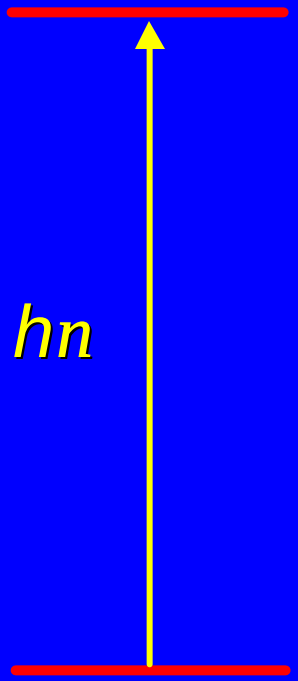
13.20

Ultraviolet-Visible (UV-VIS) Spectroscopy

Gives information about conjugated π electron systems

Transitions between electron energy states



gaps between electron energy levels are greater than those between vibrational levels

gap corresponds to wavelengths between 200 and 800 nm

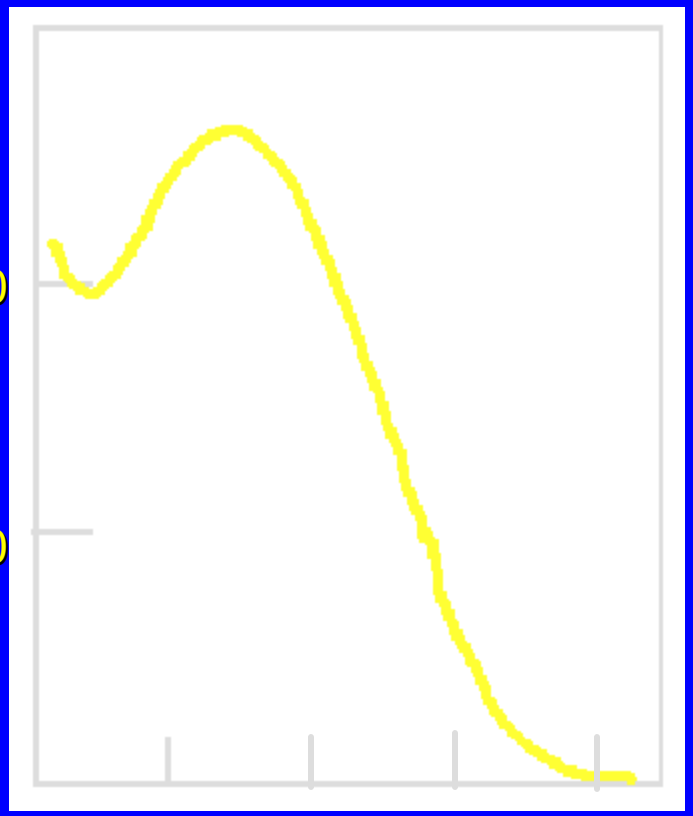
Conventions in UV-VIS

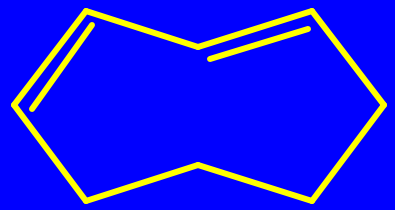
X-axis is wavelength in nm (high energy at left, low energy at right)

λ_{max} is the wavelength of maximum absorption and is related to electronic makeup of molecule—especially π electron system

Y axis is a measure of absorption of electromagnetic radiation expressed as molar absorptivity (ε)

UV Spectrum of cis,trans-1,3-cyclooctadiene

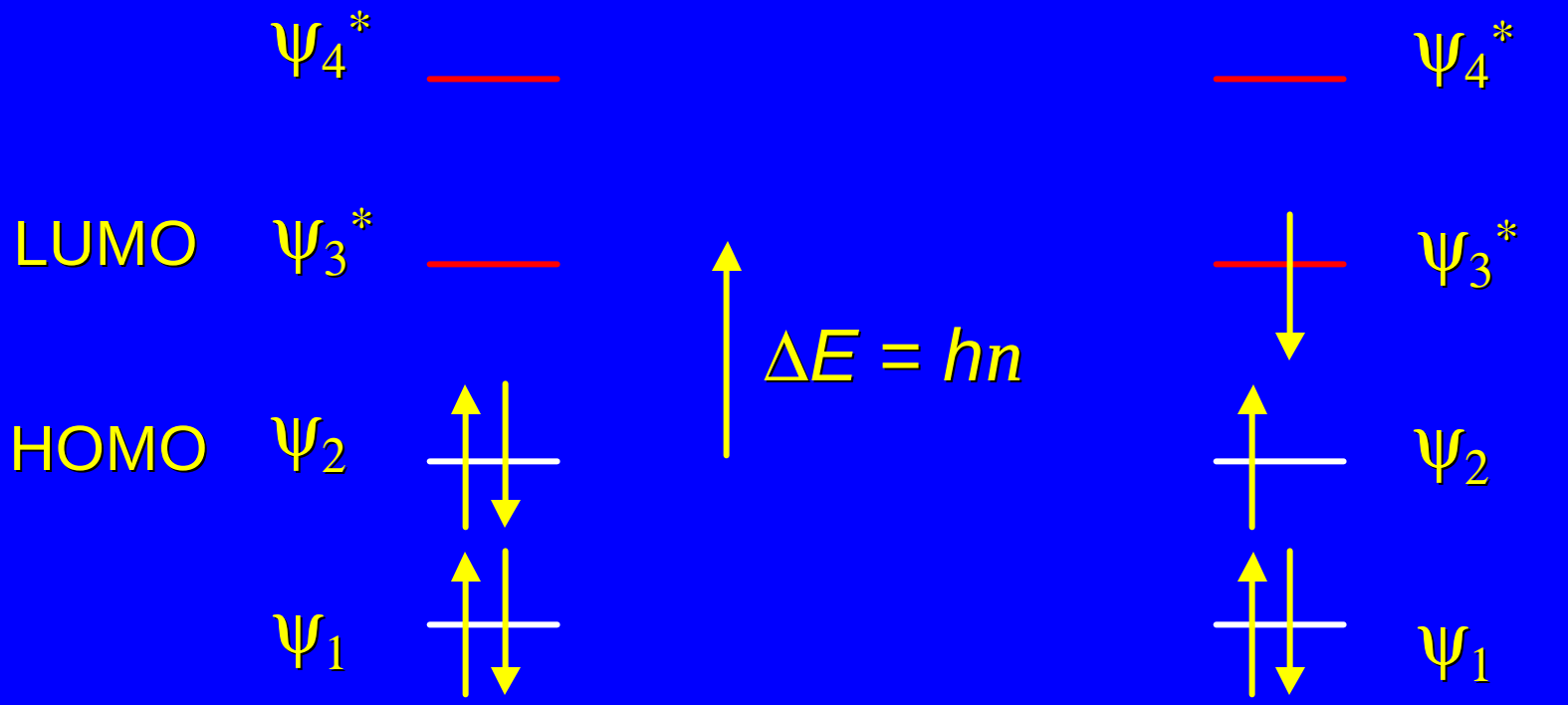




λ_{max} 230 nm

ε_{max} 2630

pÆp Transition in cis,trans-1,3-cyclooctadiene*



Most stable π-electron configuration

π-Electron configuration of excited state

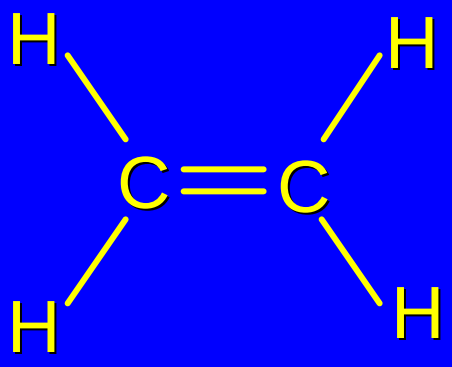
pÆp Transition in Alkenes*

HOMO-LUMO energy gap is affected by substituents on double bond

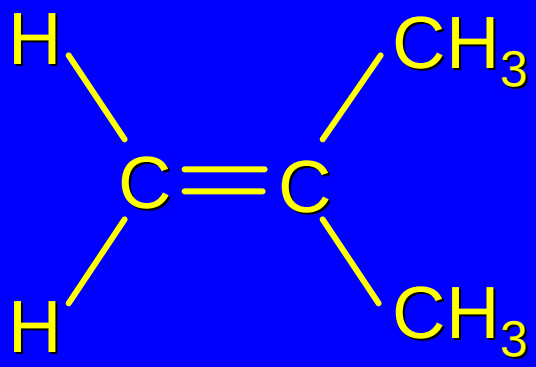
as HOMO-LUMO energy difference decreases (smaller ΔE), λ_{max} shifts to longer wavelengths

Table 13.5 (p 525)

Methyl groups on double bond cause λ_{max} to shift to longer wavelengths



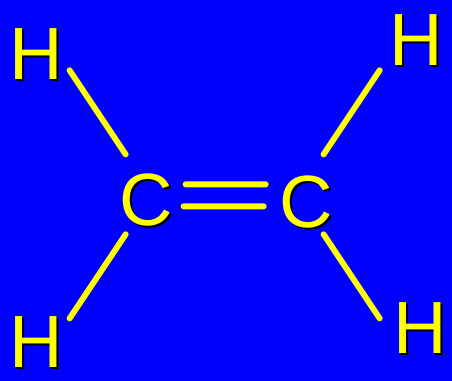
λ_{max} 170 nm



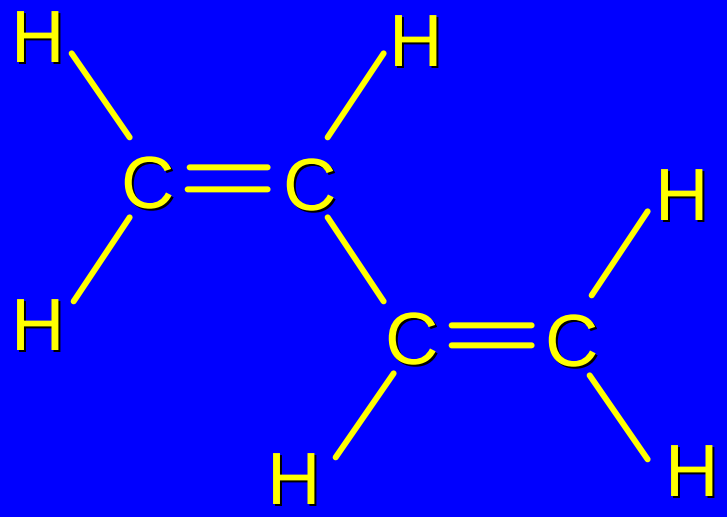
λ_{max} 188 nm

Table 13.5 (p 525)

Extending conjugation has a larger effect on λ_{max}; shift is again to longer wavelengths

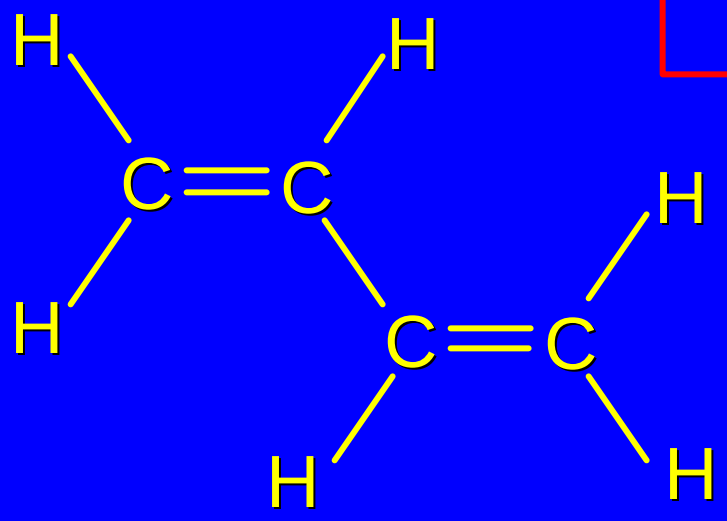


λ_{max} 170 nm

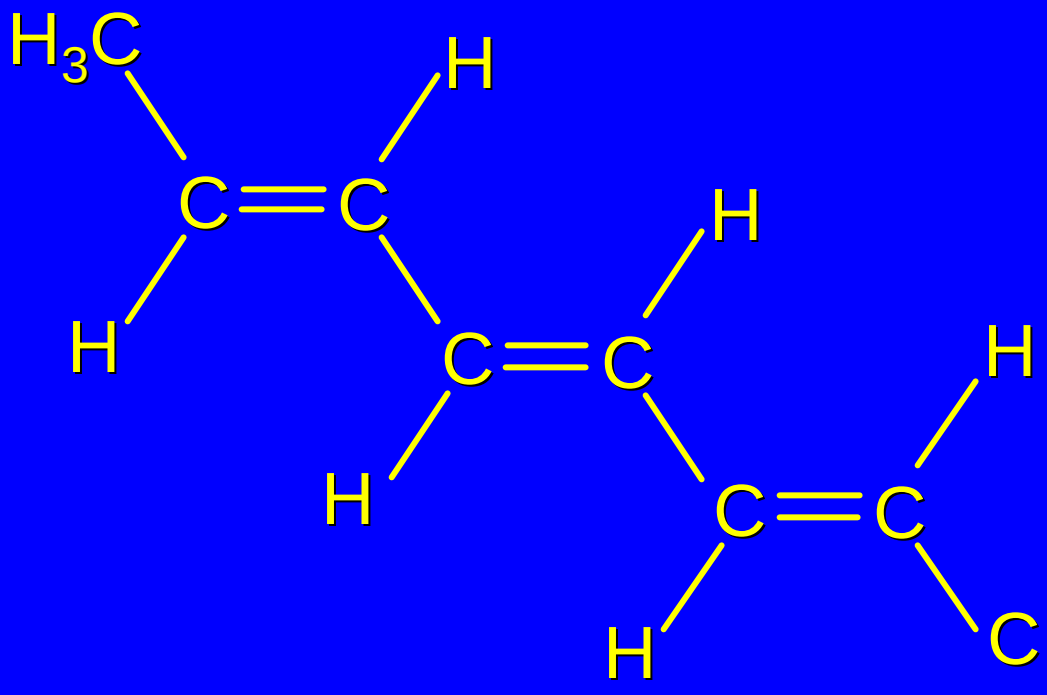


λ_{max} 217 nm

Table 13.5 (p 525)



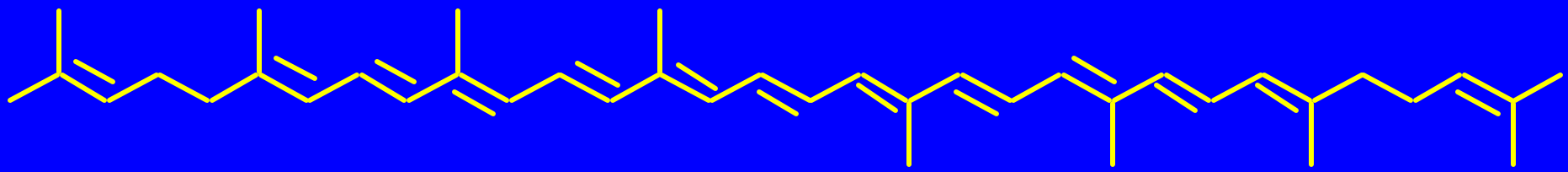
λ_{max} 217 nm
(conjugated diene)



λ_{max} 263 nm
conjugated triene plus
two methyl groups

Lycopene

orange-red pigment in tomatoes



λ_{max} 505 nm