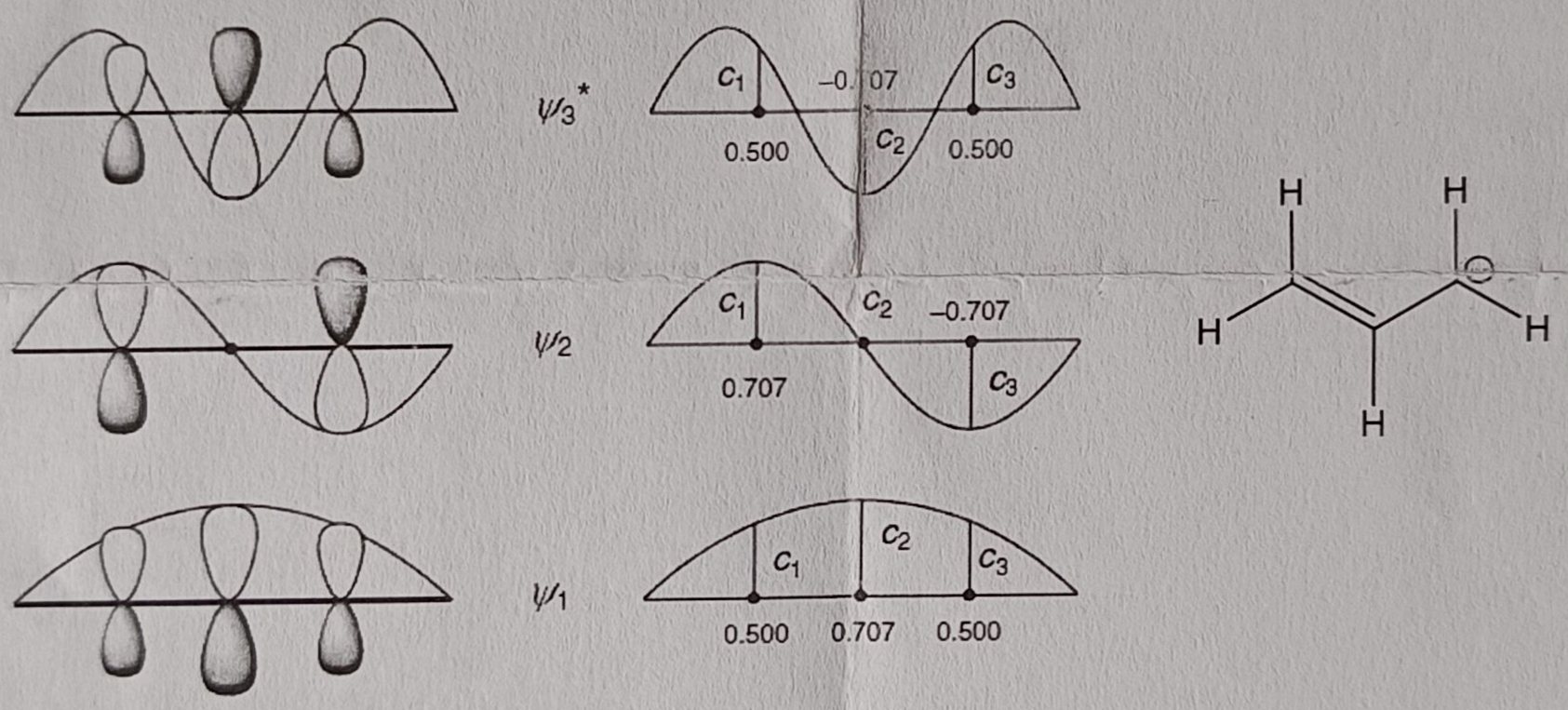
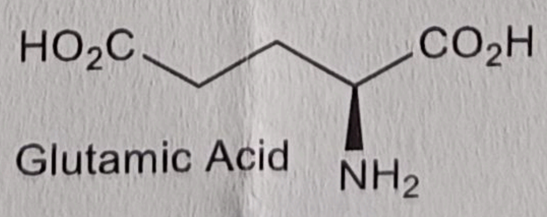
CH1101, Autumn 2024
Endsem Exam
06.12.2024, 10:00 am-12:30 pm
Total marks: 50
Special instruction: You must attempt all questions.

1. Consider a heterodiatomic molecule AB and its internuclear axis is the z-axis. Sketch the overlap situations for the following pairs of orbitals and comment on the nature of their overlap integrals (S>0 or S<0 or S=0): [1s(A)+1s(B)], [1s(A)+2p_x(B)], [1s(A)–2p_x(B)], [2p_x(A)+2p_x(B)], [2p_z(A)+2p_z(B)] **[5]**
2. Consider an element X with an atomic number 8. Sketch two side-by-side MO diagrams, one for X_2 and another for X_2^{2-} with properly labelling the orbitals and their g/u symmetries. Compare the X–X bond orders, bond lengths, and bond energies with brief justification. Comment on the magnetic behavior of X_2 and X_2^{2-}. **[10]**
3. Sketch two side-by-side MO diagrams of CO, one by considering the s-p orbital hybridization and the other without the hybridization concept. Which one of the two diagrams better justify the CO as a ligand when it binds to a metal and why? **[10]**
4. The MOs for allyl anion are provided below. Although it is not apparent from the chemical structure shown here, allyl anion is experimentally found to be symmetrical. Explain this based on the MOs provided. **[4]**

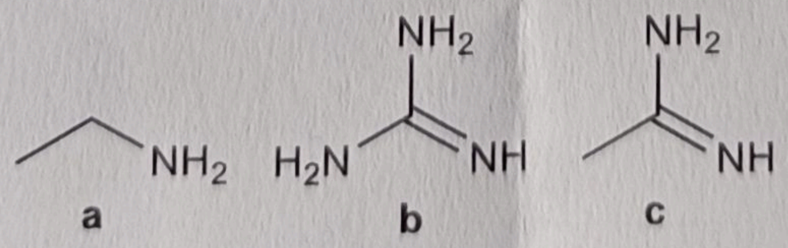


5. Explain the various pK_a values (2.19, 4.25 and 9.67) for the naturally occurring amino acid glutamic acid. Say which pK_a belongs to which functional group and explain your answer. **[4]**

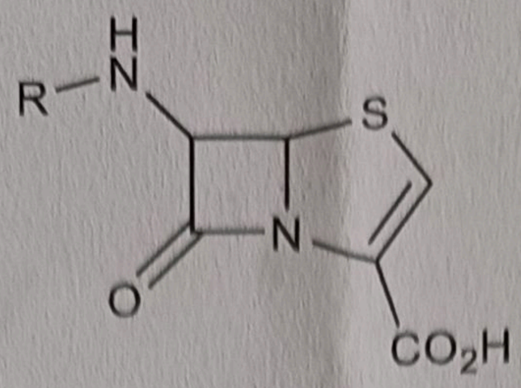


Glutamic Acid

6. Arrange the following compounds in order of increasing basicity. Explain your answer. **[4]**



7. You all have heard about penicillin, the first antibiotic. The general structure is shown below. Do you think any conjugation is present in any part of the molecule? Draw resonance structures to show the delocalization. **[3]**

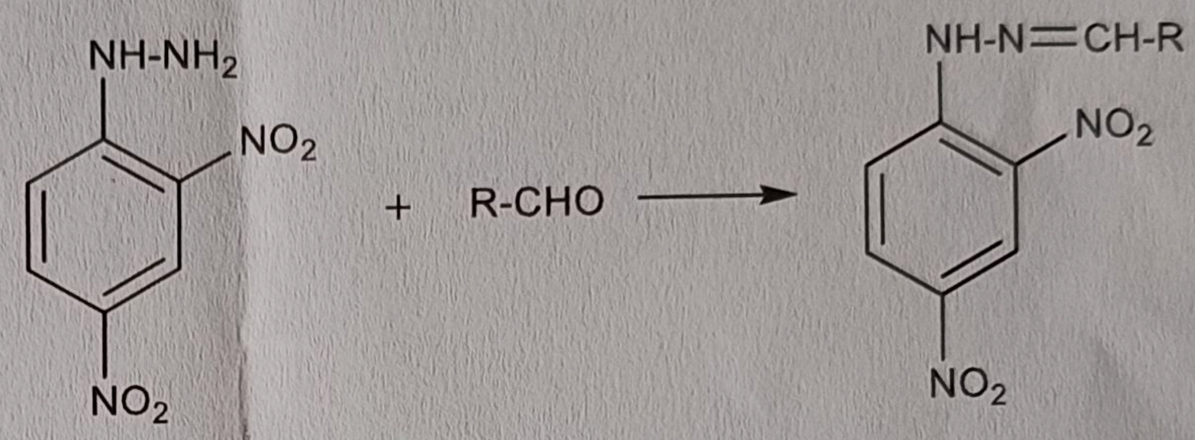


8. 2,4-dinitrophenylhydrazine (DNP) is used for the qualitative identification of aldehydes and ketones since the products are nicely colored. Suppose that you are asked to identify the contents of three bottles whose labels have fallen off. One bottle contained butanal, one contained trans-2-butenal, and one contained trans-3-phenyl-2-propenal. The 2,4-dinitrophenylhydrazones prepared from the contents of the bottles have the following characteristics. λ_{max} denotes the wavelength at which the molecule has the highest absorption of light. Identify which bottle contains which aldehyde. Explain why different aldehydes produced different colors in the product. **[4]**

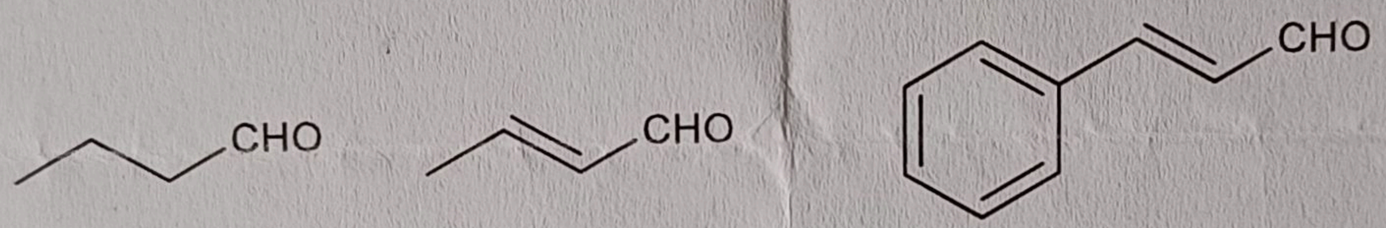
Bottle 1: λ_{max} 377 nm; orange color

Bottle 2: λ_{max} 358 nm; yellow color

Bottle 3: λ_{max} 394 nm; red color

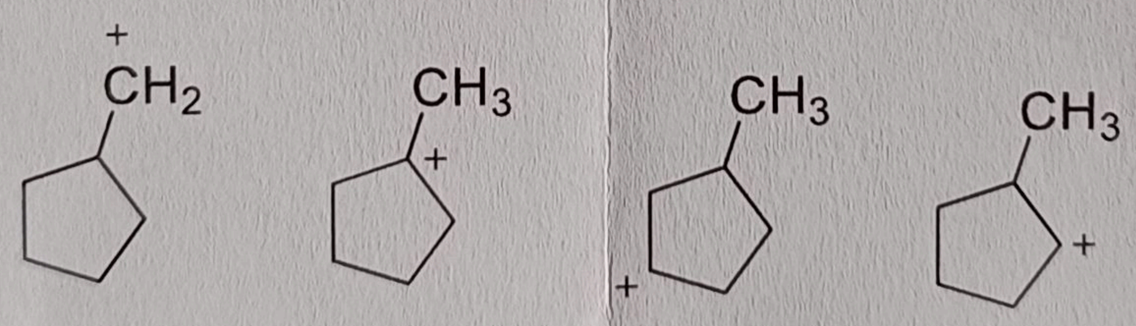


DNP



Butanal **Trans-2-butenal** **Trans-3-phenyl-2-propenal**

9. Which of the following isomeric carbocations is the most stable? Explain based on the concept of σ-conjugation (use MOT). **[3]**



10. All alkyl carbocations are typically unstable and short-lived species. However, Geoge Olah was successful in proving the existence of tert-butyl carbocation from tert-butyl alcohol in liquid SO_2 by using the following condition. Explain the reason behind choosing the different reagents like HF and SbF_5 and SO_2 as the solvent. **[3]**