CML100 2018-19 II semester Major

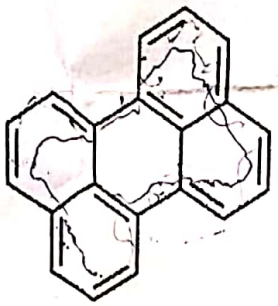
Time: 120 min

April 29, 2019

All your work should be shown to be eligible for partial marking.

$c = 3.0 \times 10^8\,\mathrm{m\,s^{-1}}$; $h = 6.626 \times 10^{-34}\,\mathrm{J\,s^{-1}}$; $m_e = 9.109 \times 10^{-31}\,\mathrm{kg}$.

1. Perylene, structure given below, is a planar molecule.



As a zeroth approximation we consider the π-electrons of perylene as freely moving in a square box of length L.

(a) Write the quantum numbers and energies of all the occupied electronic states in increasing order of energy. [2]

(b) What would be length of the box if the absorption spectrum of perylene shows a maximum at $\lambda = 435\,\mathrm{nm}$? [2]

(c) Another model treats the π-electrons of perylene as moving in a rectangular box with a length of 0.72 nm and a width of 0.48 nm. What is the Schrödinger equation satisfied by a π-electron in this case? Write the wavefunction of the highest occupied state. [1]

(d) For the model in Q. 1c, at what wavelength is the maximum in the absorption spectrum expected? [1]

2. Less than two weeks ago there was excitement following the detection of the species HeH^+ in interstellar space. One website called HeH^+ "elusive molecule, first in universe."

(a) Write the Hamiltonian for this species in atomic units. [1]

(b) A possible LCAO MO for the system is $\psi = c(\psi_{He^+} + \psi_H)$, where ψ_{He^+} and ψ_H are the normalized 1*s* wavefunctions of He^+ and H respectively. Ignoring pre-multiplicative constants, what are the functional forms of ψ_{He^+} and ψ_H? [1]

(c) Show how you would determine c in the expression for ψ in Q. 2b. Use standard notation where required. What is the physical significance of all terms in your answer? [1.5]

(d) Obtain an expression for the approximate energy of ψ_{MO}. [1.5]

3. An electron in H-atom is in the state $\psi(r,\theta,\phi) = \frac{1}{4\sqrt{2\pi a_0^3}} \frac{r}{a_0} e^{-\frac{r}{2a_0}} \sin\theta\cos\phi$.

(a) What is the energy of the electron in atomic units? [0.5]

(b) Plot ψ as a function of x. [0.5]

(c) What is x position of the electron in this state? $\int_0^\infty z^n e^{-az}\,dz = \frac{n!}{a^{n+1}}$. [2]

(d) At what radial distance from the nucleus is the electron most likely to be found? [1]

(e) In this state, what is the orbital angular momentum and its z-projection? [1]

4. Decide whether the following statements are true or false giving a brief thermodynamic reasoning. No reasoning, no marks. [4 × 1]

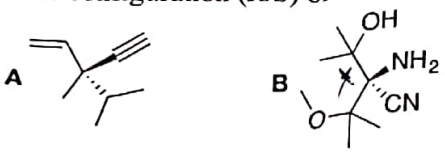
(a) The entropy of a material can never decrease.

(b) A body in thermal and mechanical equilibrium with a reservoir at constant temperature and pressure will have the lowest value of Gibbs energy for that body.

(c) The chemical potential of any species that can be exchanged between two phases will always be equal.

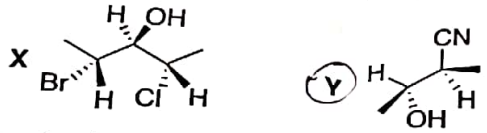
(d) If A is the free surface area of a liquid and γ its surface tension, the quantity $Ad\gamma$ represents thermodynamic work.

5. (a) Tell the absolute configuration (*R*/*S*) of the given compounds **A** and **B**. **(2)**



(b) L-(+)-Lactic acid has specific rotation: +2.67° (c = 2.51 in water at 15 °C), a solution containing mixture of *d*-Lactic acid and *l*-Lactive acid has specific rotation −1.84° (c = 2.51 in water at 15 °C). What is percentage of (+)-Lactic acid present in this mixture. **(2)**

(c) Draw Fischer Projections given chiral compounds **X** and **Y**. **(2)**

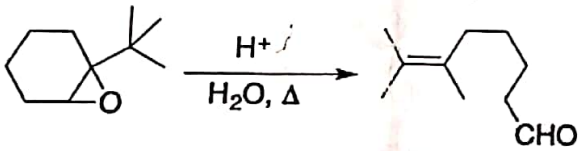


6. (a) Write the structures and absolute configuration of all products obtained from the reaction of (*E*)-pent-2-ene with bromine (Br_2). **(2)**

(b) The reduction of (*S*)-4-methylhexan-3-one with $NaBH_4$ in presence of chiral catalyst gives exclusively one stereoisomer as a major product. In this reaction "hydride" attacks from "*Re*" face of ketone. Write the IUPAC name and structure of this product. **(2)**

(c) Define prochiral molecule, explain it with examples? **(2)**

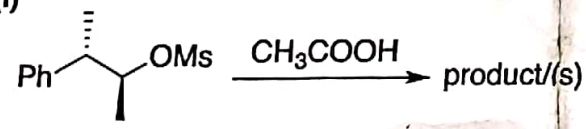
7. (a) Write stepwise mechanism for following transformation. **(2)**



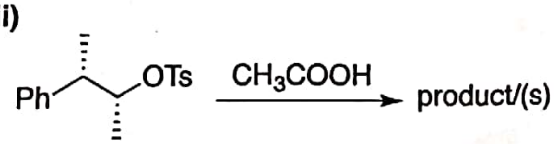
(b) How will you synthesize 4-hydroxy-4-phenylbutan-2-one from 1-phenyl-ethene. **(2)**

8. (a) Write the product/(s) formed in the given reaction **(i)** and **(ii)**. **(2)**

(i)



(ii)



(b) Write the structure of **M, N, O** and **P** in the following reaction. **(2)**