5. This question is about colourful compounds

Colourful molecules are found in leaves (β-carotene and chlorophyll), blood (haemoglobin), skin (melanin), and multivitamin supplements. They are all organic compounds with alternating single and double bonds, and we will now explore how this pattern leads to colour.

(a) A simple molecule with alternating single and double bonds is buta-1,3-diene. Draw its skeletal structure.

Buta-1,3-diene is colourless because it does not absorb visible light. It does absorb in the UV at a wavelength, λ, of 210 nm. This absorption is caused by the electrons in the double bonds moving between different energy levels. The difference between levels is given by:

$$\Delta E = \frac{hc}{\lambda}$$

where h is the Planck constant and c is the speed of light in vacuum. ΔE is also related to the length of the molecule, L, via:

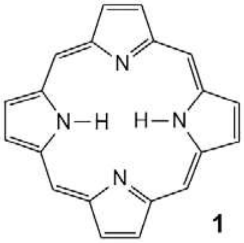
$$\Delta E = \frac{(2n+1)h^2}{8m_e L^2}$$

where m_e is the mass of the electron and n is the number of double bonds.

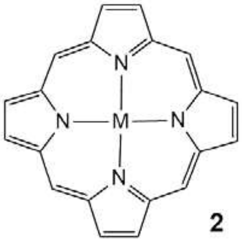
(b) **(i)** Calculate the energy difference, ΔE, for the UV absorption in buta-1,3-diene in J.

(ii) Using this energy difference, calculate the length, L, in Å.

Porphine (**1**) absorbs visible light, forming bright red crystals. Its coordination complexes with metals (**2**) are also coloured and found in chlorophyll and haemoglobin. It has been determined that the magnesium complex (M = Mg) absorbs at 571.4 nm, and the zinc complex (M = Zn) absorbs at 568.7 nm.



1



2

As with buta-1,3-diene, the wavelength is related to the size of the molecule, now via:

$$\lambda = \varepsilon d^2$$

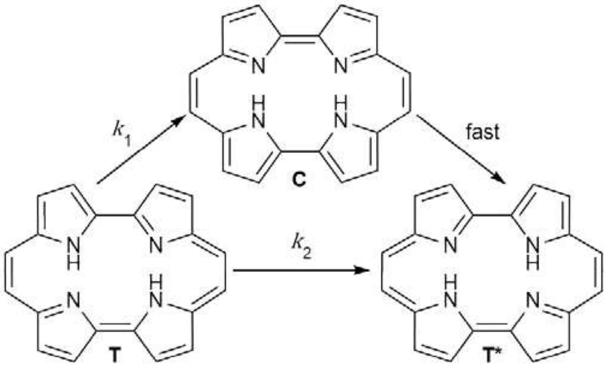
where d is the distance between nitrogen atoms on opposite sides of the ring and ε is a proportionality constant which is assumed to be the same for **1** and **2**. The N–Mg bond length is 2.052 Å.

(c) **(i)** Calculate the proportionality constant ε in $Å^{-1}$ to four significant figures.

(ii) Calculate the length of the N–Zn bond in Å to four significant figures.

(iii) Calculate the absorption wavelength of porphine **1** (for which d = 4.112 Å) in nm to four significant figures.

Porphycene is an isomer of porphine that has attracted attention as a molecular switch. The hydrogen atoms in porphycene can “hop” across the ring, interconverting between two stable *trans*-states (**T** and **T***) that are the on/off positions of the switch. There is also an unstable *cis*-state **C**. The trans-states can interconvert via the cis-state with rate constant k_1, or directly with rate constant k_2.



At high temperatures $k_1 >> k_2$ and so the direct conversion of **T** → **T*** can be ignored. The following rate equation and kinetic data were obtained for the isomerisation.

$$k_1 = A\exp\left(-\frac{E_a}{RT}\right)$$

T / K	k_1 / s^{-1}
493	3.31×10^{12}
393	1.32×10^{12}

(d) Under such conditions, calculate the activation energy, E_a, for **T** → **T*** using the Arrhenius law and the above data.

The transformation is much faster at 100 K than expected from the Arrhenius law because the direct conversion of **T** → **T*** now dominates the reaction. This is due to quantum tunnelling. The rate constant k_2 has a non-Arrhenius temperature dependence

$$k_2 = \left(\frac{2E_a}{\mu}\right)^{\frac{1}{2}}\frac{\alpha RT}{E_a}\exp\left(-\alpha\left(2-\frac{\alpha RT}{E_a}\right)\right)$$

where μ is a scaled molar mass with units of m^2 kg mol^{-1} and α is a dimensionless constant. This expression can be simplified by combining some of the terms together to form new terms β and γ.

$$k_2 = T\left(\frac{\beta}{\gamma}\right)^{\frac{1}{2}}\exp(-2\alpha+\beta T)$$

(e) Express β and γ in terms of α, μ, E_a, and R.

The equation can be further rearranged to give

$$\ln\left(\frac{k_2}{T}\right) = \beta T + i$$

(f) Use the following data to calculate β in K^{-1}.

(If you do not get an answer to this question, use $\beta = 9.456 \times 10^{-4}$ K^{-1} in further calculations)

T / K	k_2 / s^{-1}
83	8.74×10^{10}
61	6.23×10^{10}

The value of the constant α can be shown to be 2.235.

(g) Calculate the activation energy E_a.