B.Sc. 1st Semester (Honours) Examination, 2018 (CBCS)

Subject : Chemistry

Paper : CC-I (Theory)

Time: 2 Hours **Full Marks: 40**

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

1. Answer *any five* questions from the following: 2×5=10

(a) What do you mean by specific rotation of an optically active compound? Why is it called so?

(b) Draw the labeled orbital picture of ketene and but-1, 3-diene.

(c) Arrange the following carbocations in order of their stability:
cyclopropenium ion, triphenylmethyl cation, tertiary butyl cation

(d) Arrange the following oxyanions in order of their increasing basicity:

$H_3CO^-, PhO^-, HO^-, (CH_3)_3CO^-, CH_3COO^-$.

(e) Draw the structure of (2Z, 4R, 5E)-4-chlorohepta-2, 5-diene molecule.

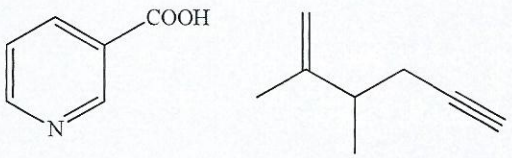
(f) Draw the Fischer Projection of threo-4-chloro-3-hydroxyhexanal and convert it to Newman and Sawhorse representation.

(g) Draw the ground state HOMO of hexatriene.

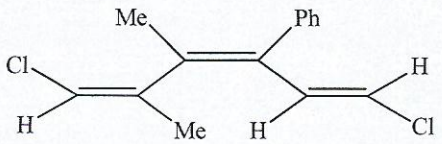
(h) Carbocation at the bridge-head position is not possible — Explain with a suitable example.

2. Answer *any two* questions from the following: 5×2=10

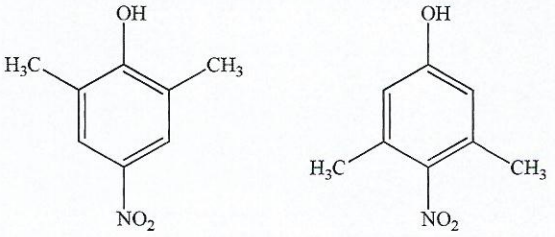
(a) (i) Give the IUPAC names for the following compounds:



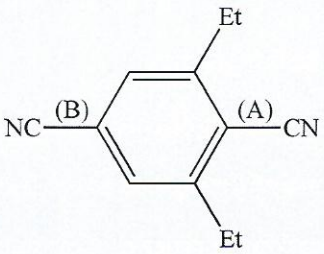
(ii) Name the compound with E/Z symbols:



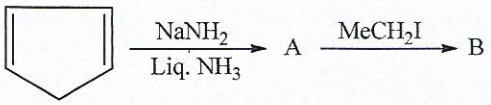
(iii) Which of the following two isomeric phenols is stronger acid and why? 2+1+2=5



(b) (i) The bond energy of which C-CN bond (A or B) is greater? Justify.



(ii) Give the product:



State why A is very stable? 2+3=5

(c) (i) Draw the shape/geometry of singlet and triplet carbenes.

(ii) Suggest a method for the resolution of a racemic mixture of an acid.

(iii) Bond dissociation energy and bond energy are not always same — Justify with example. 2+2+1=5

(d) (i) Write three major factors that influence the stabilization of carbanions. Illustrate your answer with suitable examples.

(ii) Azulene is a non-benzenoid compound. Account for its aromaticity and relatively high dipole moment. 3+2=5

3. Answer *any two* questions from the following: 10×2=20

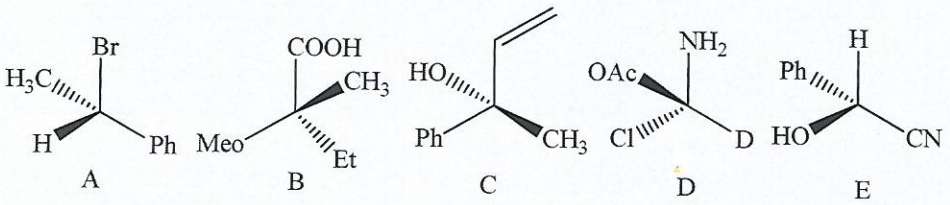
(a) (i) The first ionization constant of maleic acid ($K_1 = 1 \cdot 41 \times 10^{-2}$) is much higher than that of fumaric acid ($K_1 = 9 \cdot 3 \times 10^{-4}$) whereas the second ionization constant of fumaric acid ($K_2 = 3 \cdot 62 \times 10^{-5}$) is much higher than that of maleic acid ($K_2 = 8 \cdot 5 \times 10^{-7}$). How would you explain the observation?

(ii) Draw the MOs of cyclobutadiene and show those in Frost's diagram.

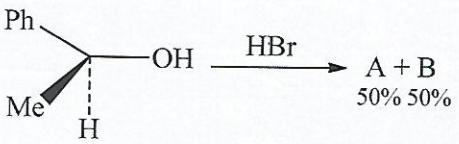
(iii) Enantiomers behave similarly under all physical and chemical conditions — Justify or criticize.

(iv) Draw all possible stereoisomers of Ph CH(OH)CH = CHMe 3+3+2+2=10

(b) (i) Designate the organic compounds (A–E) according to R/S Nomenclature.



(ii) Complete the reaction with stereochemistry.

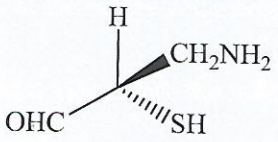


(iii) Determine the point groups in case of *o*-xylene, *m*-xylene and *p*-xylene.

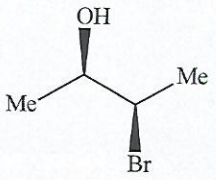
(5×1)+(1+1)+(1+1+1)=10

(c) (i) Assign the following organic compound as D/L — system of nomenclature:

(a)



(b)



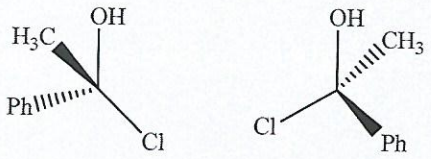
(ii) Difluorocarbene ($:CF_2$) exists in singlet state while diphenyl carbene ($:CPh_2$) prefers triplet state — Explain with orbital diagram.

(iii) Draw the shapes of $Ph_3\dot{C}$ and $Ph_2\dot{C}H$ free radicals. Compare the electrophilicity of the carbenes: $Me_2C:$ & $(MeO)_2C:$

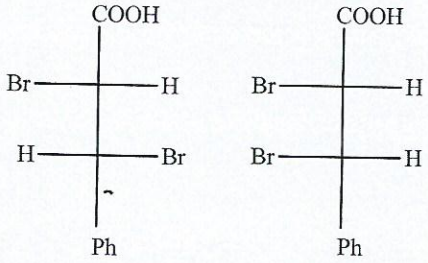
(iv) Indicate a carbon centre which is achirotopic but stereogenic. Give an example of a compound which is cis but (E). 2+3+3+2=10

(d) (i) Assign the following pairs as enantiomers, diastereomers and homomers.

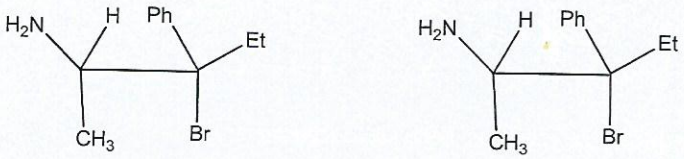
(I)



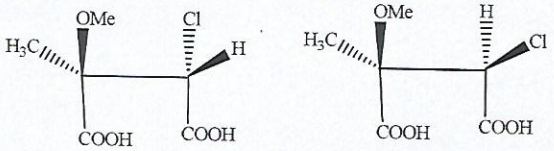
(II)



(III)



(IV)



(ii) Write the resonating structures for the carbocation $MeC^{\oplus}(OMe)NMe_2$ and indicate the stablest one. Indicate the electrophilic centres for cyclohexenone. Draw the shapes of cyclooctatetraene and its dianion.

$(4\times1)+(2+2+2)=10$