1. **Benzene absorbs at 260 nm, corresponding to the HOMO – LUMO transition.**

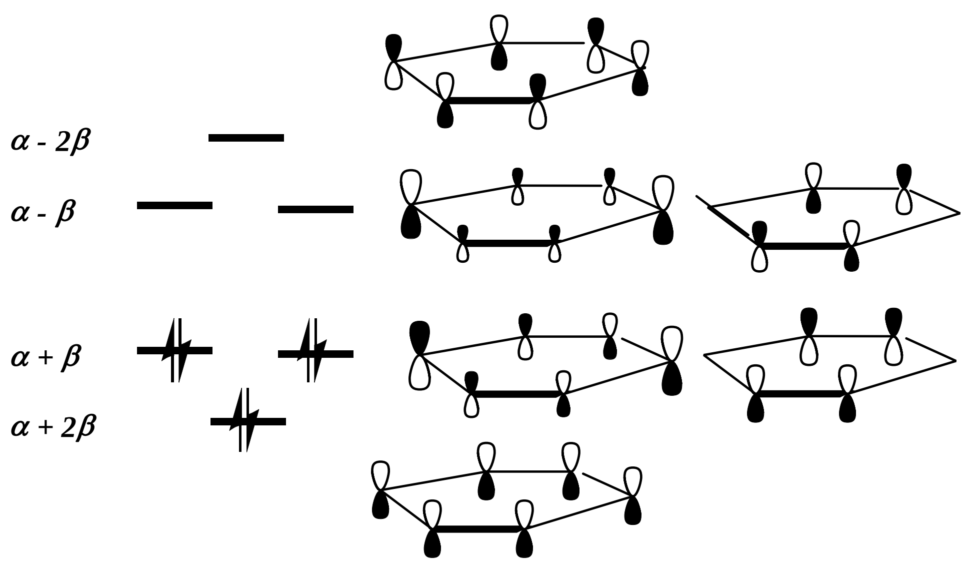
(a) **What is the spectroscopic value of β in eV and Joules.**

The wavelength, λ, is related to the energy (in Joules) using Planck's relationship, $E = \frac{hc}{\lambda}$ where $h = 6.626 \times 10^{-34}$ J s (Planck's constant) and $c = 2.998 \times 10^{8}$ m s^{-1} (speed of light).

Hence, the wavelength of 260 nm = 260×10^{-9} m corresponds to:

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1})}{(260 \times 10^{-9}\ \text{m})} = 7.6 \times 10^{-19}\ \text{J}$$

The energy levels for the π orbitals of benzene are shown below:



The HOMO has energy $\alpha + \beta$ and the LUMO has energy $\alpha - \beta$. The HOMO – LUMO gap is thus equal to 2β. Hence,

$$2\beta = 7.6 \times 10^{-19}\ \text{J so}\ \beta = 3.8 \times 10^{-19}\ \text{J}$$

As 1 eV = 1.602×10^{-19} J:

$$\beta = 3.8 \times 10^{-19}\ \text{J} = = \frac{3.8 \times 10^{-19}}{1.602 \times 10^{-19}}\ \text{eV} = 2.4\ \text{eV}$$

(b) **Calculate the total energy of the π electrons in benzene using this value**

Benzene has 2 electrons in the orbital with energy $\alpha + 2\beta$ and 4 electrons in the two orbitals with energy $\alpha + \beta$. The total energy of the 6 π electrons is therefore:

$$E = 2 \times (\alpha + 2\beta) + 4 \times (\alpha + \beta) = 6\alpha + 8\beta$$

The total bonding energy is 8β:

$$E_{\text{bonding}} = 8\beta = 8 \times (3.8 \times 10^{-19}\ \text{J}) = 3.1 \times 10^{-18}\ \text{J}$$
$$E_{\text{bonding}} = 8\beta = 8 \times (2.4\ \text{eV}) = 19\ \text{eV}$$

(c) An isolated C=C π bond has energy α + β. What is the total energy of the π electrons in three C=C bonds.

Three C=C bonds corresponds to 3 × 2 π electrons. If the energy of each is $\alpha + \beta$, the total energy is

$$E = 6 \times (\alpha + \beta) = 6\alpha + 6\beta$$

The total bonding energy is 6β:

$$E_{\text{bonding}} = 6\beta = 6 \times (3.8 \times 10^{-19}\ \text{J}) = 2.3 \times 10^{-18}\ \text{J}$$
$$E_{\text{bonding}} = 6\beta = 6 \times (2.4\ \text{eV}) = 14\ \text{eV}$$

(d) Using your answer to (b) and (c), what is the aromatization energy?

The difference in energy between the π electrons in benzene and in three C=C bonds is:

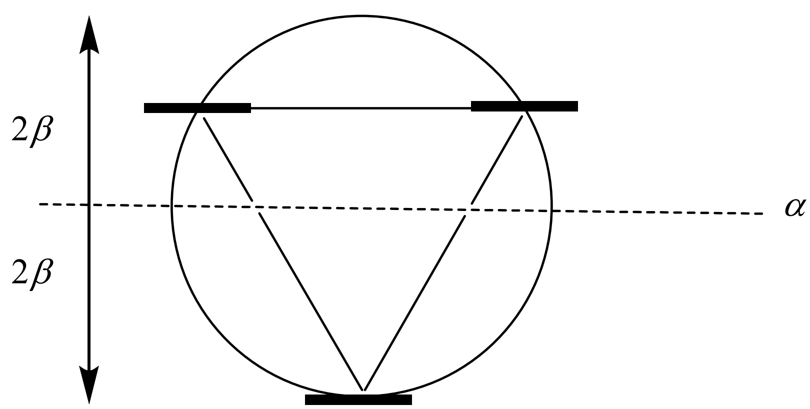
$$\begin{aligned}\Delta E &= 8\beta - 6\beta = 2\beta \\ &= 2 \times (3.8 \times 10^{-19}\ \text{J}) = 7.6 \times 10^{-19}\ \text{J} \\ &= 2 \times (2.4\ \text{eV}) = 4.8\ \text{eV}\end{aligned}$$

As 1 mol corresponds to 6.022×10^{23} molecules, this corresponds to:

$$\Delta E = (7.6 \times 10^{-19}\ \text{J}) \times (6.022 \times 10^{23}\ \text{mol}^{-1}) = 460000\ \text{J} = 460\ \text{kJ}$$

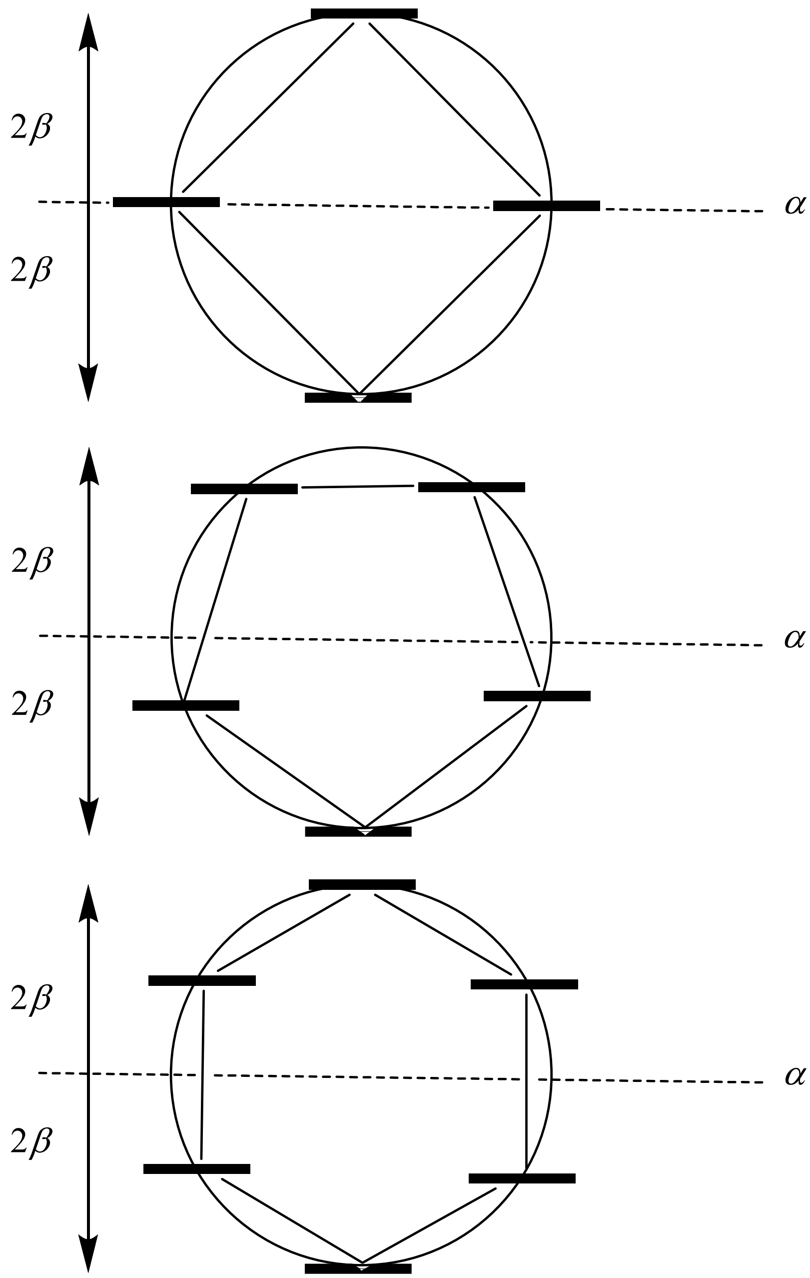
2. Draw a circle and inscribe an equilateral triangle inside such that one vertex lies at the 6 o'clock position. The points at which the two figures touch are the π energy levels.

The energies of the three π orbitals of C_3H_3 are shown as bold lines below. If the circle has a radius of 2β, the positions of the lines correspond to their energies.



3. Repeat for 4, 5 and 6 membered rings.

The energies of the four π orbitals of C_4H_4, the five π orbitals of C_5H_5 and the five π orbitals of C_5H_5 are shown as bold lines on the figures below. If the circle has a radius of 2β, the positions of the lines correspond to their energies.


2β
2β
α
2β
2β
α
2β
2β
α