1. Polyenes of high molecular weight   (9 p)

Ziegler-Natta catalyst is used in the synthesis of high molecular weight polyenes. One of the elements of the multicomponent catalyst mixture is $Al_2(C_2H_5)_6$, which self-ignites on contact with oxygen. As a result, it produces a white metal oxide **A**, carbon dioxide and water (**reaction 1**). $Al_2(C_2H_5)_6$ also reacts with water vapour present in the air, producing a white hydroxide **B** and a gaseous hydrocarbon **C** (**reaction 2**).

a) Write the balanced equations for reactions **1–2**.   (2)

When polymerised in the presence of the Ziegler-Natta catalyst, 1,3-butadiene forms stereoregular (i.e. with defined stereochemical composition) polybutadiene chains:
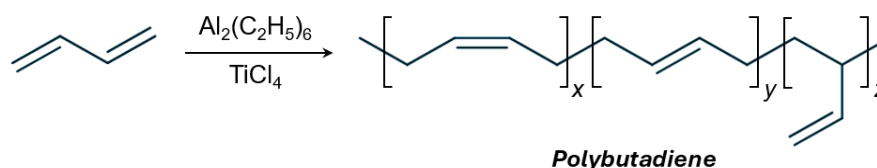
Polybutadiene

b) Choose a formula of the compound that forms during dissociation of $Al_2(C_2H_5)_6$.   (1)
- ☐ $Al(C_2H_5)_3^-$
- ☐ $Al(C_2H_5)_3^+$
- ☐ $Al(C_2H_5)_3^{\cdot}$ (radical)
- ☐ $Al(C_2H_5)_3$

c) Choose what type of addition polymerisation is occurring in the case of the polybutadiene synthesis.   (1)
- ☐ Anion initiated polymerisation
- ☐ Cation initiated polymerisation
- ☐ Radical initiated polymerisation
- ☐ Coordination polymerisation

During laboratory analysis it was found that the molecular weight of the synthesised polybutadiene was 108180 g·mol^{-1}. The number of *trans* double bonds in the following molecular chain was twice greater than that of the vinyl groups. While the $x : y$ ratio is 23.5.

d) Calculate the values of subscripts x, y and z in the aforementioned polybutadiene molecular chain.   (2)

Acrylonitrile butadiene styrene (ABS) is a synthetic plastic from which Lego bricks are made. Addition polymer ABS consists of acrylonitrile ($H_2C=CH-CN$), 1,3-butadiene and styrene ($C_6H_5-CH=CH_2$) monomers. It is known that an ABS polymer chain (M_{ABS} = 8390 g·mol^{-1}) contains 2.672% of nitrogen by mass, while 1.929 g of bromine reacts completely in a 1 : 1 molar ratio with 1,3-butadiene subunits, which are present in 2.155 g of ABS.

e) Calculate the number of subunits N and mass percentage of acrylonitrile, 1,3-butadiene and styrene in the ABS polymer chain.   (3)

2. CO$_2$ capture   (10 p)

The scheme below describes sodium hydroxide assisted direct CO_2 capture from air. The given method allows for the production of pure CO_2 for further use or storage. CO_2 absorber, precipitator, calciner and slaker are reactors, where the enthalpies of reactions taking place in them are -84.8, -11.6, -81.9 and 178.3 kJ·mol^{-1}, respectively.
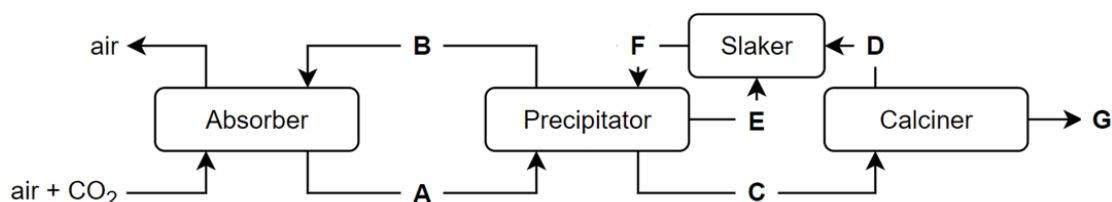
a) Using the given standard enthalpies of formation and calculations, determine the formulas of compounds **A–G**. (7)

Compound	NaOH $_{(aq)}$	Na$_2$CO$_3$ $_{(aq)}$	CO$_2$ $_{(g)}$	CaO $_{(s)}$	Ca(OH)$_2$ $_{(aq)}$	CaCO$_3$ $_{(s)}$	H$_2$O $_{(l)}$
ΔH_f° (kJ$\cdot$mol^{-1})	−469.1	−1130.7	−393.5	−635.1	−1002.8	−1206.9	−285.8

The cost of CO$_2$ capture can be derived from the price of metal carbonate decomposition. In the case of compound **C**, the respective cost is 100€ per 1 tonne of CO$_2$. Metal carbonates with lower decomposition enthalpies can be used to reduce the cost.

b) Calculate the cost of decomposition for both MgCO$_3$ and ZnCO$_3$, if in 2024 the price of electric energy in Estonia is 1$\underline{00}$€·MWh^{-1}. ΔH_f°(MgCO$_3$ $_{(s)}$) = −1095.8 kJ$\cdot$mol^{-1}, ΔH_f°(MgO $_{(s)}$) = −601.6 kJ$\cdot$mol^{-1}, ΔH_f°(ZnCO$_3$ $_{(s)}$) = −814.2 kJ$\cdot$mol^{-1} and ΔH_f°(ZnO $_{(s)}$) = −348.0 kJ$\cdot$mol^{-1}. (2)

c) Considering the chemical properties of Mg and Zn, choose which of the following compounds would suit best for CO$_2$ capture and release. (1)

☐ MgCO$_3$
☐ ZnCO$_3$
☐ Compound **C**

3. A shiny riddle (13 p)

A small town in North America has a name similar to that of the mineral oxide **A** of element **Z**, in which the mass percentage of oxygen (w_0) is 20.05%. Among the minerals of **Z**, **X$_3$YZ$_2$** (w_Z = 32.90%) and **XYZ$_4$** (w_Z = 62.61%) are especially important, since in addition to **Z** they contain precious metals **X** and **Y**. Moreover, metals **X** and **Y** are located in the same group of the periodic table.

a) Using calculations, determine the formulas of oxide **A** and elements **X–Z**. (4)

The reaction of the oxide **A** with hydrogen peroxide and water produces an ortho acid **B**. Upon heating of the ortho acid **B**, oxide **C** is obtained. The reaction of the oxide **A** with sulfur tetrafluoride (SF$_4$) gives a binary compound **D** and a gas that smells like burnt matches. The heating of the oxide **C** together with barium oxide in a 1 : 1 molar ratio gives a salt **E**. The reaction of the salt **E** with fluorosulfuric acid (FSO$_2$OH) produces a strong monoprotic oxyacid **F** (w_0 = 6.68%) that contains the element **Z**, an insoluble barium salt and a strong mineral acid. In the reaction, fluorosulfuric acid acts only as a donor of fluorine atoms. When compounds **F** and **D** are mixed together, salt **G** is formed, which contains **Z** in both the cation and anion.

b) Determine the formulas of **B–G**. (6)

Element **Z** is used in the synthesis of semiconductors in solar panels. The reaction of **Z** with sodium borohydride (NaBH$_4$) gives a binary salt **H** and two gases. The reaction is carried out in liquid ammonia to minimise the reagents' exposure to water, since the hydrolysis of **H** produces gas **I** with a rotten garlic smell. Semiconductor **J** (w_Z = 53.16%) is obtained by mixing cadmium(II) chloride with **H**.

c) Determine the formulas of **H–J**. (3)

## 4. Famous names in the synthesis of Amphidinolide E (13 p)

Amphidinolides are compounds with strong anticancer activity, which can be isolated from algae

belonging to the *Amphidinium* genus. Amphidinolide E can be synthesised from two simpler compounds **D** and **I**. In the first step of the synthesis of **D**, the starting material is oxidised to aldehyde **A**. In the second step, a nucleophilic addition reaction happens while the third step is a rearrangement of functional groups.
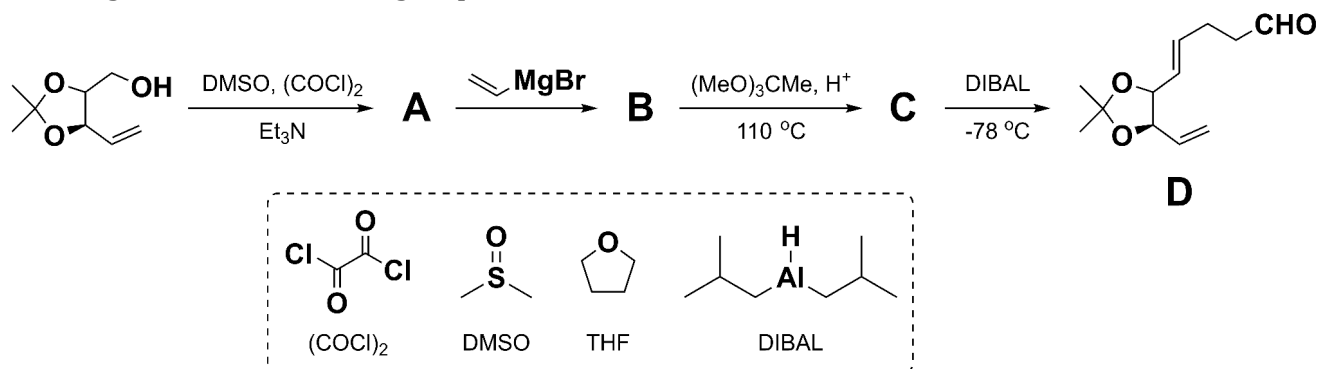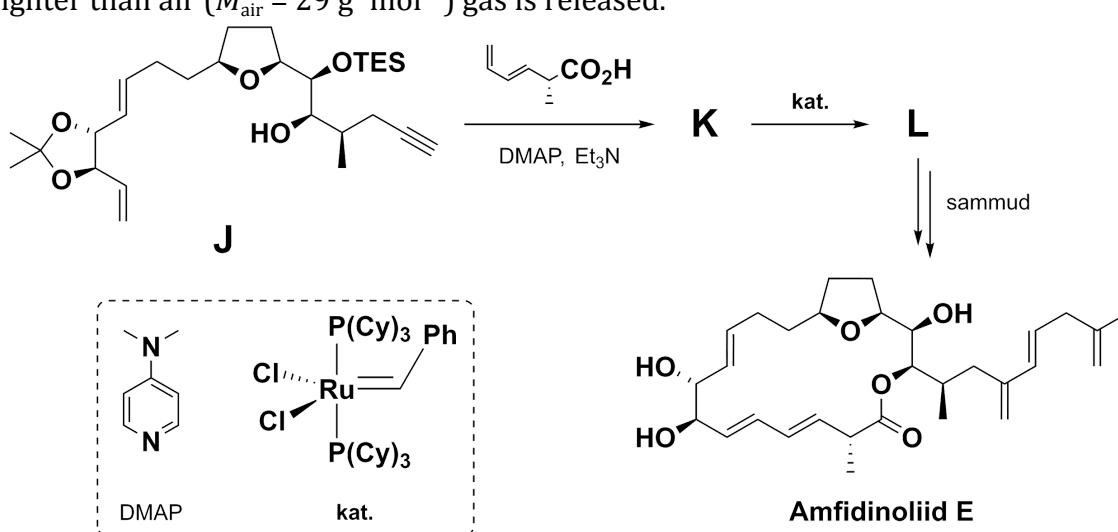
a) Draw the structures of compounds **A–C** without showing stereochemistry. (3)

b) Choose the name of the reaction happening in the step **B → C**. (1)
   ☐ Claisen–Johnson rearrangement
   ☐ Gabriel synthesis reaction
   ☐ Wittig reaction

c) From the list of scientists, choose the name of the French chemist (1871–1935), after whom the organometallic reagent (Nobel prize 1912) used in step **A → B** was named. (1)
   ☐ Markovnikov
   ☐ Grignard
   ☐ Claisen
   ☐ Suzuki

In **E → F** − the second step of the synthesis of **I** − oxidation happens. In the third step **F → G**, the double bond equivalent increases by one − in the first reaction a geminal dibromo intermediate is formed through a Wittig-type transformation, which can then be consequently eliminated to form a multiple bond. 9-BBN or *banana borane* is a reducing agent similar to diborane (B_2H_6). $NaIO_4$ is a strong oxidant.
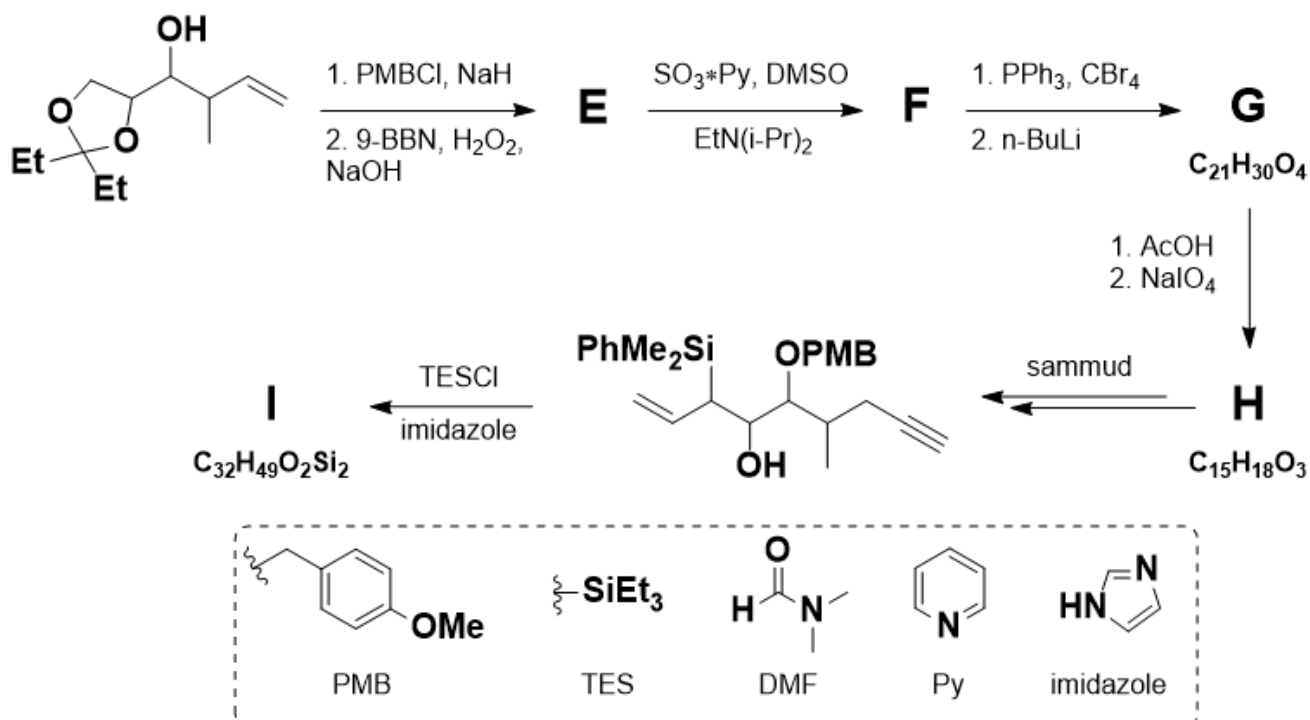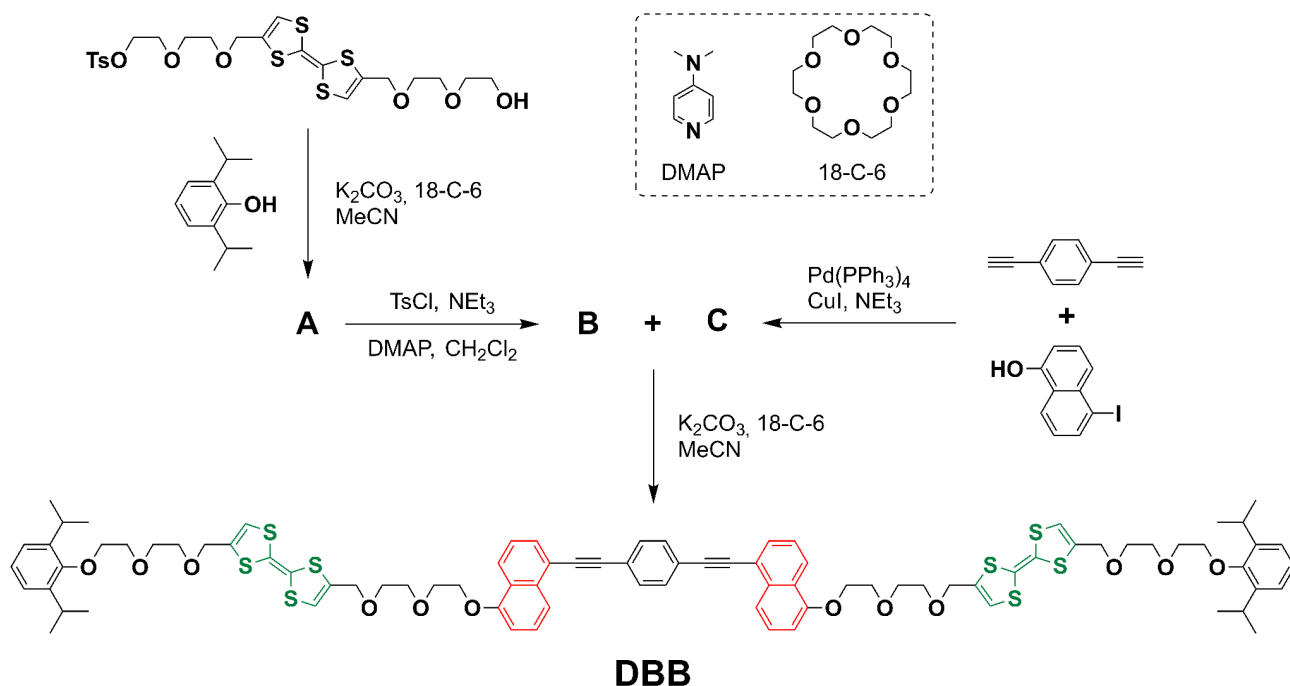
d) Draw the structures of compounds **E–I** without showing stereochemistry. (5)
Compound **J** is synthesised from **D** and **I**. In the step **K → L** the 18-membered cycle is formed and a lighter than air (M_{air} = 29 g·mol^{-1}) gas is released.

e) Draw the structures of compounds **K** and **L** without showing stereochemistry. (2)
f) Choose, what is the name of the catalyst marked as **kat.** (1)
  ☐ Lindlar catalyst
  ☐ Ziegler–Natta catalyst
  ☐ Friedel–Crafts catalyst
 ☐ Grubbs catalyst

5. Molecular muscles (9 p)
Rotaxanes are supramolecular structures that are mechanically locked together through noncovalent interactions. Rotaxanes consist of a round macrocycle (shown in blue in the problem), which is threaded by a long dumbbell-shaped molecule. Such complex structures are used in the synthesis of artificial molecular machines. Dumbbell-shaped **DBB** can be produced according to the following synthesis scheme:

a) Draw the structures of compounds **A-C**. (4)
b) Choose, what is the purpose of the crown ether (18-C-6). (1)

- ☐ Solvent
- ☐ Nucleophile
- ☐ Radical initiator
- ☐ Cation chelating ligand

The following scheme synthesis scheme shows the preparation of a rotaxane:
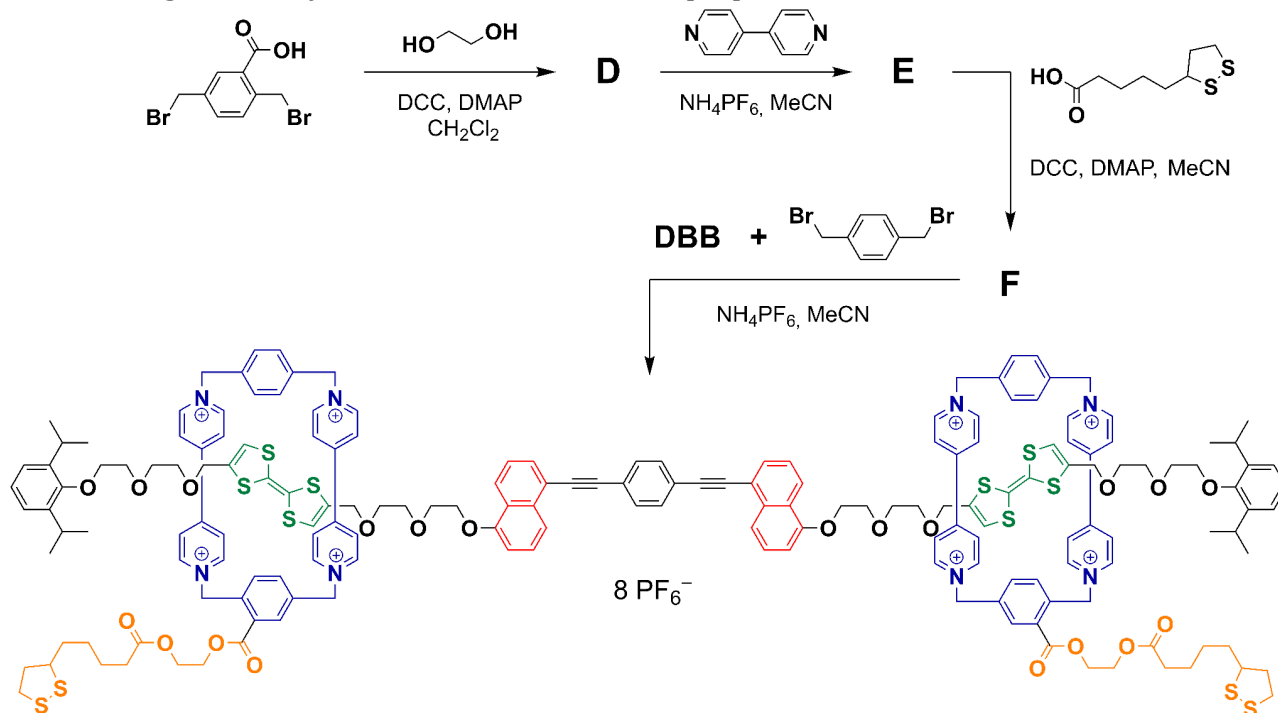
c) Draw the structures of compounds **D-F**, for **E** and **F** draw only the cations. (3)

Molecular muscles, that extend and contract similarly to biological muscles, can be built from the synthesised rotaxane. The disulfide fragments belonging to the macrocycles enable the rotaxanes to bind to the gold surface, where the aforementioned phenomena occur.

d) According to the theory of hard and soft acids and bases (HSAB), choose why polarisable sulfur atoms are suitable for binding rotaxanes to the gold surface. (1)
- ☐ Sulfur and gold are both **soft** particles, which form strong covalent bonds.
- ☐ Sulfur and gold are both **borderline** particles (with properties in between those of hard and soft particles), which form strong ionic-covalent bonds.
- ☐ Sulfur and gold are both **hard** particles, which form strong ionic bonds.

## 6. Construction of molecular muscles (8 p)

Tetrathiafulvalene fragments (shown in green in the figure) can be reversibly oxidised. Upon oxidation, the conformation of rotaxane macrocycles (shown in blue) changes due to electrostatic repulsion. The conformation change of the rotaxane that bends the gold surface is shown schematically in the following picture.
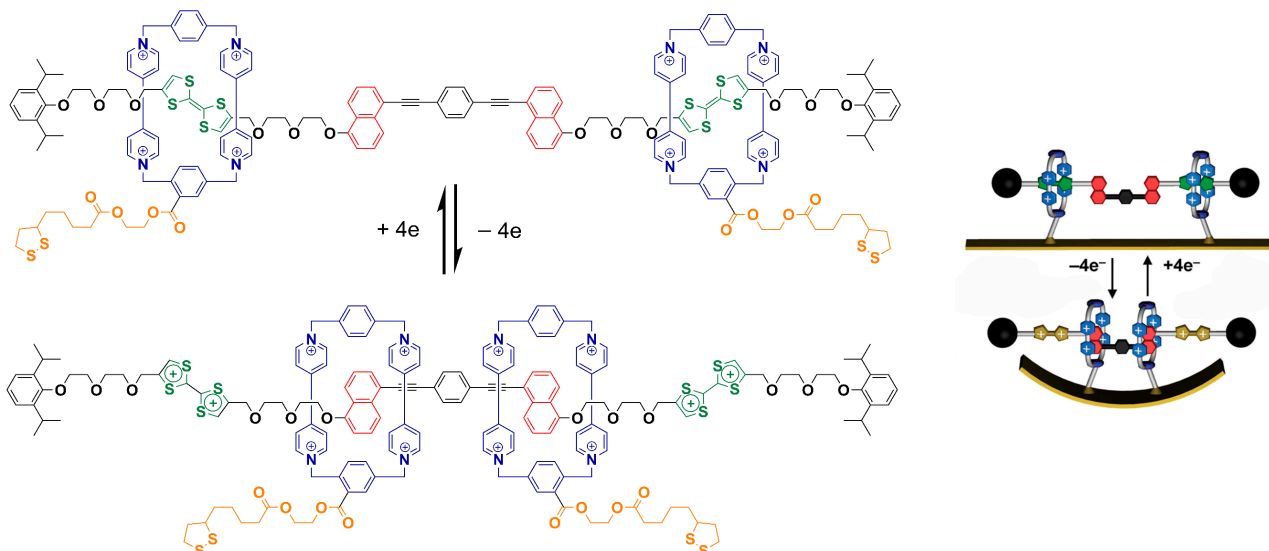
a) Considering the sulfur-containing heterocycles present in the tetrathiafulvalene fragments of the reduced and oxidised forms, determine the number of **i)** π-electrons and **ii)** if these cycles are aromatic or not. (2)

	Reduced form	Oxidised form
π-electron count		
Aromatic	☐	☐
Non-aromatic	☐	☐

For the construction of artificial muscles, a bunch of rotaxanes are bound to the gold surface. The contraction of such muscles occurs upon the simultaneous conformational change of all rotaxane molecules. All rotaxane molecules are oriented along the length of the muscle.
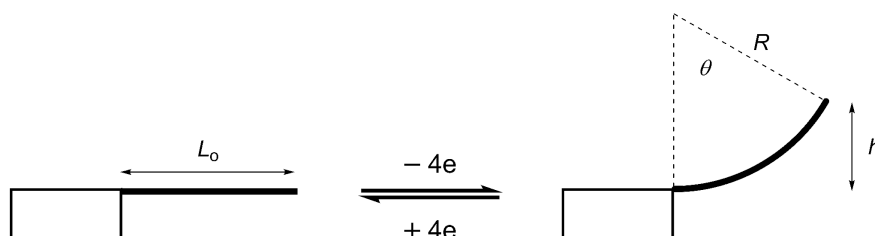
The vertical displacement h (μm) of each contracted muscle can be expressed by the following equation, where L_0 is the total length of the muscle and R is the radius of curvature:

$$h = R\left[1 - cos\left(\frac{L_0}{R}\right)\right]$$

b) Calculate **i)** the total length (L_0) and **ii)** the vertical displacement (h) of the muscle, if $\theta = 30°$ and $R = 95\underline{5}$ μm (see figure). During calculations, assume that the total length of the muscle does not change. (2)

The tension (F) on the surface of the muscle, caused by the electrostatic repulsion of the dicationic tetrathiafulvalene and the tetracationic macrocycle, can be described using Coulomb's law, where q_1 and q_2 are the magnitudes of the respective charges, ε is the relative dielectric permittivity, ε_0 is the dielectric permittivity of the vacuum and r is the distance between charges:

$$F = \frac{q_1 q_2}{4\pi\varepsilon_0\varepsilon r^2}$$

In the following figure the side view of the rotaxane molecule is shown schematically, where the blue macrocycle has moved by a distance x relative to the tetrathiafulvalene.
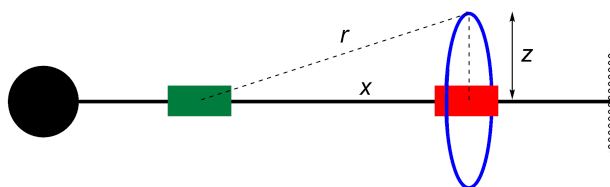
c) Derive an expression for the horizontal component F_x of the electrostatic force F, which is caused by **one** rotaxane molecule, with respect to the radius of the blue macrocycle z and the horizontal deviation x. Ignore all interactions between different rotaxane molecules. (2)

☐ $F\dfrac{x}{\sqrt{x^2+z^2}}$

☐ $F\dfrac{\sqrt{x^2+z^2}}{x}$

☐ $2F\dfrac{x}{\sqrt{x^2+z^2}}$

☐ $2F\dfrac{xz}{\sqrt{x^2+z^2}}$

Total tension on the surface of the muscle F_{tot} is proportional to the vertical displacement h, where β is a constant:

$$F_{tot} = \beta h$$

d) Calculate how many rotaxane molecules N are needed to achieve a vertical displacement of 120 μm, if β = 1500 N·m^{-1}, z = 0.50 nm, x = 1.4 nm, ε = 80, ε_0 = 8.85·10^{-12} F·m^{-1} and elementary charge e = 1.6·10^{-19} C. (2)

7. Antiarin   (9 p)

Antiarin belongs to the group of compounds used for treatment of heart weakness, but it is also quite toxic − its uses range from regulating heart pressure to being used in poison darts.

a) Determine the empirical formula of antiarin and calculate its molar mass. (1)

For many mammals, the median lethal dose (LD$_{50}$) of antiarin is 1.76·10^{-7} mol·kg^{-1} − the amount of substance lethal to half (50%) of the test group individuals within a certain time period.

b) A pill used for heart weakness treatment, with a mass of 0.22 g, contains 1.24% of the active ingredient. Calculate how many pills Alex, who weighs 70 kg, can take per day without exceeding the median lethal dose of antiarin. (2)

The pill contains the derivative of antiarin, which has an empirical formula of $C_{50}H_{54}O_{14}$. It is known that its structure contains benzene rings, while each molecule of antiarin has three residues of acid **X** attached to it.

**c)** Determine the acid **X** and draw its structure. (2)

In the stomach, acidic hydrolysis of antiarin occurs, causing the cleavage of the glycosidic bond present in the molecule.

d) Draw the structures of compounds that form during acidic hydrolysis, without showing stereochemistry. (2)

As an antidote for antiarin, Digibind is used, which is a drug containing another toxic cardiac glycoside, which is summarised by the saying "even poison can be a medicine, all depends on the dose", because it "neutralises" the toxicity of antiarin when administered in the correct dose. Sleepy Alex accidentally took one pill more than the allowed dose in the morning, which turned out to be life-threatening. The called ambulance administered n vials of Digibind to Alex:

$$n = 2·m_{total\ antiarin}\text{ (mg)·0.8 (bioavailability)}$$
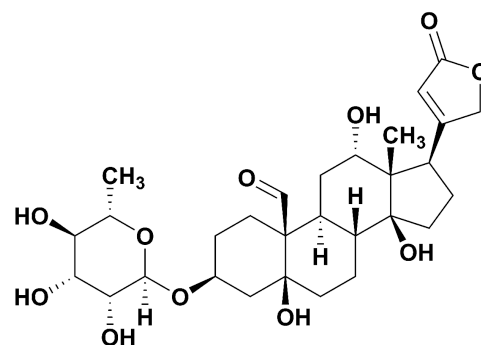
e) Calculate how many vials of the antidote were administered to Alex. (2)

## 8. Monomers and dimers (9 p)

Organometallic compounds are molecules, which contain covalent bonds between metal and carbon atoms. One of the most famous organometallic compounds is the compound **C**, which was synthesised in 1951 for the first time. Its discovery led to a breakthrough and rapid development in the field. Compound **C** resembles the shape of a burger and can be synthesised as follows:

$$2 \; \text{A} \xrightarrow[-H_2]{\text{Na}} 2\textbf{B} \xrightarrow{\textbf{X}} \textbf{C} + 2\textbf{Y}$$
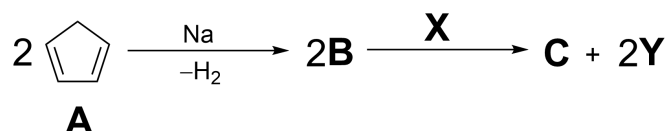
The reaction of compound **A** with sodium yields salt **B**, while releasing hydrogen gas. Upon addition of halide **X** to two equivalents of compound **B**, compound **C** is formed along with two equivalents of inorganic salt **Y**, which is widely used for cooking in everyday life. It is known that the molar mass ratio of salts **X** and **Y** is $M_X : M_Y = 2.169 : 1$.

a) Write the systematic name of compound **A**. (1)
b) Determine the chemical formulas of salts **X** and **Y**. (2)
c) Draw the structures of compounds **B** and **C**. (2)

The starting material **A** is unstable at room temperature, reacting over time with itself, forming a stable dimer **A$_2$**. Moreover, the happening pericyclic reaction is known under the names of two famous chemists. Every 8 hours approximately half of the monomer dimerises, hence why compound **A** can be stored for a long time either as a dimer or at very low temperatures. Therefore, the starting material **A** for the synthesis of compound **C** has to be freshly made, which is done by heating the dimer at high temperatures i.e. cracking:

$$\textbf{A}_2 \xrightarrow{170\,°C} 2 \; \textbf{A}$$
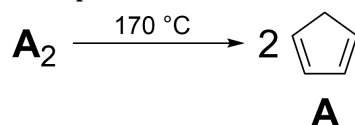
d) i) Draw the structure of dimer **A$_2$**, without showing stereochemistry and **ii)** name the reaction through which the compound **A** dimerises. (2)

During cracking the monomer has to be continuously separated from the dimer, since at higher temperatures the rate of the reverse cracking reaction i.e. dimerisation also increases. In the table below, some physical properties of compounds **A** and **A$_2$** are shown.

Compound	T_m (°C)	T_b (°C)	Miscibility with org. solvents	Miscibility with water
A	−90	40	Mixes	Does not mix
A$_2$	33	150	Mixes	Does not mix

e) Considering the data provided in the table, choose which of the following methods is suitable for separating monomer **A** from its dimer **A$_2$**. (1)
☐ Fractional distillation
☐ Rectification (repeated reflux distillation)
☐ Decantation
☐ Recrystallisation

Compound **A*** (famous analogue of compound **A**) is also widely used as a ligand in the synthesis of organometallic compounds. The use of compound **A*** is somewhat more convenient, since, unlike **A**, it does not form the corresponding dimer.
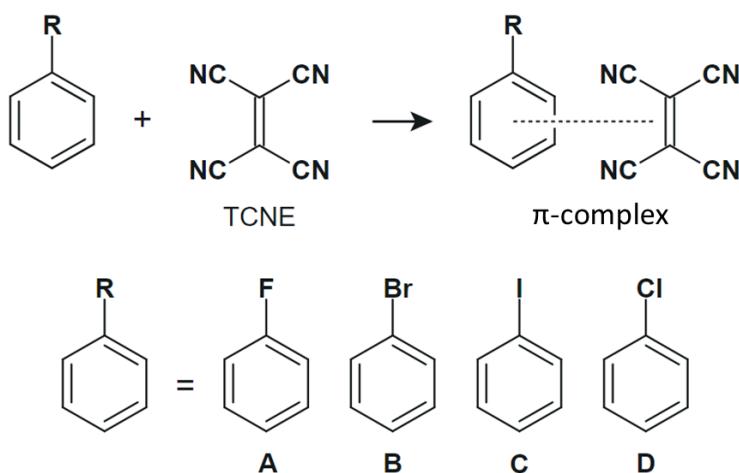
A　　　　**A***
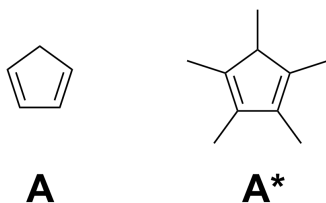
f) Choose why compound **A*** does not dimerise. (1)
- ☐ Molar mass of **A*** is too great.
- ☐ **A*** is sterically hindered (i.e. too bulky).
- ☐ Double bonds in **A*** more electron-deficient, in comparison to **A**.
- ☐ Double bonds in **A*** more electron-rich, in comparison to **A**.

9. Colourful aromatics (10 p)

Aromatic compounds form π-complexes with tetracyanoethylene (TCNE):

Electronegative cyanogroups of TCNE "pull" the electrons of the double bond to themselves, which lowers the electron density of the bond. Through this TCNE forms donor-acceptor interactions with π-electrons of the benzene ring. The colour of the π-complex depends on the ionisation potential of the compound, i.e its ability to lose electrons. The higher the ionisation potential of the compound, the higher the energy of the light it absorbs.

a) Arrange the compounds **A–D** in order of increasing ionisation potential. (2)

The following figure on the left shows the approximate absorbance curves of π-complexes between compounds **A–D** and TCNE.
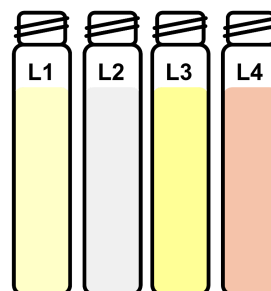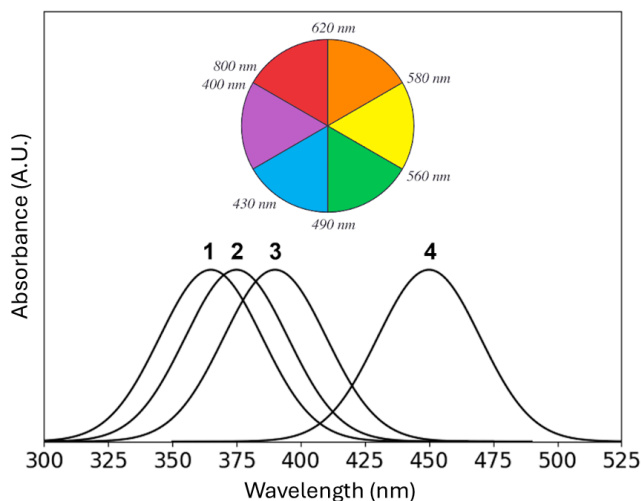
b) Determine the compounds **A–D**, corresponding to each curve **1–4**. (2)

Chemist Ben Zene mixed up vials of compounds **A–D**. To identify the compounds, Ben weighed out 10.0 mg of unknown compound from each vial into four test tubes and then added 10.00 cm^3 of a 1% TCNE solution in dichloromethane. As a result, Ben got four solutions of different colours **L1–L4** (see right-hand figure above).

c) Determine which compounds (**A–D**) contain solutions **L2** and **L4**, by using the absorbance curves and the colour wheel in the left-hand figure. (2)

Unfortunately for Ben, solutions **L1** and **L3** cannot be distinguished by a human eye since their tones are too similar, which is why he decided to use UV-Vis spectroscopy to identify the compounds contained in those solutions. According to the Beer-Lambert law, the solution's absorbance (A) is proportional to the concentration of the compound (c), extinction coefficient (ε) and the optical path length (l):

$$A = c \cdot \varepsilon \cdot l$$

Ben found in literature that the extinction coefficients for respective π-complexes of TCNE with compounds **A–D** are 2670, 577, 690 and 1400 dm^3·mol^{-1}·cm^{-1}. Thus, to carry out UV-Vis measurements, Ben transferred 1.00 cm^3 of solutions **L1** and **L3** into two measuring flasks and filled them up with dichloromethane until the 100.00 cm^3 mark, hence obtaining diluted solutions **L1'** and **L3'**. Lastly, Ben added solutions **L1'** and **L3'** into cuvettes and measured their absorbance. The diameter (optical path length l) of the cuvettes used for the measurements was exactly 1 cm.

d) Identify which compounds (**A–D**) are contained in solutions **L1** and **L3**, if absorbance values of **L1'** and **L3'** are 0.1244 and 0.0367 A.U, respectively. (4)