21st BChO, 2013, Tartu, Estonia

Problem 1 – BIO, ELECTRO – Photosynthesis

Photosynthesis consists of light and dark phase reactions. Light reactions produce NADPH and ATP, which is followed by dark reactions where the carbon dioxide is being fixed. Chlorophyll becomes excited when a light photon hits it.

a) Which one is preferably absorbed by the active chlorophyll, green (532 nm) or red (680 nm) photon?

The standard reduction potential for chlorophyll equals 0.78 V.

b) Calculate the standard reduction potential for chlorophyll for the photochemical process: Chlorophyll$^+$ + e$^-$ → Chlorophyll*, where an asterisk denotes an excited state.

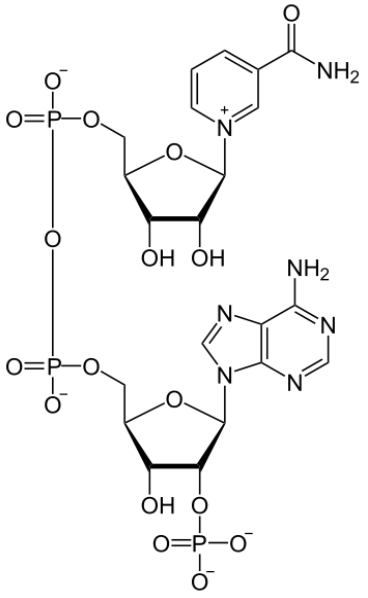
The splitting of water produces protons and dioxygen when the electrons are carried to the redox systems:

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ ($E°$ = 1.23 V)

The electrons from the reaction are used to form NADPH:

$NADP^+ + H^+ + 2e^- \rightarrow NADPH$ ($E°$ = −0.11 V)

Actually, NADP$^+$ (shown in the figure) binds two protons.



c) Mark the two new hydrogens in the NADPH structure.

d) Calculate the potential for cell conditions (pH = 7).

e) Calculate the ΔG for the NADPH formation reaction.

The accumulation of protons inside the chloroplast thylakoid creates a concentration cell.

f) Calculate the voltage of such a concentration cell if the pH outside the membrane is 7.8 but inside the membrane, the pH is 5.4.

However, nature has used a different approach – the protons are used for the preparation of ATP. The protons synthesized in the inner side of the membrane pass out through the spinning enzyme ATP synthase, producing ATP from phosphate and ADP: ADP + P_i → ATP + H_2O ($\Delta G°$ = +30.5 kJ mol^{-1}).

g) Draw the structure of ATP.

h) Calculate ΔG for ATP hydrolysis in real cell conditions if the ATP concentration is twice larger than ADP concentration and the phosphate concentration is 5 mM.

i) Calculate the approximate number of protons needed for the preparation of one ATP molecule.

The following are the dark reactions, which do not need light to function, just a supply of energetic compounds and CO_2. Carbon dioxide is bound in a cascade of reactions called the Calvin cycle. Some of the intermediates in the Calvin cycle are used to make glucose as well as other bioorganic compounds.

The NADPH reducing properties are used in the third reaction of the cycle, where 1,3-bisphosphoglycerate is converted to glyceraldehyde-3-phosphate.

j) Write the equation with correct chemical structures.

It also takes 18 ATP molecules to prepare one glucose molecule.

k) Write the sum reaction for the dark phase of photosynthesis per one glucose molecule.

l) Calculate Gibbs energy for this reaction in cell conditions.

In summary, green plants utilize sunlight to convert CO_2 and H_2O to organic compounds (glucose $C_6H_{12}O_6$) and O_2. The reaction ΔG = 2880 kJ mol^{-1} and ΔS = −257 J mol^{-1} K^{-1}.

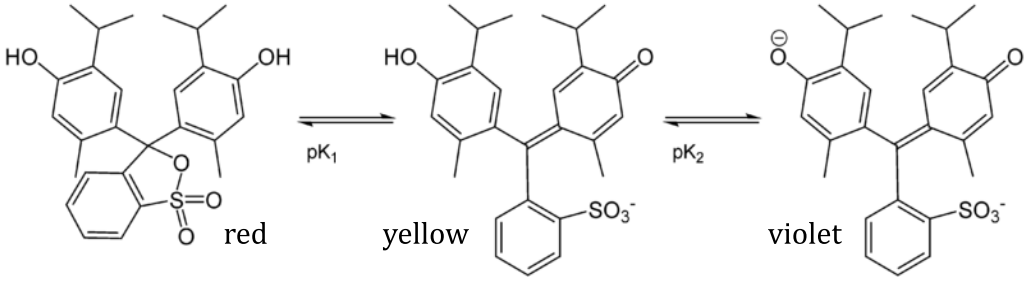
m) Calculate the minimum number of photons (λ = 680 nm) required to make one molecule of glucose from CO_2 and H_2O.

n) Comment on the spontaneity of this reaction at 25 °C and other temperatures.

Problem 2 – CALC, EQUIL – Phenolsulfonphthalein

For determination of the endpoint in an acid-base titration, mainly two methods are used – either using an indicator or potentiometric titration. One possible indicator is phenolsulfonphthalein.

pH	*A*
5.02	0.0043
7.42	0.0350
8.32	0.2116
9.23	0.6828
10.26	0.9631
12.61	1.0076



Unfortunately, not all indicators are applicable for all acid-base titrations. A suitable indicator needs to have its transition range (the pH range where the indicator changes color) near the equivalent point of the titration curve. The transition range is mostly the pH range where the ratio of protonated and deprotonated form of the indicator changes from 1 : 10 to 10 : 1 or vice versa. To validate if phenolsulfonphthalein is a suitable indicator, its pK_{a2} value was determined using the spectrophotometric method. In order to do this, the absorbance of phenolsulfonphthalein was measured (λ = 590 nm) at different pH values (the concentration of phenolsulfonphthalein and optical length were kept constant). The obtained results are indicated in the table. It is known that at the lowest measured pH, only HA^- occurs in the solution and at the highest measured pH, only A^{2-} occurs. It is also known that Beer's law is additive:

$$A = A(HA^-) + A(A^{2-}) = \varepsilon(HA^-)l[HA^-] + \varepsilon(A^{2-})l[A^{2-}]$$

where ε is the molecular absorbance coefficient and *l* is the optical length in the cuvette.

a) Derive a formula to evaluate the pK_{a2} values according to the previously described information.

b) Calculate the estimated pK_{a2} values (4 values) and the average pK_{a2} value according to the data given in the table.

50.00 cm^3 of 0.01000 M ammonia (pK_b = 4.75) is titrated with HCl (0.1000 M).

c) Calculate the pH of the titration solution if **i)** 4.90, **ii)** 5.00, and **iii)** 5.10 cm^3 of the titrant is added to the solution.

d) Can phenolsulfonphthalein be used as an indicator for this titration?

50.00 cm^3 of 0.01000 M acetic acid (pK_a = 4.76) is titrated with NaOH (0.1000 M).

e) Calculate the pH of the titration solution if **i)** 4.90, **ii)** 5.00, and **iii)** 5.10 cm^3 of the titrant is added to the solution.

f) Can phenolsulfonphthalein be used as an indicator for this titration?

Problem 3 – STRUCT – Hydrides

Hydrogen is a versatile element. It forms a wide range of binary compounds with metallic and nonmetallic elements. With transition metals, hydrogen forms so-called metallic or interstitial hydrides. When chromium is electrodeposited at low temperatures, a face-centered cubic chromium hydride CrH_x can be produced. The unit cell of this hydride may be described as consisting of chromium atoms in a face-centered cubic arrangement and hydrogen atoms located in tetrahedral holes of this cell.

a) Write a theoretically possible chemical formula for chromium hydride assuming that all tetrahedral holes were filled with hydrogen atoms.

In reality, metallic hydrides are nonstoichiometric compounds, e.g., palladium forms hydride $PdH_{0.7}$ instead of theoretically possible PdH. This hydride forms upon passing hydrogen gas over palladium. On the other hand, on heating, palladium hydride readily releases hydrogen gas. This fact has an important commercial application – palladium is used for the purification of hydrogen gas and could be used as a fuel tank for hydrogen-powered cars.

The hydrogen storage capacity of a palladium-based fuel tank may be characterized by the ratio V(liquid H_2)/V(solid hydride) when both volumes contain the same amount of hydrogen atoms. Density of liquid H_2 is 0.0710 g cm^{-3}. Density of $PdH_{0.7}$ is 12.1 g cm^{-3}.

b) Calculate V(liquid H_2)/V(solid hydride) ratio for $PdH_{0.7}$.

Another type of hydride are ionic or salt-like hydrides. These compounds contain H^- ions. Unknown metal **M** forms hydride $\mathbf{M}H_x$, where x is an integer number. When 1.000 g of $\mathbf{M}H_x$ reacted with excess water, 3.216 dm^3 of gas was collected over water at 25 °C and 100.00 kPa pressure. Vapor pressure of water at a given temperature is 23.0 mm Hg.

c) Determine the unknown metal **M**.

Crystalline structure of $\mathbf{M}H_x$ could be described as follows: H^- ions arranged in a face-centered cubic lattice and metal ions occupy some holes in this lattice. The lattice constant is a. Let us assume that we have a sample of $\mathbf{M}H_x$ that consists of very small cubic crystals of exactly the same size. For a short time, this sample was exposed to open air. Due to the reaction with water vapor, all surface H^- ions were transformed into OH^- ions. However, ions inside of the crystals remained unchanged. After that, the sample was investigated using ^{1}H-NMR-spectroscopy. There are two peaks (for H^- and OH^-) in the ratio, accordingly 150 : 1 in the resulting spectrum.

d) Determine the edge length (expressed as a multiple of a) of the crystals in the sample.

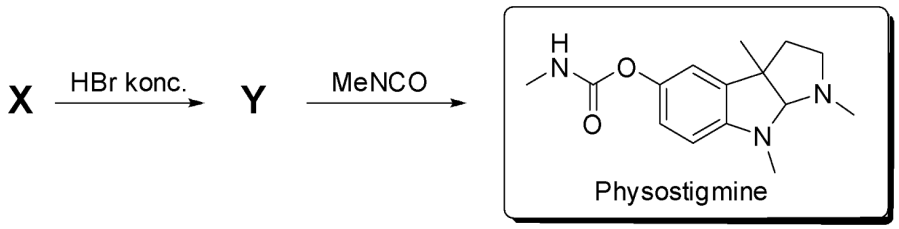
With non-metals, hydrogen forms covalent hydrides. Some of these compounds consist of small molecules, some are polymeric substances.

Boron forms a wide range of binary compounds with hydrogen. The simplest of these compounds is diborane B_2H_6.

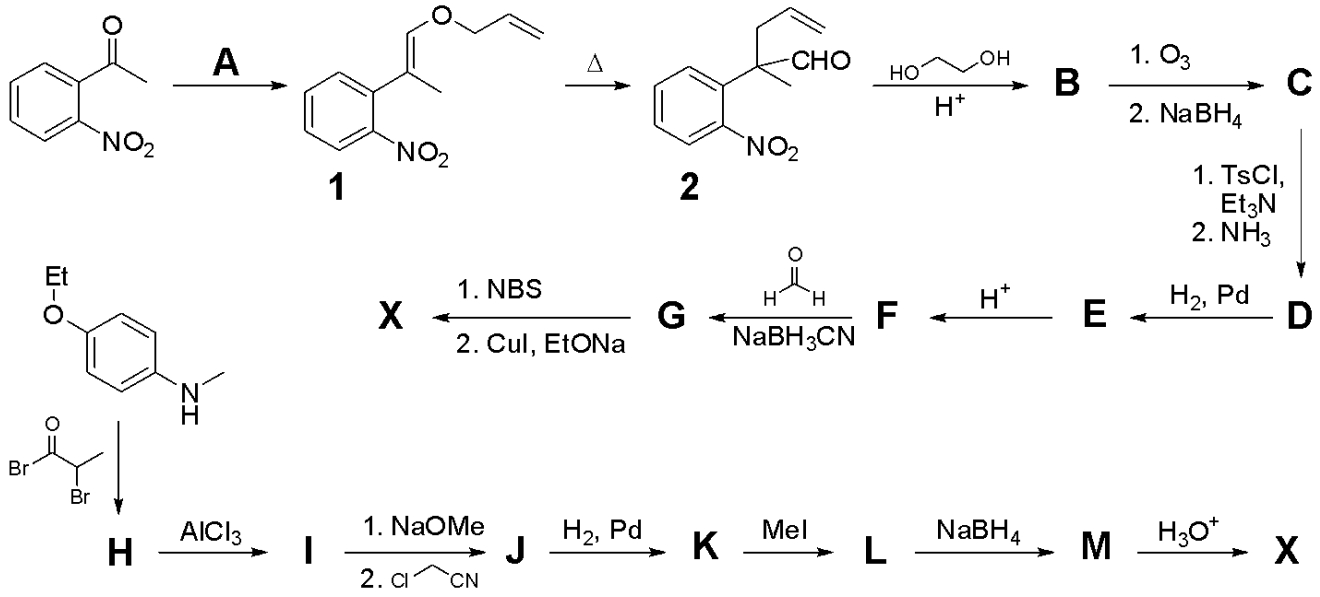
e) Draw a spatial structure of a B_2H_6 molecule.

Problem 4 – BIO, SYNTH – Physostigmine

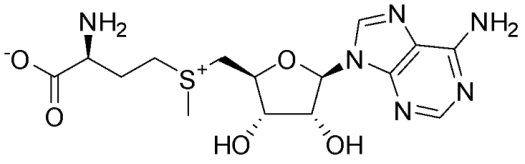
Physostigmine is a reversible acetylcholinesterase inhibitor that can be extracted from *Physostigma venenosum* beans. This compound can be used to treat myasthenia gravis, glaucoma and Alzheimer's disease. In addition, physostigmine enhances short-term memory. Physostigmine is easily obtained from compound **X**:

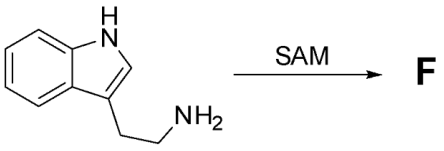


Compound **X** can be produced using two different methods:



The tricyclic compound **F** is biosynthesized from tryptamine with the aid of methylating coenzyme S-adenosylmethionine (SAM):


S-adenosyl methionine



Tryptamine

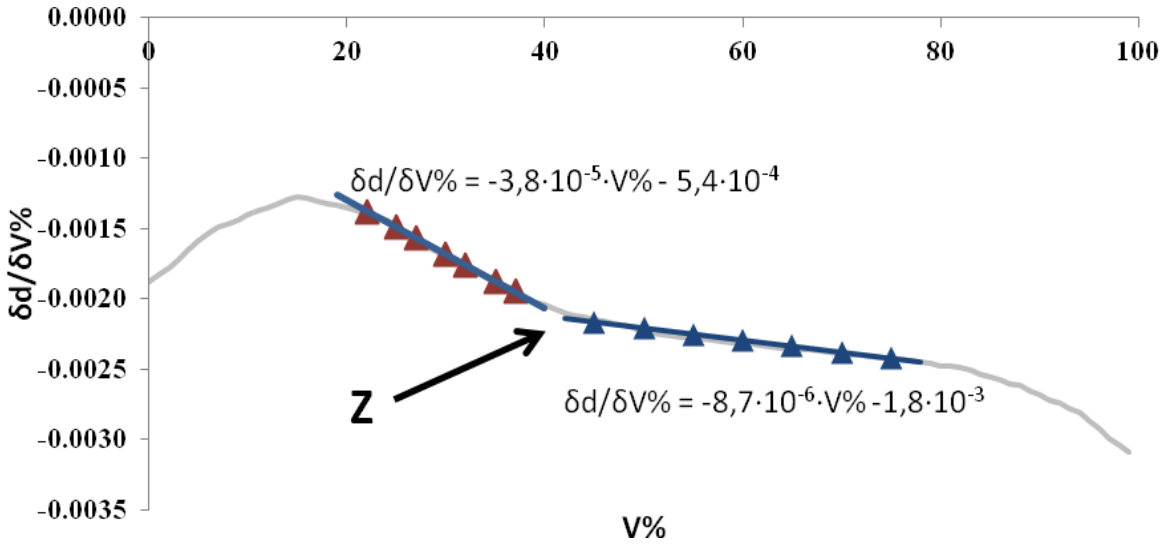
a) Provide skeletal formulas for the compounds **A**–**M**, **X** and **Y**.

b) Provide mechanisms for the biosynthesis of compound **F** and the transformation of **1** to **2**.

c) Write the number of possible physostigmine stereoisomers.

Problem 5 – THERMO – A national drink

It may seem that famous Russian chemist Dmitri I. Mendeleev (1834–1907) dedicated his life to the periodic table of elements. However, Mendeleev wrote his doctoral thesis, "A Discourse on the Combination of Alcohol and Water", where he investigated the relationship between density and composition of solutions. Mendeleev's experiment was repeated using data available on the web and the graph shown below was obtained. It shows derivatives of the density against the volume fraction of the ethanol in solution plotted as a function of the volume fraction of the ethanol. In the graph, there are several extreme points and one of them is marked as **Z**. Such extreme points Mendeleev explained by the formation of ethanol-water hydrates. Density of ethanol is 0.789 g cm^{-3}.



a) Calculate the composition of ethanol-water hydrate **Z**, where composition is expressed as volume fraction of ethanol in water. Does it fit the Russian vodka standard of 40%?

b) Calculate the composition of hydrate **Z** expressed as mass fraction and molar fraction of ethanol in solution. If you were unable to solve question **a)**, you may assume that **Z** corresponds to 40% ethanol (volume fraction).

c) Point out the main intermolecular forces acting between the ethanol and the water molecules in the hydrate.

Pure ethanol is a colorless liquid with a boiling point of 78.37 °C (pressure p = 101.33 kPa), while at 20.00 °C its vapor pressure is 5.95 kPa. Assume that all enthalpy and entropy changes given and calculated in this problem are temperature-independent.

d) Calculate the molar enthalpy and entropy of vaporization of ethanol.

e) Compare the obtained value with molar enthalpy of vaporization of water, which is 44.0 kJ mol^{-1} at 80 °C. Explain why the obtained enthalpy value is greater/smaller than the enthalpy of vaporization of water.

Ethanol is widely used in homemade window cleaning solutions but it is not very effective as ethanol quickly evaporates. It also may be used as a window cleaner for cars during winter.

f) Calculate the melting point for 35% (mass fraction) ethanol solution. The cryoscopic constant for water is 1.85 K kg mol^{-1}.

Ethanol is also used as an additive in biofuel. The leading country in the use of ethanol as a gasoline additive is Brazil, where fuel E25 contains 25% (volume fraction) ethanol while the rest is petrol. Let's assume that the petrol consists of pure octane (ρ_{octane} = 0.703 g cm^{-3}).

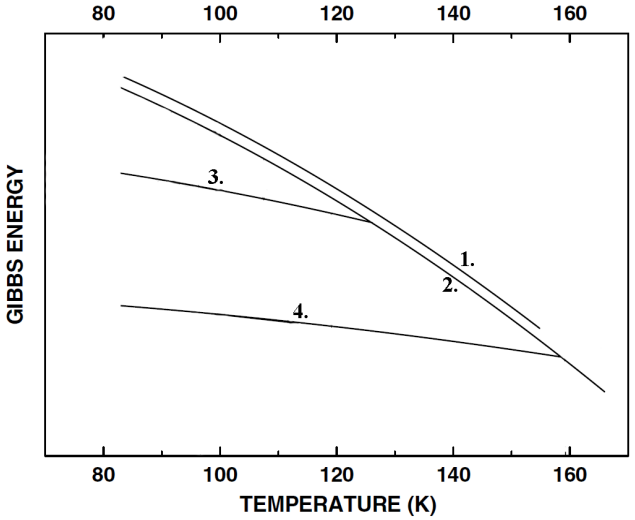
g) Calculate the enthalpy of combustion for octane and ethanol (in kJ per mol) using average bond enthalpies given in Table. Calculate the heat ratio between combustion of 1.0 kg of ethanol and combustion of 1.0 kg octane.

Chemical bond	C–H	C–C	C–O	O=O	H–O	C=O
ΔH(bond), kJ mol^{-1}	413	348	358	498	463	804

h) Enthalpy of the chemical reactions can be calculated using the standard enthalpies of formation. Using the data from Table, calculate the enthalpy of combustion of ethanol and identify the main reason for differences between values calculated here and in question **g)**.

Compound	Ethanol (l)	Carbon dioxide (g)	Water (l)
$\Delta H°$, kJ mol^{-1}	−277.0	−393.5	−285.0

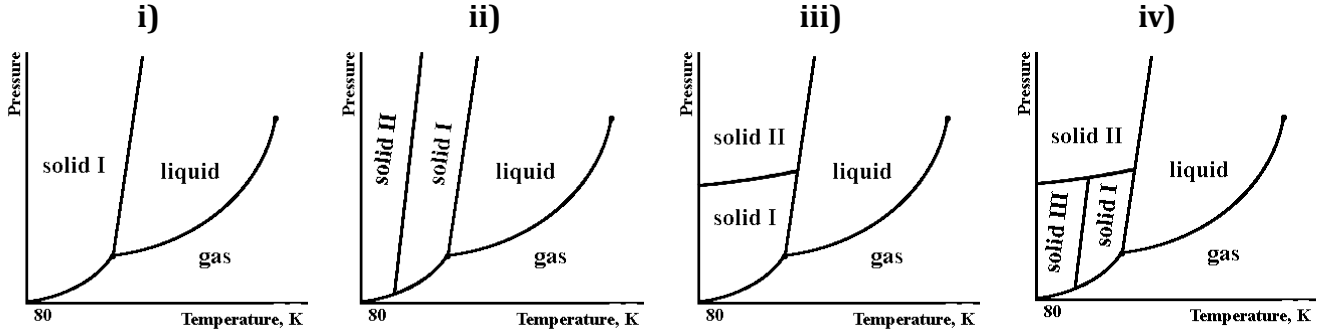
At low temperatures, ethanol exists in solid state and it has been detected that there are two different polymorphic modifications of ethanol. Gibbs energy curves for different phases of ethanol are shown below.



i) Identify these curves as corresponding to **i)** liquid ethanol, **ii)** thermodynamically stable solid form, **iii)** metastable solid form, and **iv)** supercooled liquid and explain your choice.

j) Determine the melting point of the thermodynamically stable and metastable forms.

k) Which of the following phase diagrams can correspond to ethanol? What are the limitations for pressure for selected diagrams, if there are any? Show these limitations by marking the pressure that corresponds to the data given in Figure 2.



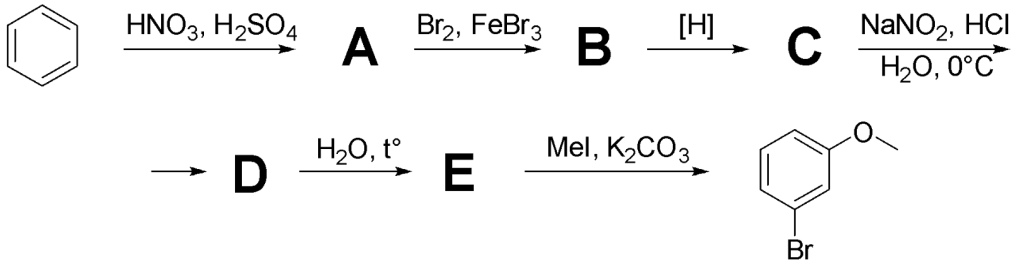
Problem 6 – MECH, SYNTH – Benzyne

Some of the most fascinating types of reactions are those involving the intermediacy of benzyne. Benzyne is benzene minus two adjacent hydrogens, producing a formal triple bond – C_6H_4. The structure of benzyne has been examined both experimentally and theoretically, and the alkyne representation is most widely accepted, although two other structures are considered significant resonance contributors. Using IR spectroscopy, the vibrational frequency of the triple bond in benzyne was assigned to be 1846 cm^{-1}; an unstrained alkyne has a vibrational frequency of approximately 2150 cm^{-1}.

a) What does this say about the relative strength of the benzyne triple bond compared to unstrained alkyne? Circle correct answer(s): **i)** stronger; **ii)** longer; **iii)** weaker; **iv)** shorter.

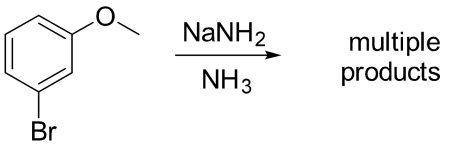
Due to the extreme reactivity of arynes, they must be generated in situ. In the early days of benzyne chemistry, harsh conditions were needed to generate benzynes from aryl halide and a strong base. Consider the following scheme for the synthesis of *m*-bromoanisole, which is then used as a substrate for an experiment involving a benzyne intermediate.

b) Suggest structures for **A**, **B**, **C**, **D**, and **E**.



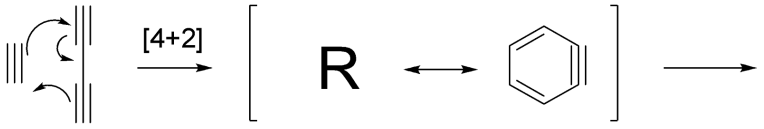
The reaction of *m*-bromoanisole with amide anion in liquid ammonia could potentially give multiple benzyne intermediates and multiple products.

c) Suggest structures for all possible intermediate benzyne(s) and all possible final products after the workup step!



A hexadehydro-Diels-Alder (HDDA) reaction was developed to generate benzyne intermediates in a very sensitive manner. HDDA involves the cycloaddition of 1,3-diyne and alkyne.

d) Draw the structural formula of the resonance structure R.



Consider the following scheme, in which a novel benzyne generation approach was used.

d) Suggest the structures for **F**, **G**, **H** and **I**.