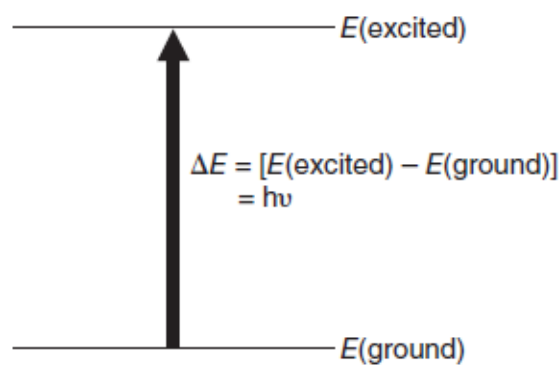


FIGURE 10.1 The excitation process.

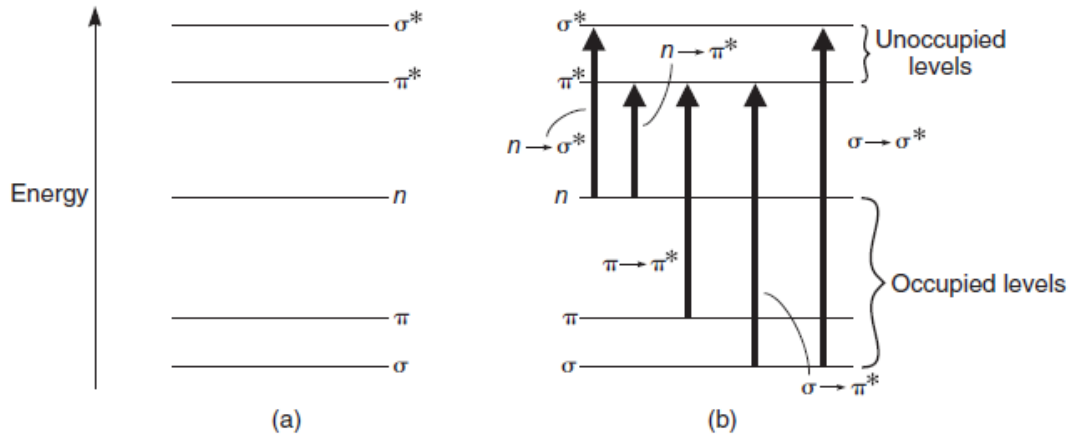


FIGURE 10.2 Electronic energy levels and transitions.

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

Increasing energy ↑	$\sigma \longrightarrow \sigma^*$	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

Electronic energy levels in aromatic molecules are more complicated than the ones depicted here. Section 10.14 will describe the electronic transitions of aromatic compounds.

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.

PRINCIPLES OF ABSORPTION SPECTROSCOPY

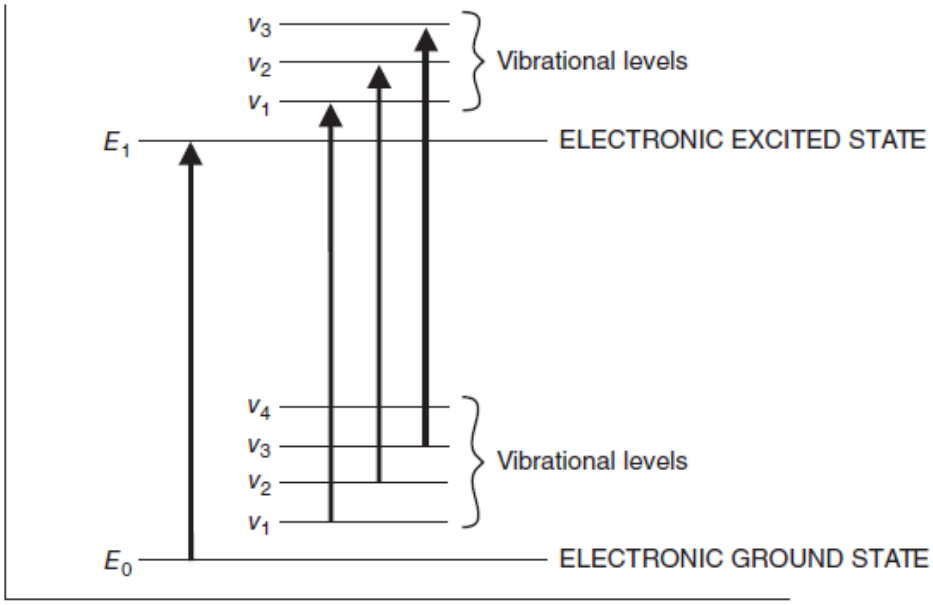


FIGURE 10.3 Electronic transitions with vibrational transitions superimposed. (Rotational levels, which are very closely spaced within the vibrational levels, are omitted for clarity.)

$A = \log(I_0/I) = \varepsilon c l$ for a given wavelength

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 10.1) 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.

10.4 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.

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.

10.5 PRESENTATION OF SPECTRA

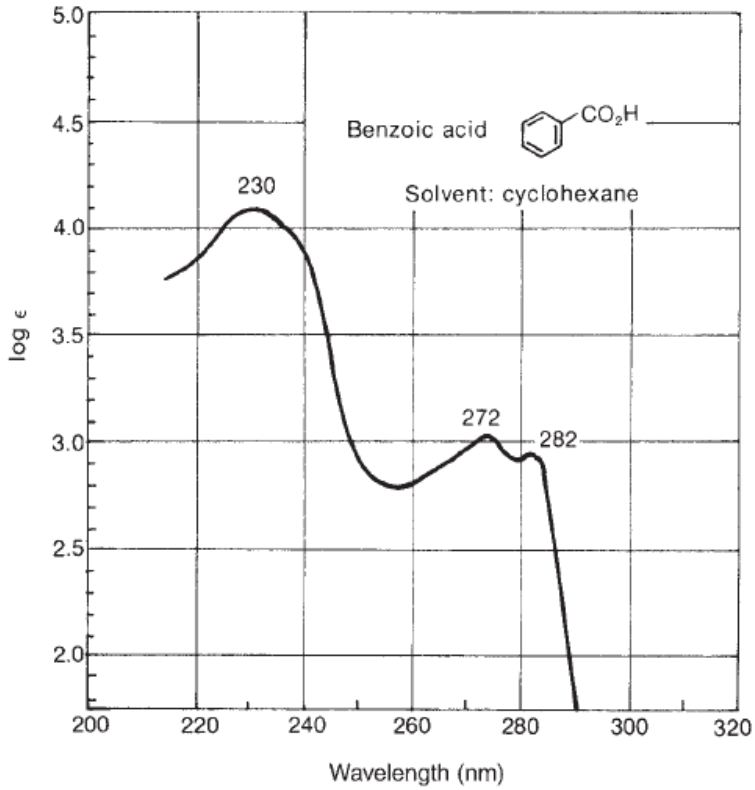


FIGURE 10.4 Ultraviolet spectrum of benzoic acid in cyclohexane. (From Friedel, R. A., and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, New York, 1951. Reprinted by permission.)

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

10.6 SOLVENTS

Of the solvents listed in Table 10.1, 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.

TABLE 10.1
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

A second criterion for a good solvent is its effect on the fine structure of an absorption band. Figure 10.5 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.

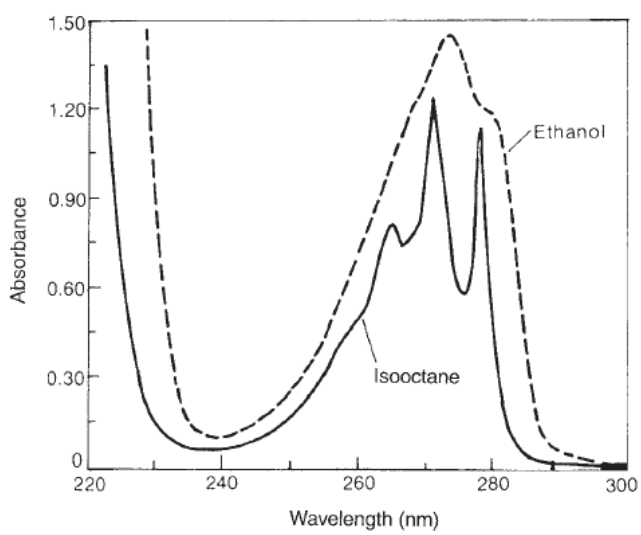


FIGURE 10.5 Ultraviolet spectra of phenol in ethanol and in isooctane. (From Coggeshall, N. D., and E. M. Lang, *Journal of the American Chemical Society, 70*, 1948: 3288. Reprinted by permission.)

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 10.2 illustrates typical effects of a series of solvents on an electronic transition.

TABLE 10.2
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

Table 10.3 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).

TABLE 10.3
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_2CO	$\pi \rightarrow \pi^*$	180	3.0
$R_2C{=}CR_2$	$\pi \rightarrow \pi^*$	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

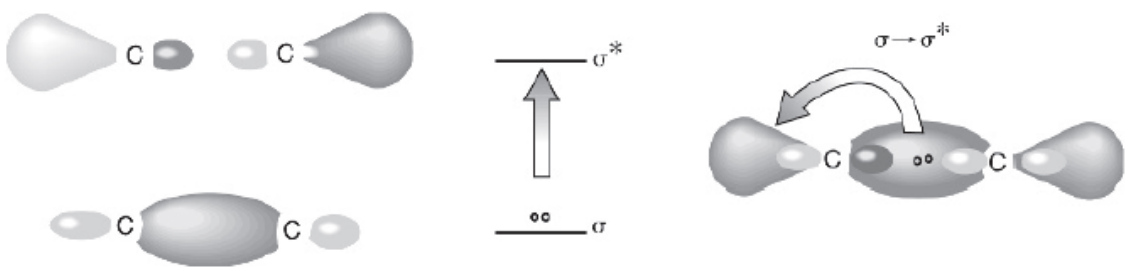


FIGURE 10.6 $\sigma \rightarrow \sigma^*$ transition.

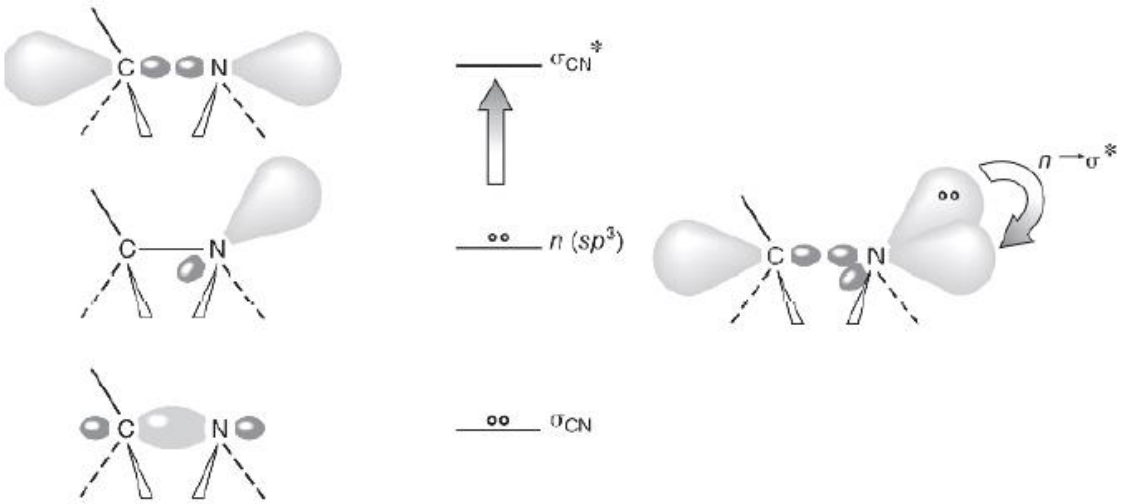


FIGURE 10.7 $n \rightarrow \sigma^*$ transition.

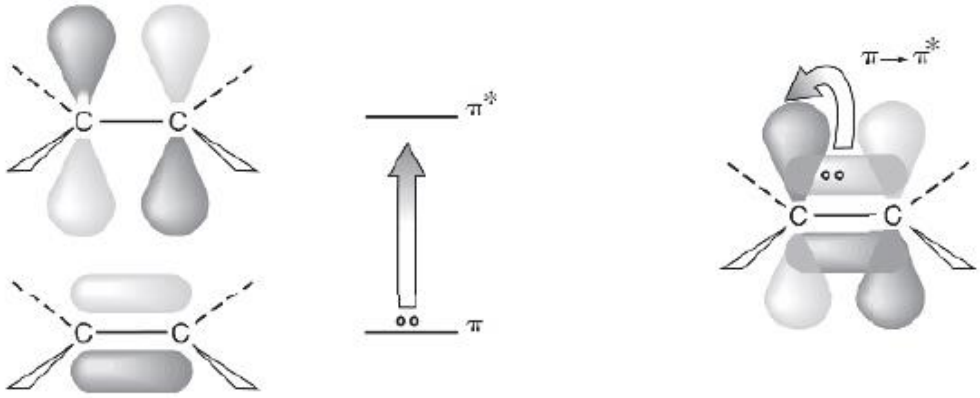


FIGURE 10.8 $\pi \rightarrow \pi^*$ transition.

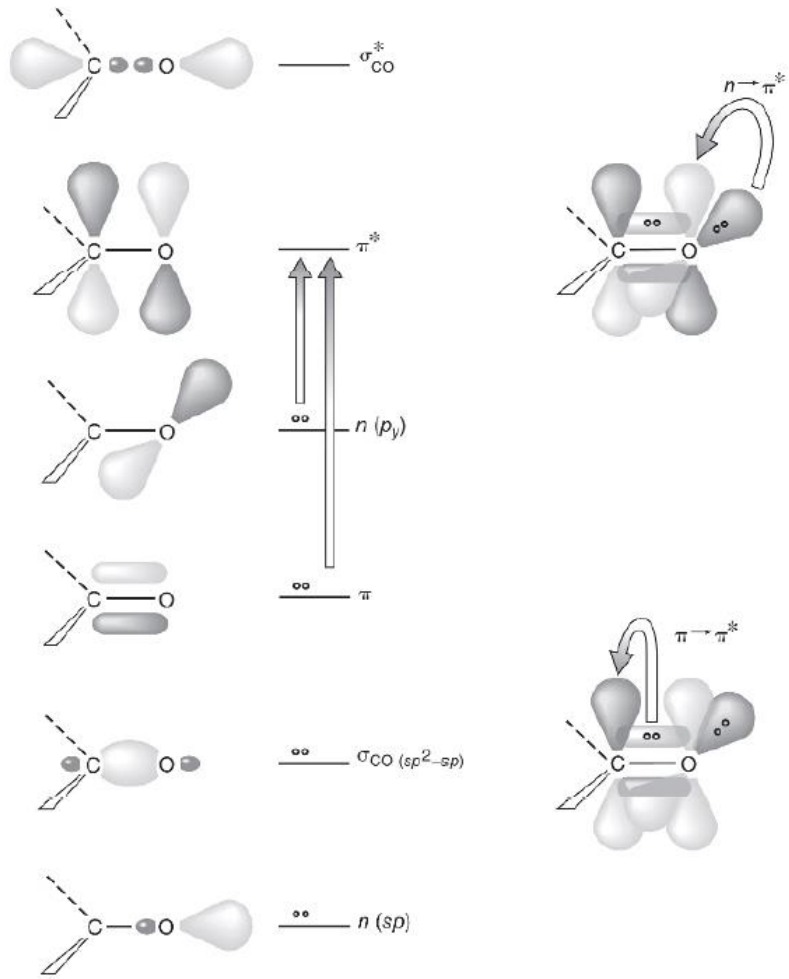


FIGURE 10.9 Electronic transitions of the carbonyl group.

10.8 THE EFFECT OF CONJUGATION

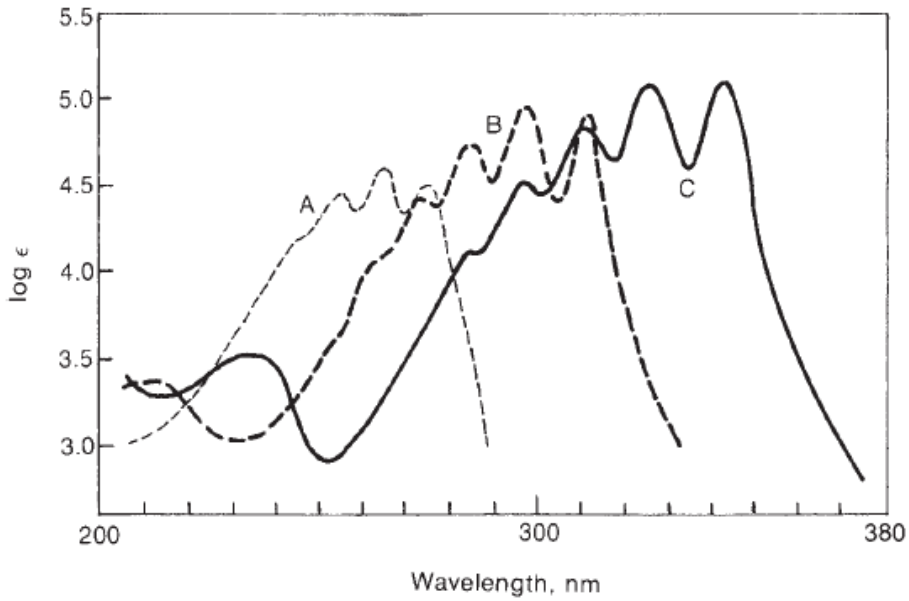


FIGURE 10.10 $CH_3{-}(CH{=}CH)_n{-}CH_3$ ultraviolet spectra of dimethylpolyenes. (a) $n = 3$; (b) $n = 4$; (c) $n = 5$. (From Nayler, P., and M. C. Whiting, *Journal of the Chemical Society*, 1955: 3042.)

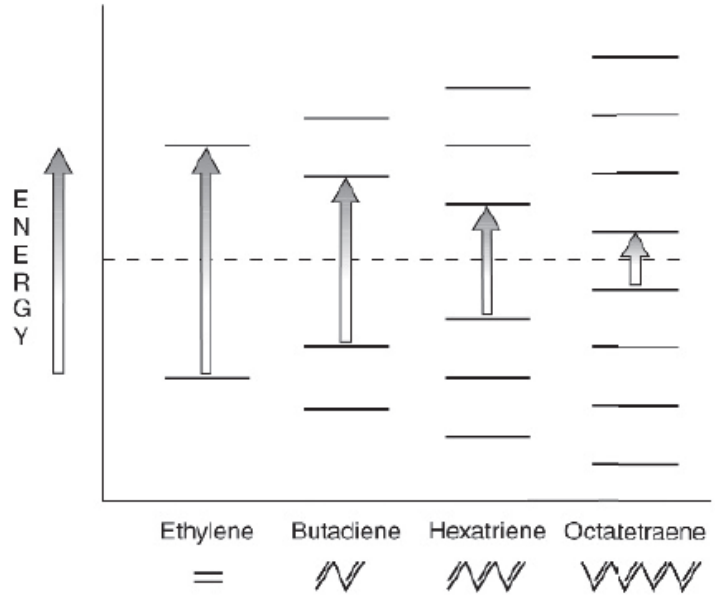
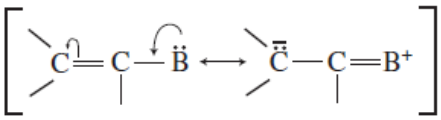


FIGURE 10.13 A comparison of the $\pi \rightarrow \pi^*$ energy gap in a series of polyenes of increasing chain length.

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.



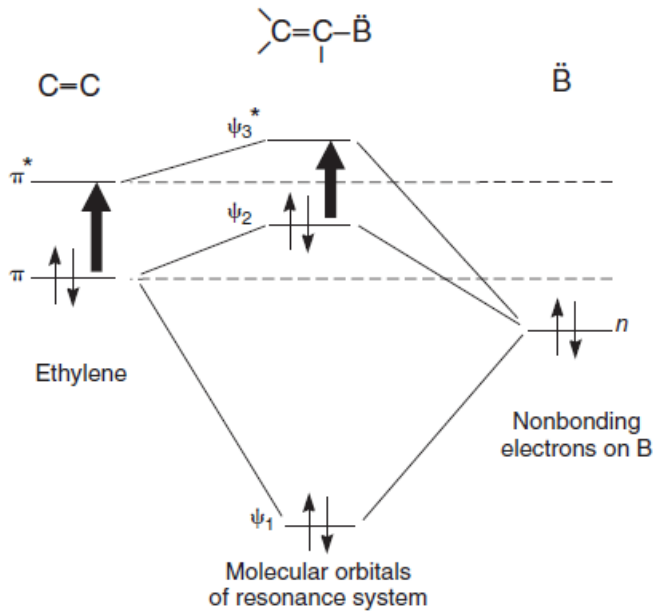
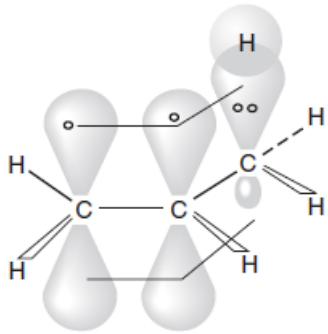


FIGURE 10.14 Energy relationships of the new molecular orbitals and the interacting π system and its auxochrome.

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.