13.20

Ultraviolet-Visible (UV-VIS) Spectroscopy

Gives information about conjugated $\pi$ electron systems
Transitions between electron energy states

\[ \Delta E = h \nu \]

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)

$\lambda_{\text{max}}$ is the wavelength of maximum absorption and is related to electronic makeup of molecule—especially $\pi$ electron system

Y axis is a measure of absorption of electromagnetic radiation expressed as molar absorptivity ($\varepsilon$)
UV Spectrum of cis,trans-1,3-cyclooctadiene

$\lambda_{\text{max}} = 230 \text{ nm}$

$\varepsilon_{\text{max}} = 2630$

Molar absorptivity ($\varepsilon$)

Wavelength, nm
$\pi \otimes \pi^*$ Transition in cis, trans-1,3-cyclooctadiene

\[ \psi_1^{\downarrow \downarrow} \quad \psi_2^{\uparrow \downarrow} \quad \psi_3^{\ast \downarrow} \quad \psi_4^{\ast \uparrow} \]

LUMO \hspace{2cm} \Delta E = h\nu \hspace{2cm} \text{HOMO}

Most stable \hspace{2cm} \pi$-Electron
\[ \psi_1 \quad \psi_2 \quad \psi_3^* \quad \psi_4^* \]
\pi$-electron \hspace{2cm} configuration of
configuration \hspace{2cm} excited state
HOMO-LUMO energy gap is affected by substituents on double bond as HOMO-LUMO energy difference decreases (smaller $\Delta E$), $\lambda_{\text{max}}$ shifts to longer wavelengths
Methyl groups on double bond cause $\lambda_{\text{max}}$ to shift to longer wavelengths.

$\lambda_{\text{max}}$ 170 nm

$\lambda_{\text{max}}$ 188 nm
Extending conjugation has a larger effect on $\lambda_{\text{max}}$; shift is again to longer wavelengths.

$\lambda_{\text{max}} \approx 170 \text{ nm}$

$\lambda_{\text{max}} \approx 217 \text{ nm}$
$\lambda_{\text{max}}$ 217 nm
(conjugated diene)

$\lambda_{\text{max}}$ 263 nm
conjugated triene plus two methyl groups
Lycopene

orange-red pigment in tomatoes

\[ \lambda_{\text{max}} \approx 505 \text{ nm} \]