

Ultra-Violet / Visible Spectroscopy- Section 3

Effective Factors on Absorbance

- Solvent characteristics:
 - ✓ non/polar
 - ✓ non/protic
 - ✓ hydrogen bonding ability
 - ✓ solvent-solute interactions can affect electron levels
 - ✓ hence affect E & ν & λ required for electron transitions
- Concentration of solute: number of chromophores
- Effective factors can change:
 - ✓ position of absorption curve
 - ✓ intensity of absorption curve
 - ✓ shape of absorption curve

TABLE 7.1
SOLVENT CUTOFFS

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

Example: UV Absorption Curve of Phenol in Ethanol & Isooctane

position of absorption curve
intensity of absorption curve
shape & pattern of absorption curve

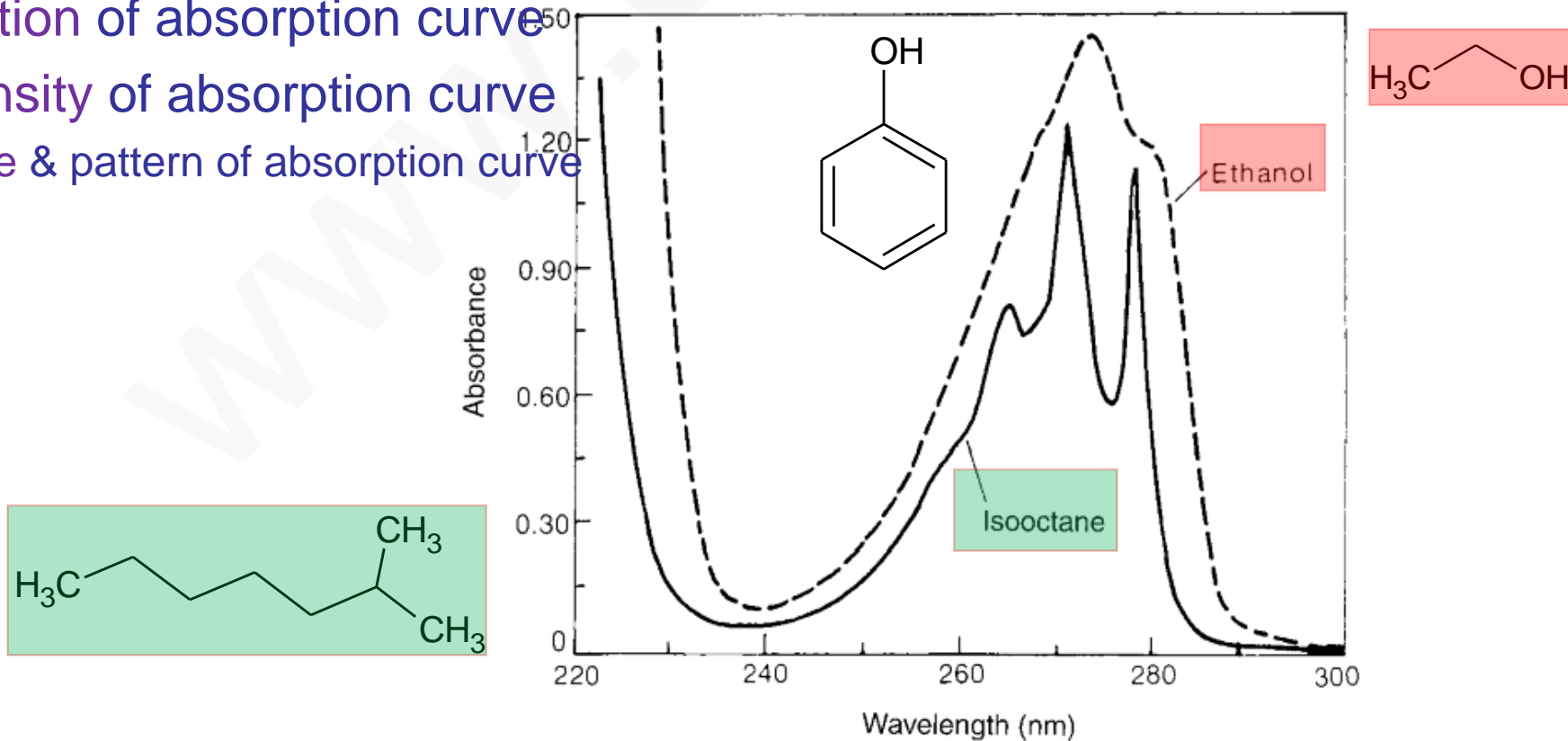


FIGURE 7.5 Ultraviolet spectra of phenol in ethanol and in isooctane. (From Coggeshall, N. D., and E. M. Lang, *Journal of the American Chemical Society*, 70 (1948): 3288. Reprinted by permission.)

Chromophore in UV Absorption

- Atoms & functional groups which are responsible for absorption of UV radiation
- Two common types of chromophores:
 - ✓ those which contain only π electrons: undergo π - π^* transitions
 - ✓ those which contain π electrons & nonbinding (n) electrons: provide two types of electron transitions: π - π^* & n - π^* transitions

Auxochrome in UV Absorption

- Auxochrome is also called color enhancing group
- Atoms & functional group which:
 - ✓ does **not** change sample's **absorption** characteristics
 - ✓ **changes** absorption characteristics of a **chromophore**
- Common auxochromes: OH; Me; OMe; X; amine

Common Changes in UV Absorption Curves

- **Red shift** or **bathochromic** effect:
 - ✓ shift the curve to **right** side:
 - ✓ shift λ_{\max} to **right** side: longer λ
 - ✓ by presence of auxochrome or by change in sample solvent
- **Blue shift** or **hypsochromic** effect:
 - ✓ shift the curve to **left** side:
 - ✓ shift λ_{\max} to **left** side: shorter λ
 - ✓ by removal of a conjugation or by change in sample solvent
- **Hypochromic** effect: hypo-chromism:
 - ✓ **decrease** the intensity of absorption
- **Hyperchromic** effect: hyper-chromism:
 - ✓ **increase** the intensity of absorption

Electron Transition for C-C Bond in Alkane

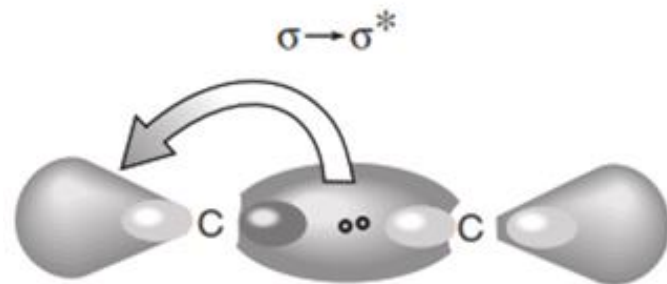
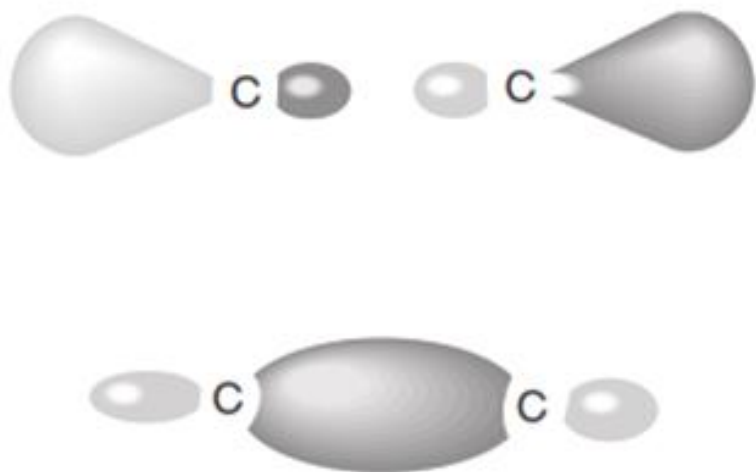
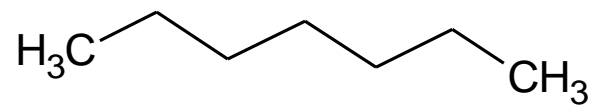
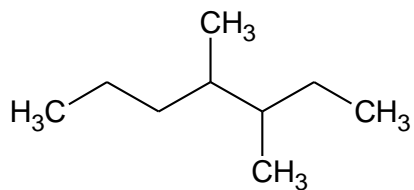


FIGURE 7.6 $\sigma \rightarrow \sigma^*$ transition.

Electron Transition for Functional Groups Possessing Non-Bonding Electron Pair

- Functional groups possessing non-bonding electron pair

Includes $n\text{-}\pi^*$ transitions:

- ✓ -O-H in alcohol (R-OH): 175-200nm
- ✓ -O-C in ether (R-O-R')
- ✓ -N-H in amine (R-NH₂; R-NH-R'; R-N(R')R''): 175-200nm

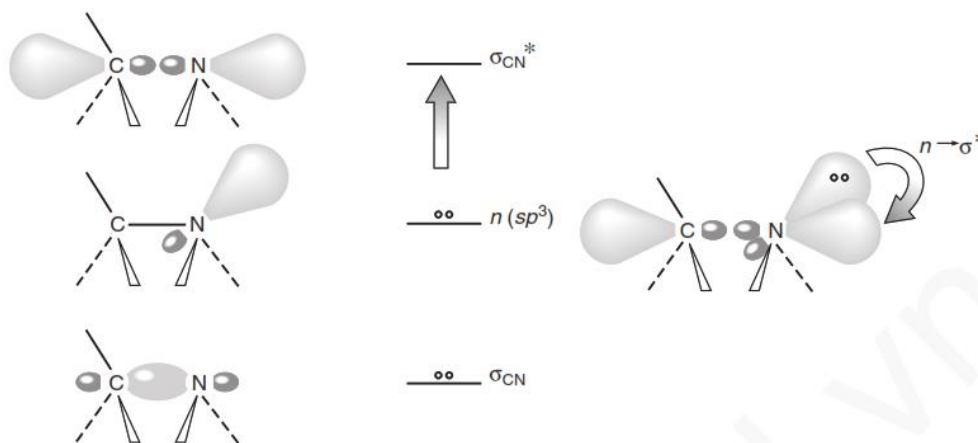


FIGURE 7.7 $n \rightarrow \sigma^*$ transition.

- ✓ -S-H in thiol (R-SH): 200-220nm
- ✓ -S-C in thio-ether (R-S-R')

Electron Transition for Un-Saturated Functional Groups: C-C Bond in Alkene

- Alkene: $\pi - \pi^*$ transition: $\lambda_{\max} = \dots$ nm
- Alkyne: $\pi - \pi^*$ transition: $\lambda_{\max} = \dots$ nm

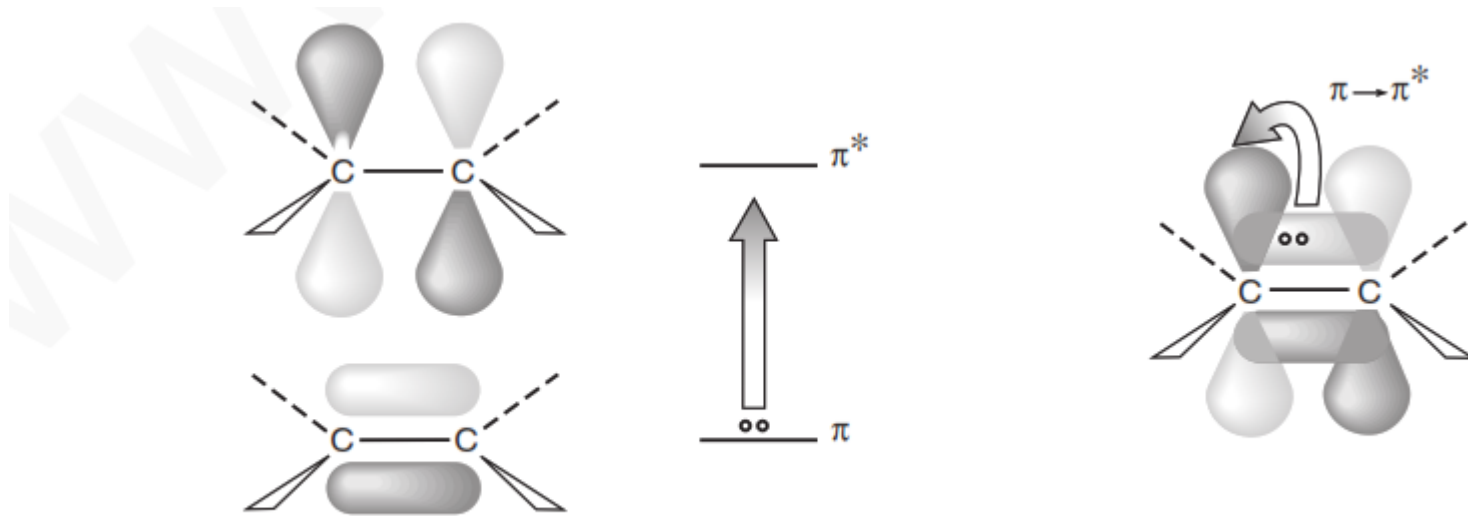


FIGURE 7.8 $\pi \rightarrow \pi^*$ transition.

Electron Transition for Alkene: Ethylene

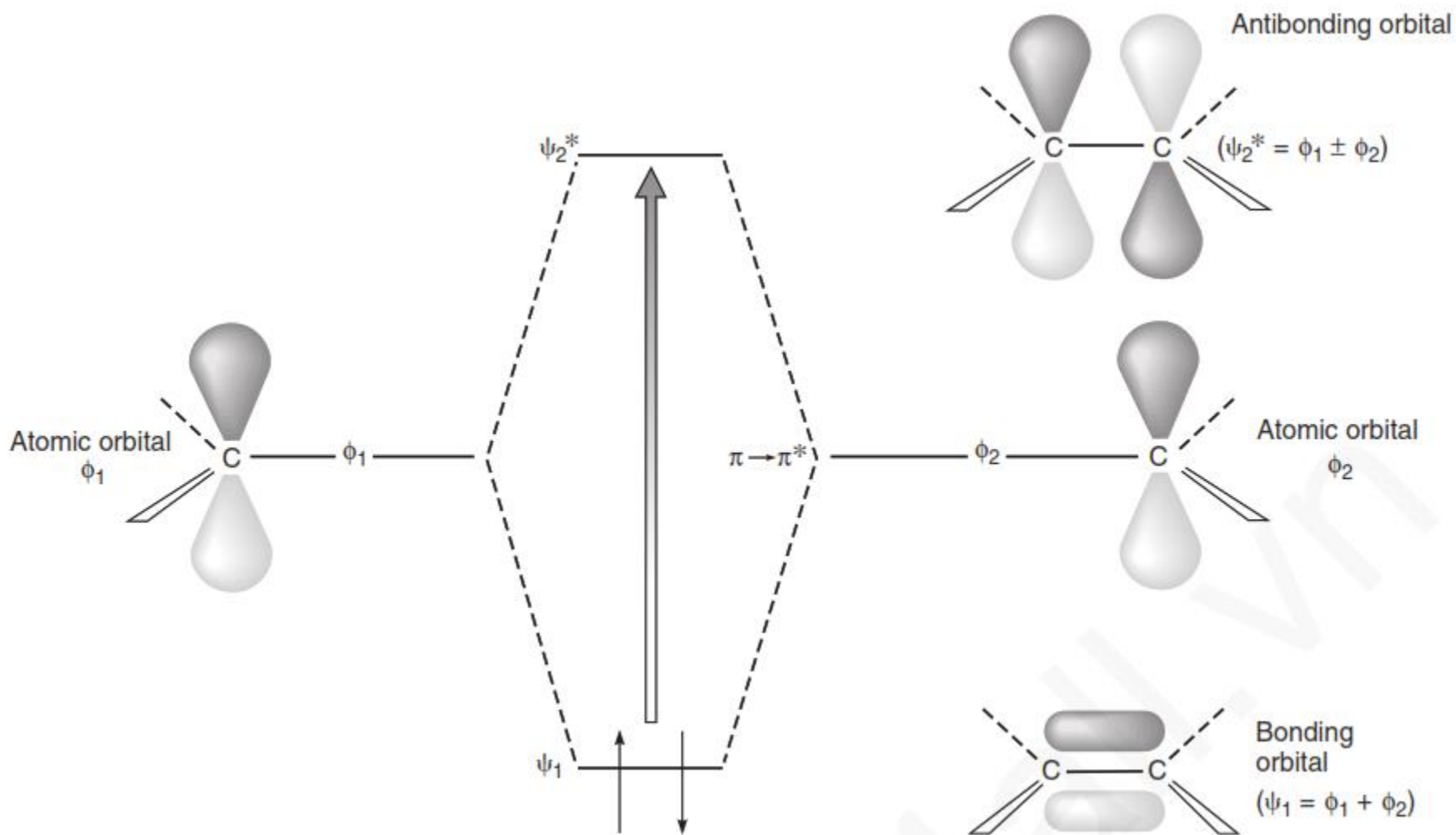


FIGURE 7.11 Formation of the molecular orbitals for ethylene.

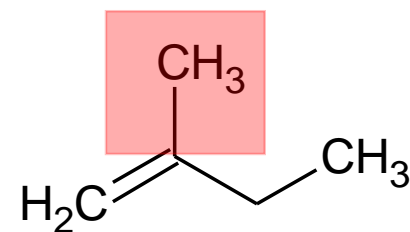
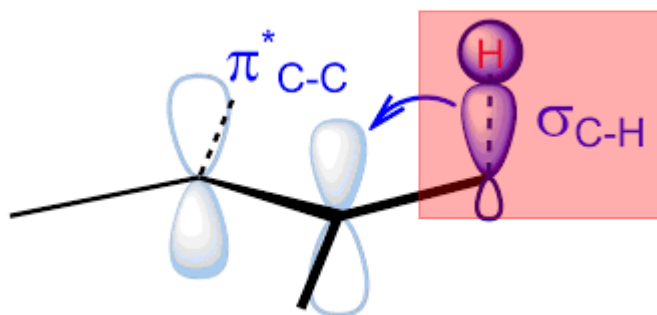
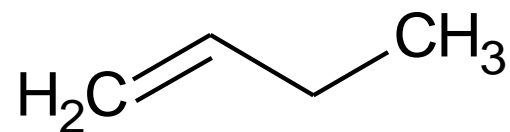
Electron Transition for Ethylene with Alkyl Group as Substitute: Hyper-conjugation

- Hyper-conjugation of $\sigma - \pi$ provides:

✓ bathochromic effect

&

✓ hyperchromic effect



Comparing Electron Transition for Ethylene & 1,3-Butadiene

- Conjugated dienes: $\lambda_{\text{max}}=217\text{-}245\text{nm}$; $\epsilon = 20,000$ to $26,000$

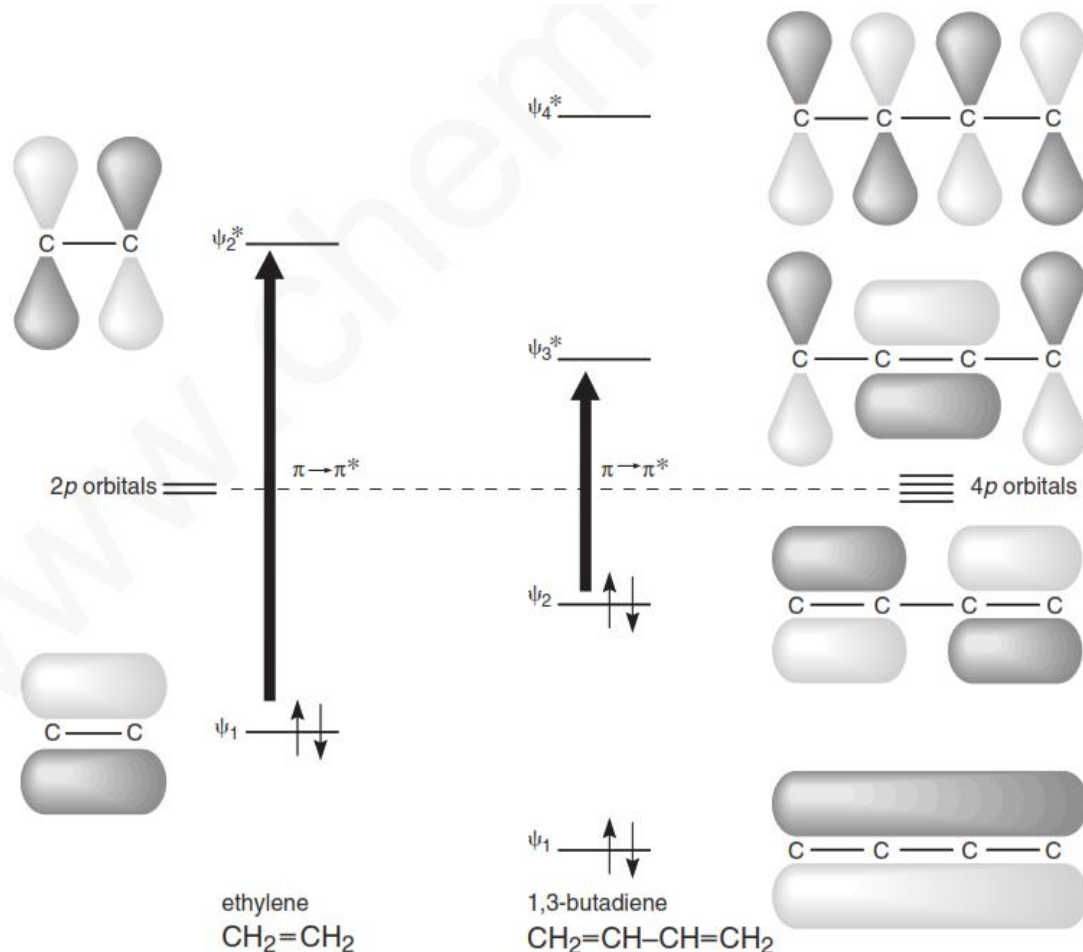
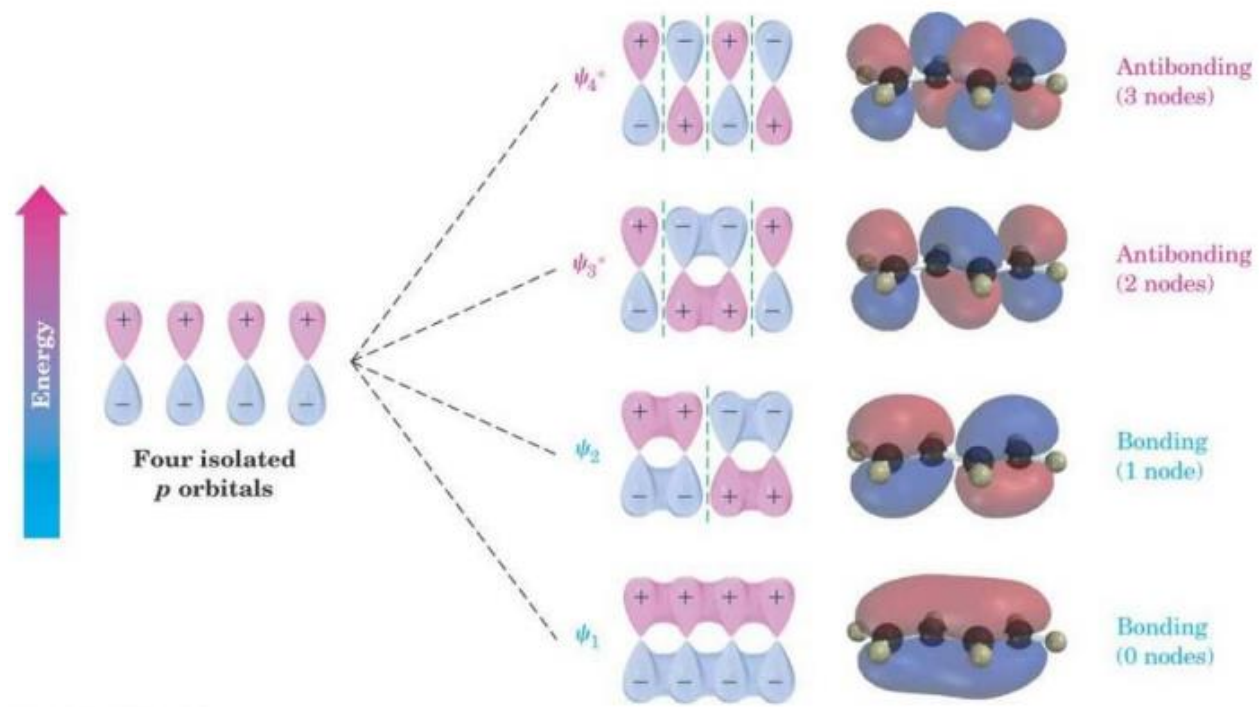
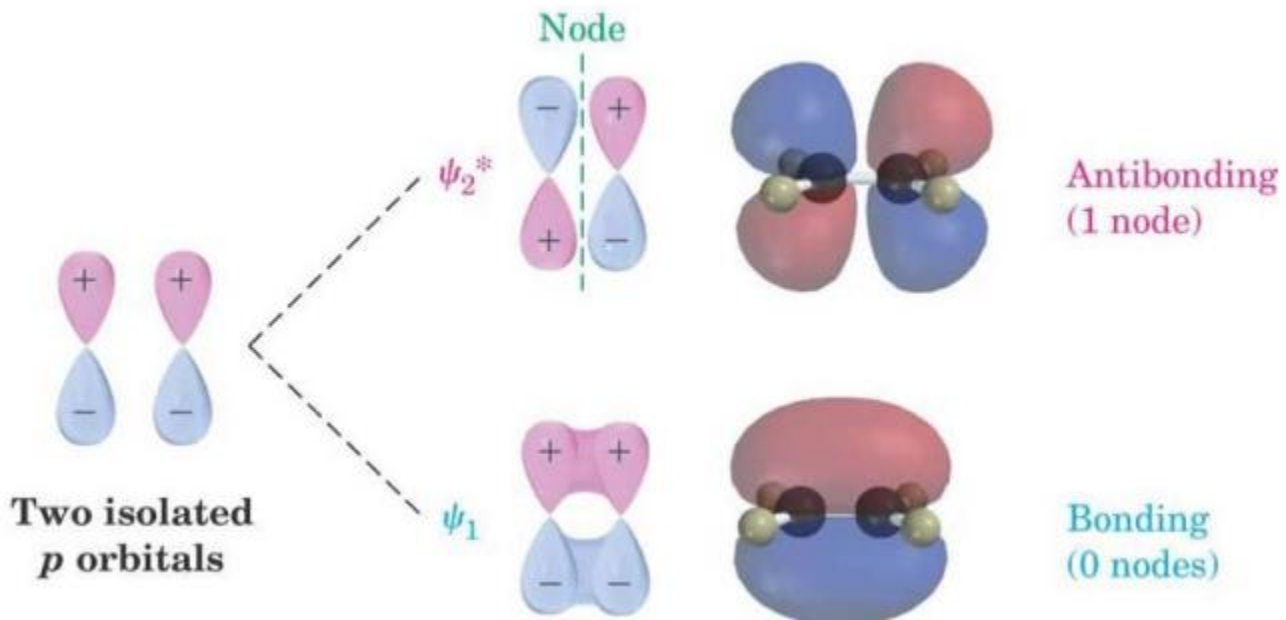
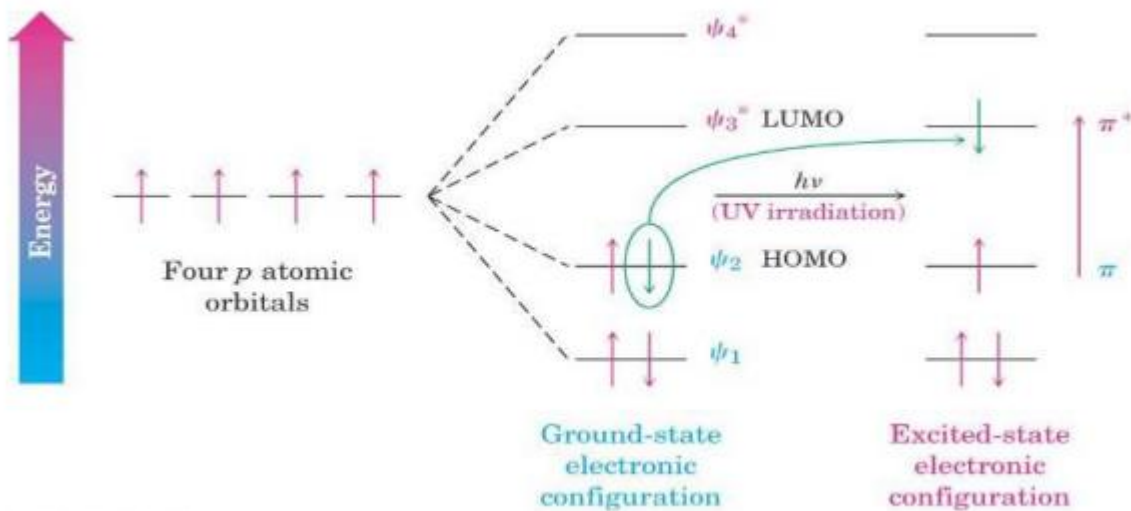


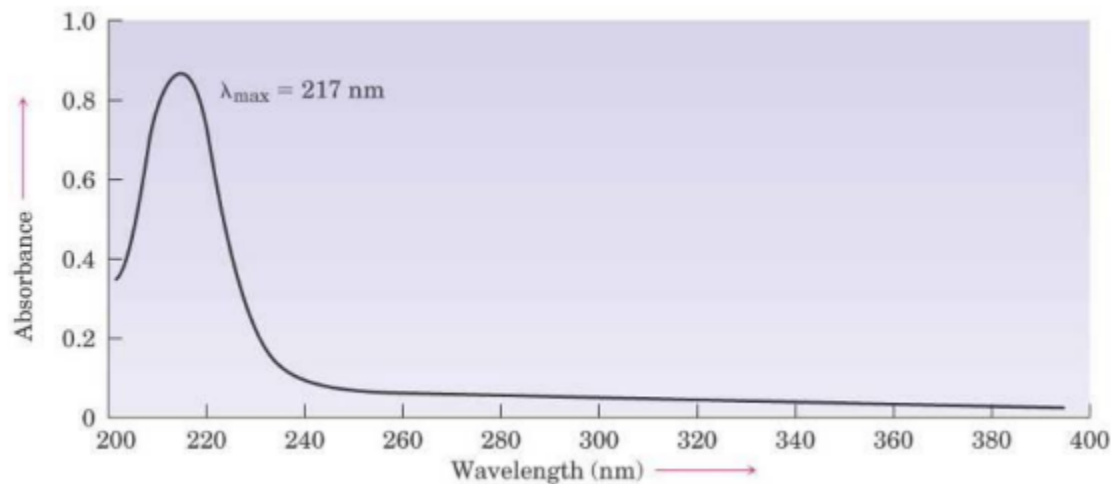
FIGURE 7.12 A comparison of the molecular orbital energy levels and the energy of the $\pi \rightarrow \pi^*$ transitions in ethylene and 1,3-butadiene.



UV Spectrum for Butadiene



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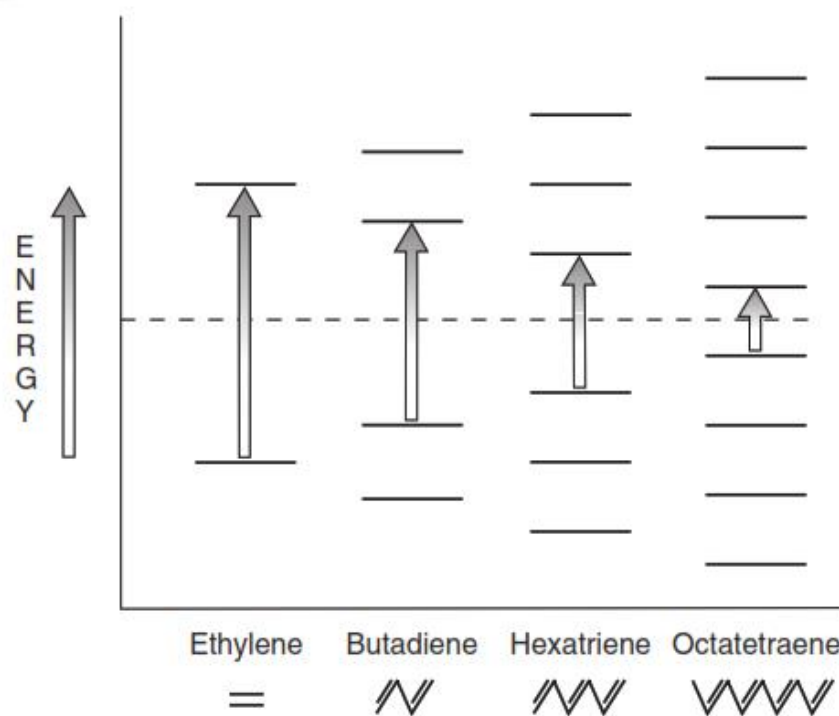
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Electron Transitions for Alkenes & Polyenes

- Polyenes as conjugated dienes:
- ✓ $\lambda_{\max} = 217 - 260 - \dots - 460 \dots \text{ nm}$; $\epsilon = 20,000 \text{ to } 35,000$

	$\lambda_{\max.} \text{ (nm)}$	ϵ
$-\text{C}=\text{C}-$	170	16 000
$-\text{C}=\text{C}-\text{C}=\text{C}-$	220	21 000
$-\text{C}=\text{C}-\text{C}=\text{C}-\text{C}=\text{C}-$	260	35 000

FIGURE 7.13 A comparison of the $\pi \rightarrow \pi^*$ energy gap in a series of polyenes of increasing chain length.



- Discuss about the effect of **alkyls** as substitutes on dienes.

UV Spectra for a Couple of Conjugated Dimethyl-Polyenes (n)

- A: $n = 3$
- B: $n = 4$
- C: $n = 5$

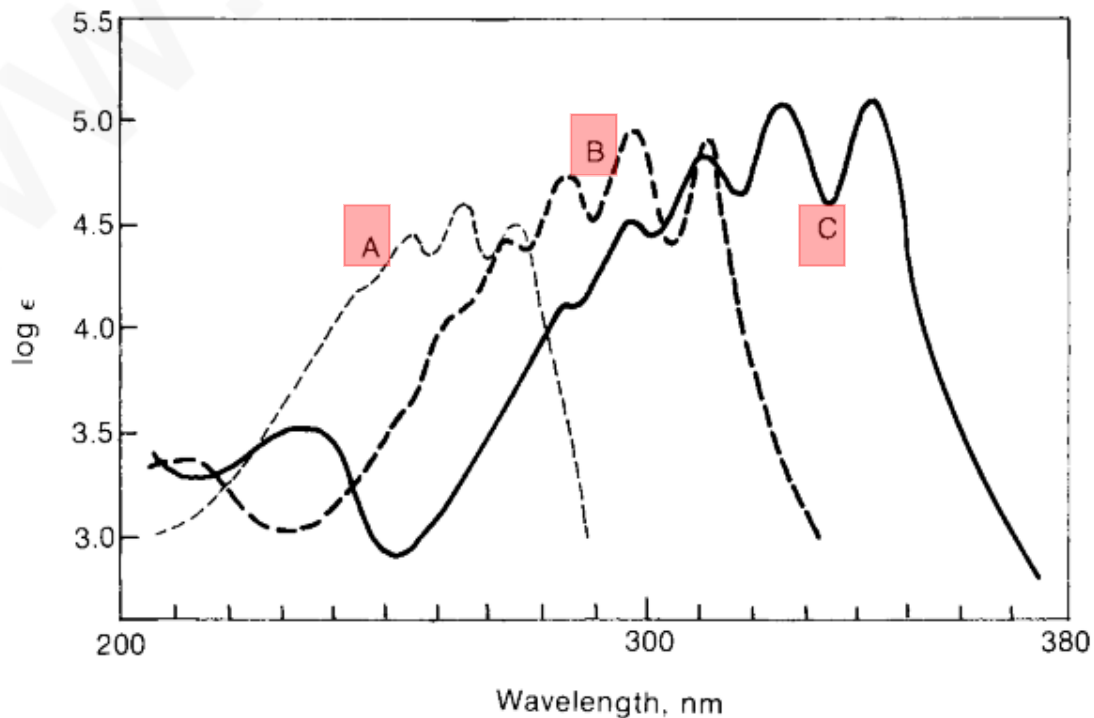
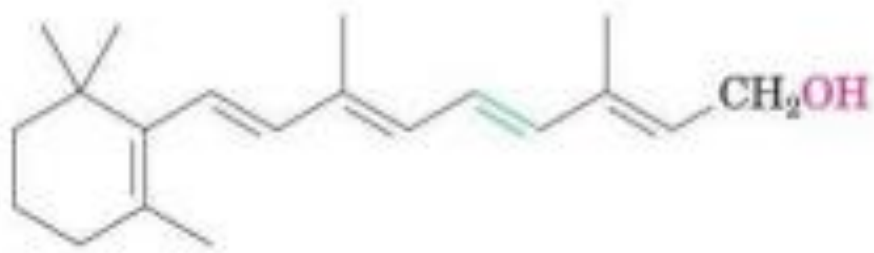
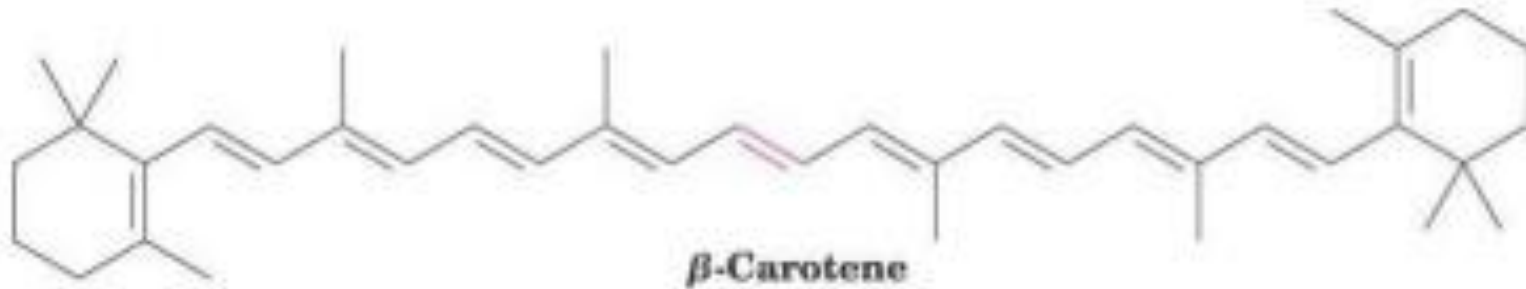


FIGURE 7.10 $\text{CH}_3-(\text{CH}=\text{CH})_n-\text{CH}_3$ ultraviolet spectra of dimethylpolyenes. (a) $n = 3$; (b) $n = 4$; (c) $n = 5$. (From Naylor, P., and M. C. Whiting, *Journal of the Chemical Society* (1955): 3042.)

Conjugated Alkenes & Carbonyls as Chromophores

TABLE 7.4
EFFECT OF CONJUGATION ON ELECTRONIC TRANSITIONS

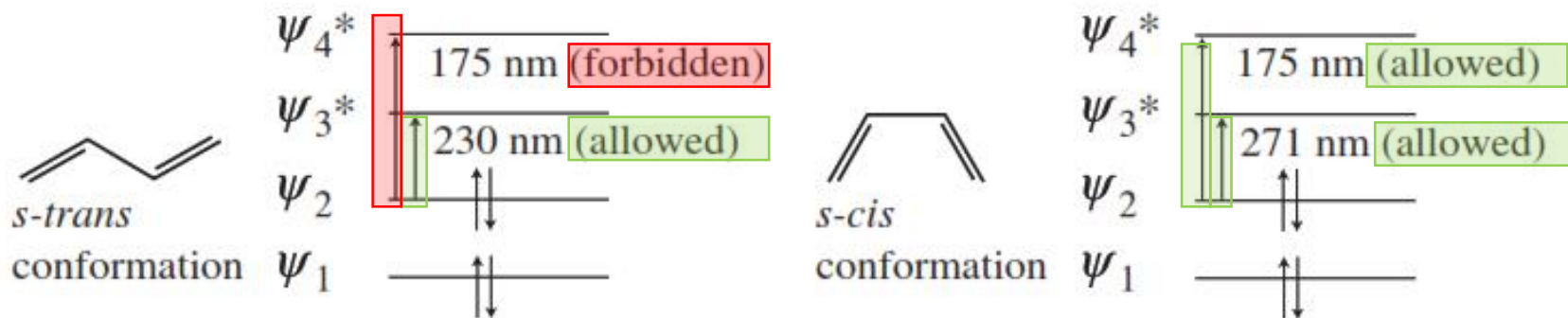
	λ_{\max} (nm)	ϵ
Alkenes		
Ethylene <chem>H2C=CH2</chem>	175	15,000
1,3-Butadiene <chem>H2C=CH-CH=CH2</chem>	217	21,000
1,3,5-Hexatriene <chem>H2C=CH-CH=CH-CH=CH2</chem>	258	35,000
β -Carotene (11 double bonds)	465	125,000
Ketones		
Acetone		
$\pi \rightarrow \pi^*$	189	900
$n \rightarrow \pi^*$	280	12
3-Buten-2-one		
$\pi \rightarrow \pi^*$	213	7,100
$n \rightarrow \pi^*$	320	27



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Electron Transitions for Stereoisomers (cis/trans) in Conjugated Alkenes (Butadiene)

- Compare allowed electron transitions in trans & cis conformations.



- Which λ is supposed to be observed as λ_{\max} for UV absorption of a sample of butadiene?

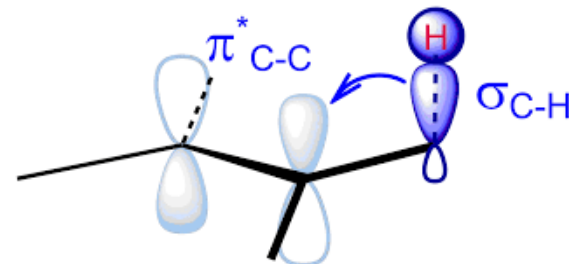
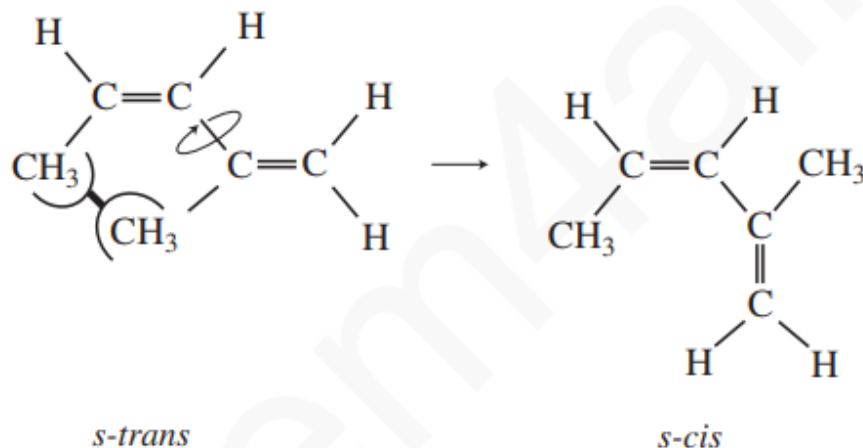
✓ conjugated dienes: $\lambda_{\max} = 217\text{-}245\text{nm}$; **insensitive** to the nature of the solvent

✓ cis conformation: longer λ & **less** intensity & **less** molar absorptivity (ϵ) is assumed

- How will absorbance be changed in λ & ϵ , if we have alkyl/s as substitute on butadiene? Next slide.

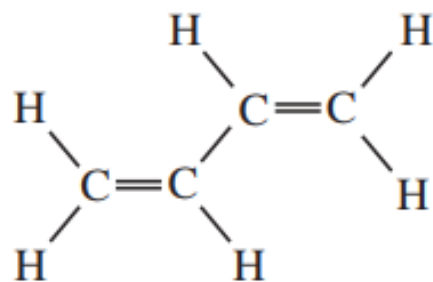
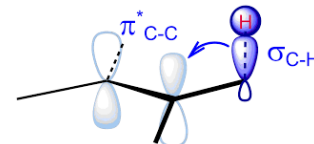
Electron Transitions for Dienes Possessing Alkyls as Substitutes

- Alkyl group provides **hyper-conjugation** of $\sigma - \pi$ on double bond's electronic characteristics:
 - hence alkyl group provides **bathochromic** effect on UV characteristics.
- Alkyl group in dienes provides **less intensity** due to the steric effect: **cis-isomer** is the more favorable isomer.

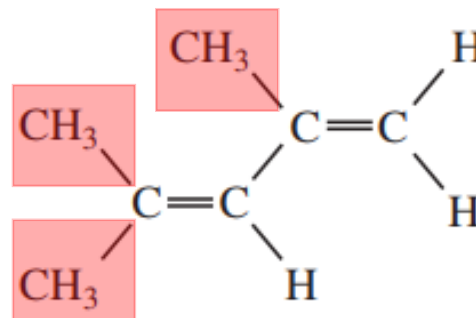


Woodward & Fieser Rules to Calculate Theoretical Maximum Absorbance Wavelength of Alkylated Dienes

- Inductive effect of alkyl: hyper-conjugation: σ - π conjugation
- Provide bathochromic effect:
- ✓ each methyl group: 5 nm bathochromic effect

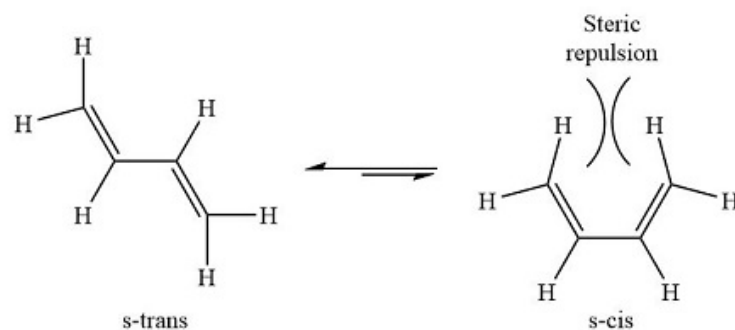
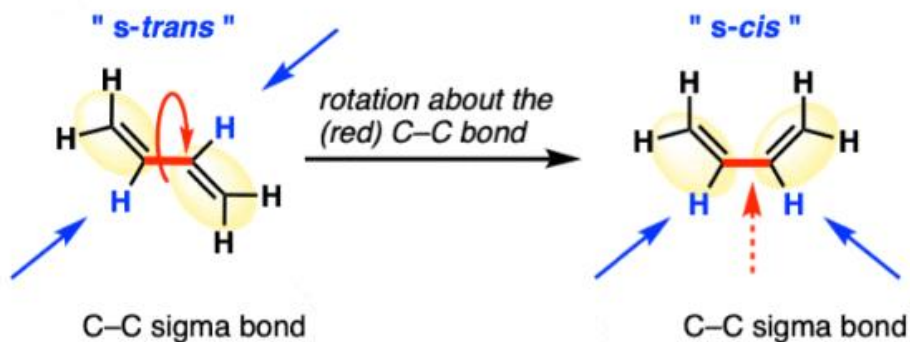


Transoid: 214 nm
Observed: 217 nm

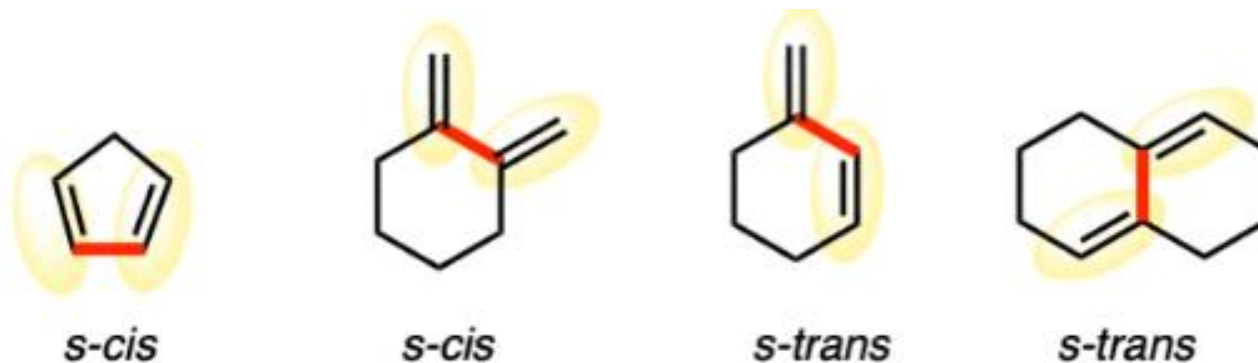


Transoid:	214 nm
Alkyl groups: $3 \times 5 =$	<u>15</u>
	229 nm
Observed:	228 nm

Compare Cis & Trans Butadiene Backbone

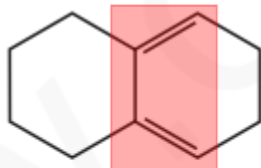


- In cyclic and locked structures:



Electron Transitions & Maximum Wavelength for Cyclic Dienes

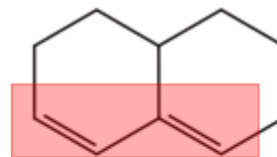
- Rigidity in conformation of **transoid** & **cisoid**, both.
- Two types due to steric conformation of double bonds:
 - ✓ homoannular diene (cisoid): **less** intensity & ϵ ; **longer** λ_{\max}
 - ✓ heteroannular diene (transoid): more intensity & ϵ ; shorter λ_{\max}



Homoannular diene (cisoid or *s-cis*)

Less intense, $\epsilon = 5,000\text{--}15,000$

λ longer (273 nm)



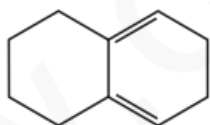
Heteroannular diene (transoid or *s-trans*)

More intense, $\epsilon = 12,000\text{--}28,000$

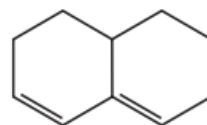
λ shorter (234 nm)

$$\Delta = 39$$

Woodward & Fieser Rules to Calculate Theoretical Maximum Absorbance Wavelength of Homo/Hetero-Annular Structures



Homoannular diene (cisoid or *s-cis*)



Heteroannular diene (transoid or *s-trans*)

TABLE 7.5
EMPIRICAL RULES FOR DIENES

	Homoannular (cisoid)	Heteroannular (transoid)
Parent	$\lambda = 253 \text{ nm}$	$\lambda = 214 \text{ nm}$
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

Electron Transition for Ethylene with a Substitute Possessing Lone Pair

- Hyper-conjugation:
 - ✓ extension of π system by resonance effect of lone pair
 - ✓ decrease conjugation due to inductive effect of heteroatom

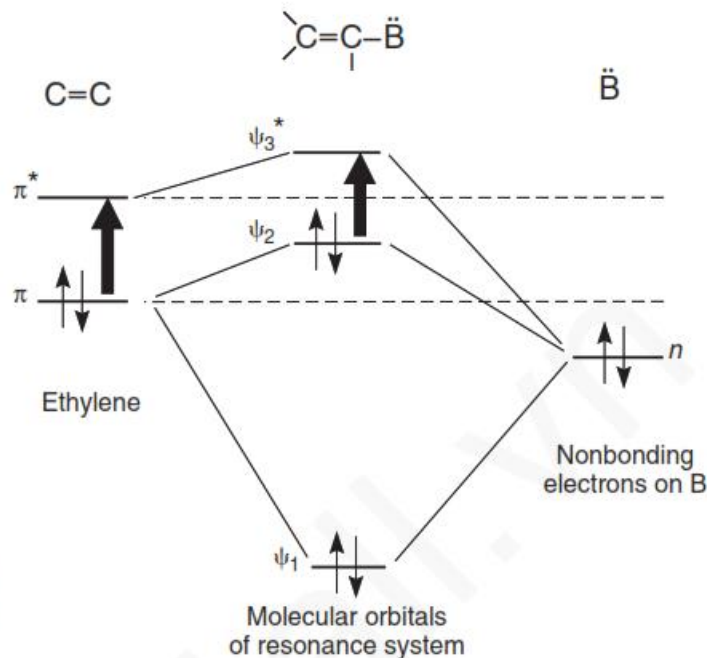
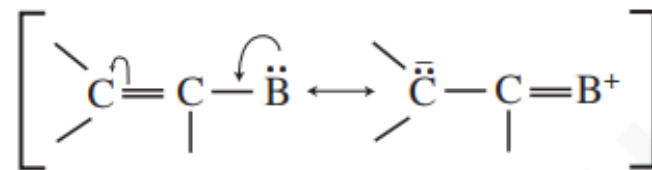
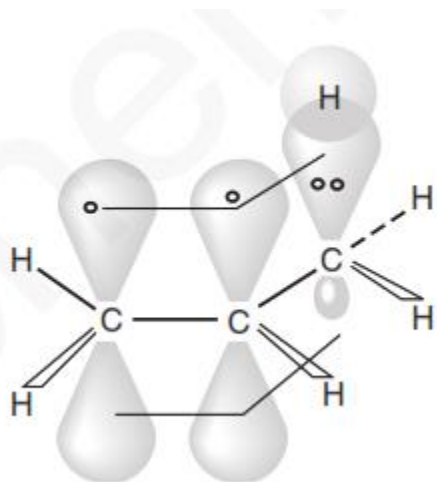


FIGURE 7.14 Energy relationships of the new molecular orbitals and the interacting π system and its auxochrome.