



52nd IChO 2020
International Chemistry Olympiad

Istanbul, Turkey

 **60**
COUNTRIES

 **166** ACADEMICS

 **235** FUTURE SCIENTIST

 23.07.2020 - 29.07.2020



Problems



52nd IChO 2020
International Chemistry Olympiad

Istanbul, Turkey

CHEMISTRY FOR A BETTER TOMORROW

July 25, 2020





Instructions

- Only write with pen. Your calculator should be non-programmable.
- This examination has **9 problems**.
- You will have **5 hours** to solve the exam.
- **Begin** only when the **START** command is given.
- All results must be written in the appropriate boxes in pen in the designated areas on the **answer sheets**. Use the back of the exam sheets if you need scratch paper. Remember that answers written outside the answer boxes will not be graded.
- Write relevant calculations in the appropriate boxes when necessary. Full marks will be given for correct answers only when your work is shown.
- The invigilator will announce a **30-minute** warning before the Stop command.
- You **must stop** working when the **STOP** command is given. Failure to stop writing will lead to the nullification of your exam.
- The official English version of this examination is available on request only for clarification.

- You are not allowed to leave your working place without permission. If you need any assistance (broken calculator, need to visit a restroom, etc), raise hand and wait until an invigilator arrives.

GOOD LUCK!

Problems & Grading Information

Problem	Title	Total Score	% of Total Score
1	Two Beauties of Turkey: the Van Cat and the Ankara Cat	24	8
2	A Tale of a Reactive Intermediate	77	10
3	(±)-Coerulescine	51	8
4	Symmetry Does Matter!	66	10
5	Konya, Carrot, Beta-Carotene, Vitamin-A, Immune System, Vision	100	14
6	Thermodynamics through an Interstellar Journey	80	12
7	Phthalocyanines	85	12
8	Boron Compounds and Hydrogen Storage	58	14
9	Quantification of Heavy Metal Ions	100	12
	TOTAL	641	100

Table of Contents

Authors	4
Physical Constants and Equations	5
Periodic Table of Elements	6
¹ H-NMR Chemical Shifts	7
Typical Coupling Constants	7
¹³ C-NMR Chemical Shifts	8
IR Absorption Frequency Table	8
Problem 1. Two Beauties of Turkey: the Van Cat and the Ankara Cat	10
Problem 2. A Tale of a Reactive Intermediate	13
Problem 3. (±)-Coerulescine.....	17
Problem 4. Symmetry Does Matter!.....	20
Problem 5. Konya, Carrot, Beta-Carotene, Vitamin-A, Immune System, Vision.....	24
Problem 6. Thermodynamics through an Interstellar Journey	28
Problem 7. Phthalocyanines	32
Problem 8. Boron Compounds and Hydrogen Storage	36
Problem 9. Quantification of Heavy Metal Ions	40

Authors

ALANYALIOĞLU, Murat, *Atatürk University*

AYDOĞAN, Abdullah, *İstanbul Technical University*

BURAT, Ayfer Kalkan, *İstanbul Technical University*

DAĞ, Ömer, *Bilkent University*

DAŞTAN, Arif, *Atatürk University*

KILIÇ, Hamdullah, *Atatürk University*

METİN, Önder, *Koç University*

ÖZTÜRK, Turan, *İstanbul Technical University*

SARAÇOĞLU, Nurullah, *Atatürk University*

TÜRKMEN, Yunus Emre, *Bilkent University*

ÜNLÜ, Caner, *İstanbul Technical University*

YILMAZ, İsmail, *İstanbul Technical University*

YURTSEVER, Mine, *İstanbul Technical University*

Editor: SARAÇOĞLU, Nurullah, *Atatürk University*

Physical Constants and Equations

Avogadro's number, $N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$

Boltzmann constant, $k_B = 1.3807 \times 10^{-23} \text{ JK}^{-1}$

Universal gas constant, $R = 8.3145 \text{ JK}^{-1} \text{ mol}^{-1} = 0.08205 \text{ atm L K}^{-1} \text{ mol}^{-1}$

Speed of light, $c = 2.9979 \times 10^8 \text{ ms}^{-1}$

Planck's constant, $h = 6.6261 \times 10^{-34} \text{ J s}$

Faraday's constant, $F = 9.6485 \times 10^4 \text{ C mol}^{-1}$

Mass of electron, $m_e = 9.1093 \times 10^{-31} \text{ kg}$

Standard pressure, $P = 1 \text{ bar} = 10^5 \text{ Pa}$

Atmospheric pressure, $P_{atm} = 1.01325 \times 10^5 \text{ Pa} = 760 \text{ mmHg} = 760 \text{ torr}$

Zero of the Celsius scale, 273.15 K

1 picometer (pm) = 10^{-12} m ; $1 \text{ \AA} = 10^{-10} \text{ m}$; 1 nanometer (nm) = 10^{-9} m

$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$

$1 \text{ cal} = 4.184 \text{ J}$

$1 \text{ amu} = 1.6605 \times 10^{-27} \text{ kg}$

Charge of an electron: $1.6 \times 10^{-19} \text{ C}$

Ideal gas equation: $PV = nRT$

Enthalpy: $H = U + PV$

Gibbs free energy: $G = H - TS$

$$\Delta G = \Delta G^0 + RT \ln Q$$

$$\Delta_r G^0 = -RT \ln K = -nFE_{cell}^0$$

Entropy change:

$$\Delta S = \frac{q_{rev}}{T}, \text{ where } q_{rev} \text{ is heat for the reversible process}$$

$$\Delta S = nR \ln \frac{V_2}{V_1} \text{ (for isothermal expansion of an ideal gas)}$$

Nernst equation: $E = E^0 + \frac{RT}{nF} \ln \frac{C_{oxidation}}{C_{reduction}}$

Energy of a photon: $E = \frac{hc}{\lambda}$

Integrated rate law

Zeroth-order: $[A] = [A]_0 - kt$

First-order: $\ln[A] = \ln[A]_0 - kt$

Second order: $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$

Arrhenius equation: $k = Ae^{-E_a/RT}$

Equation of linear calibration curve: $y = mx + n$

Lambert–Beer equation: $A = \epsilon lc$

Periodic Table of Elements

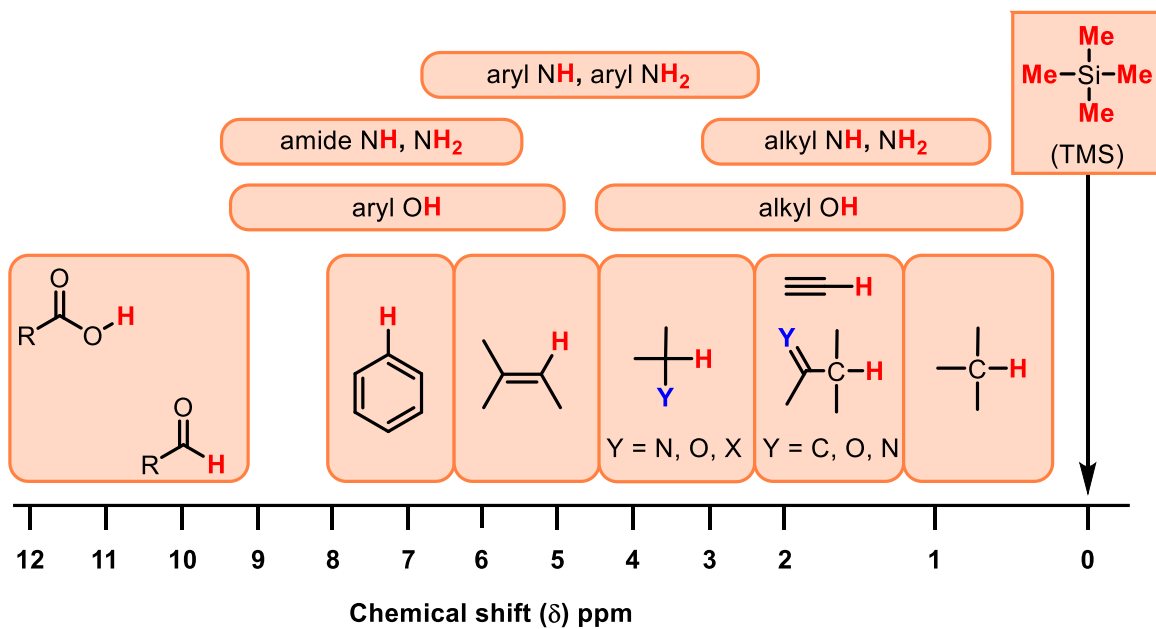
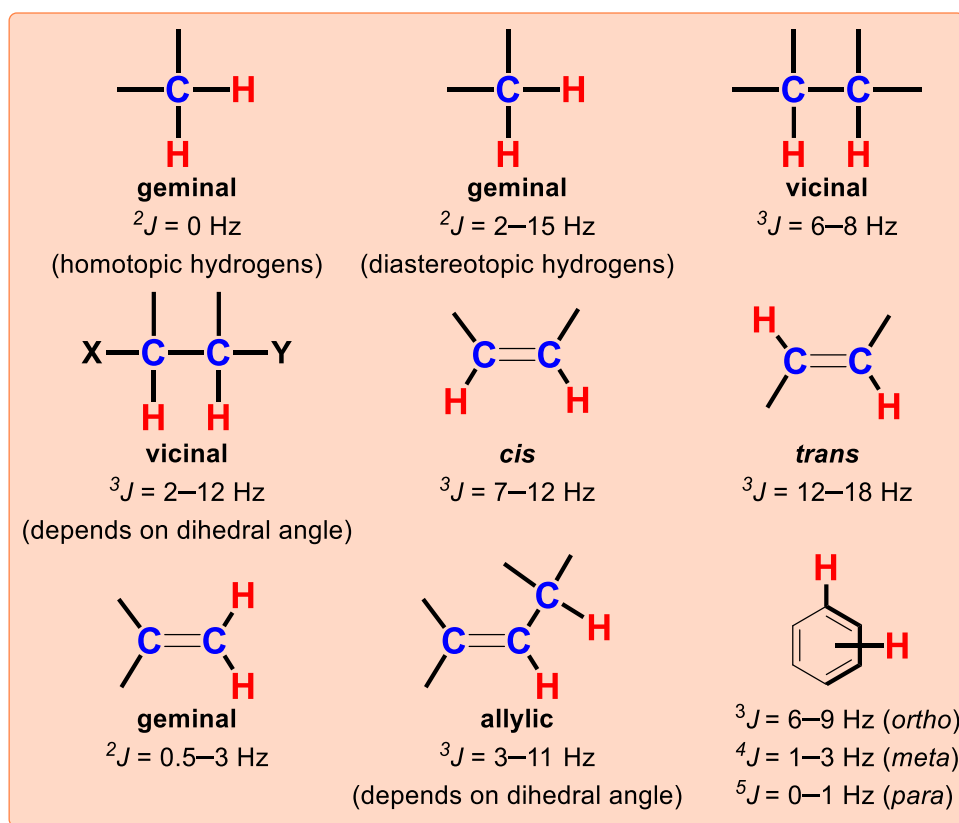
	1															18		
	1 H 1.008	2	atomic number Symbol atomic weight										13	14	15	16	17	2 He 4.003
	3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
	11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc -	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
	55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
	87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

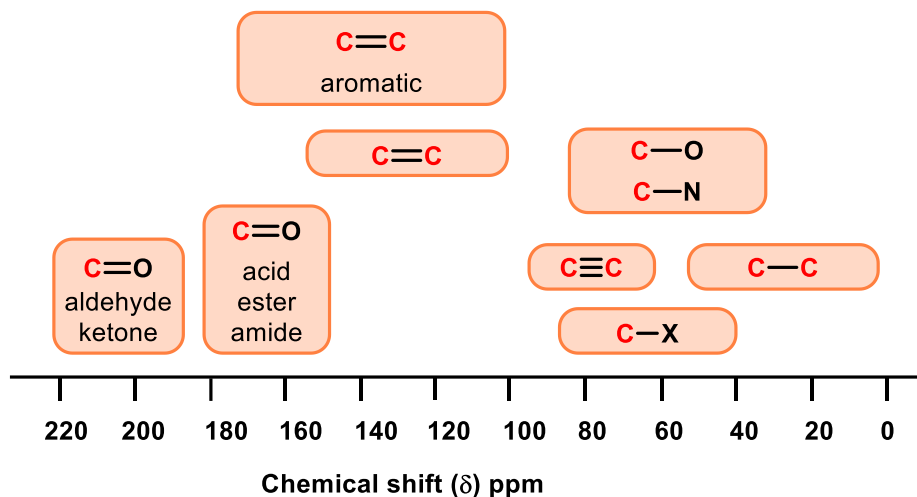
57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -



Copyright © 2018 International Union of Pure and Applied Chemistry

Reproduced by permission of the International Union of Pure and Applied Chemistry

¹H-NMR Chemical Shifts**Typical Coupling Constants**

¹³C-NMR Chemical Shifts**IR Absorption Frequency Table**

Functional Group	Type of Vibration	Absorption Frequency Region (cm^{-1})	Intensity
Alcohol			
O-H	(stretch, H-bonded)	3600–3200	strong, broad
	(stretch, free)	3700–3500	strong, sharp
C-O	(stretch)	1150–1050	strong
Alkane			
C-H	stretch	3000–2850	strong
	bending	1480–1350	variable
Alkene			
=C-H	stretch	3100–3010	medium
	bending	1000–675	strong
C=C	stretch	1680–1620	variable
Alkyl Halide			
C-F	stretch	1400–1000	strong
C-Cl	stretch	800–600	strong
C-Br	stretch	600–500	strong
C-I	stretch	500	strong
Alkyne			
C-H	stretch	3300	strong, sharp
C \equiv C	stretch	2260–2100	variable, not present in symmetrical alkynes
Amine			
N-H	stretch	3500–3300	medium (primary amines have two bands; secondary amines have one band, often very weak)

C–N	stretch	1360–1080	medium-weak
N–H	bending	1600	medium
Aromatic			
C–H	stretch	3100–3000	medium
C=C	stretch	1600–1400	medium-weak, multiple bands
Carbonyl			
C=O	stretch	1820–1670	strong
Acid			
C=O	stretch	1725–1700	strong
O–H	stretch	3300–2500	strong, very broad
C–O	stretch	1320–1210	strong
Aldehyde			
C=O	stretch	1740–1720	strong
C–H	stretch	2850–2820 & 2750–2720	medium, two peaks
Amide			
C=O	stretch	1690–1640	strong
N–H	stretch	3500–3100	unsubstituted have two bands
	bending	1640–1550	
Anhydride			
C=O	stretch	1830–1800 & 1775–1740	two bands
Ester			
C=O	stretch	1750–1735	strong
C–O	stretch	1300–1000	two bands or more
Ketone			
acyclic	stretch	1725–1705	strong
cyclic	stretch	3-membered - 1850	strong
	stretch	4-membered - 1780	strong
	stretch	5-membered - 1745	strong
	stretch	6-membered - 1715	strong
	stretch	7-membered - 1705	strong
α,β -unsaturated	stretch	1685–1665	strong
conjugation moves absorptions to lower wavenumbers			
aryl ketone	stretch	1700–1680	strong
Ether			
C–O	stretch	1300–1000 (1150–1070)	strong
Nitrile			
C \equiv N	stretch	2260–2210	medium
Nitro			
N–O	stretch	1560–1515 & 1385–1345	strong, two bands

Problem 1 8% of the total	Question	1.1	1.2	1.3	Total
	Points	14	4	6	24

Problem 1. Two Beauties of Turkey: the Van Cat and the Ankara Cat



The most beautiful of cats, the Van cat is a pure breed living only in Lake Van basin. Another endemic cat breed is the Ankara cat. They are called Angora cats. Their most important feature is their two different eye colors.

Van cat



Ankara cat



Nepeta cataria (catnip)

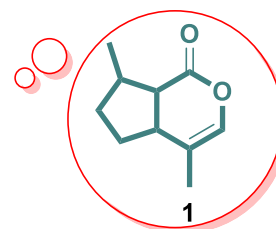


Just like people, cats can sometimes be stressed and angry. Just as people are made happy by melatonin, the stress of cats can be reduced and they can be made happy thanks to a natural product. Nepetalactone is an organic compound isolated from the plant catnip (*Nepeta cataria*), which acts as a cat attractant. Nepetalactone is a ten-carbon bicyclic monoterpene compound derived from isoprene with two fused rings: a cyclopentane and a lactone.

Cat eating catnip in the garden

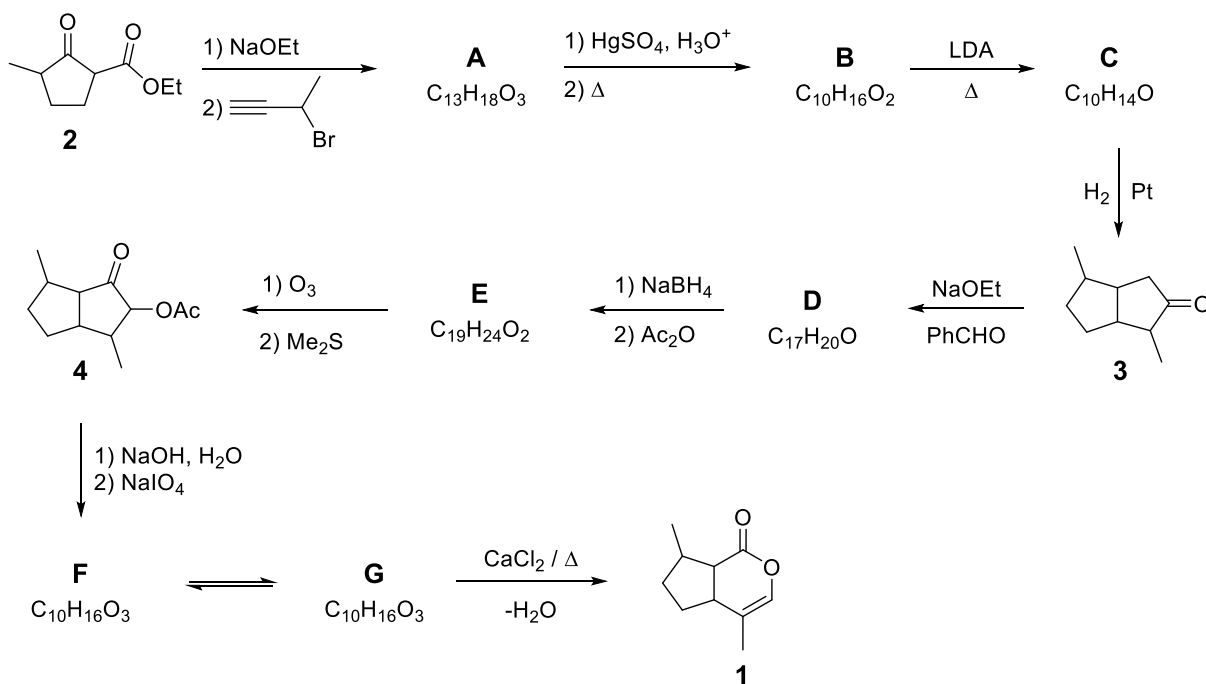


Cat's dream



Nepetalactone

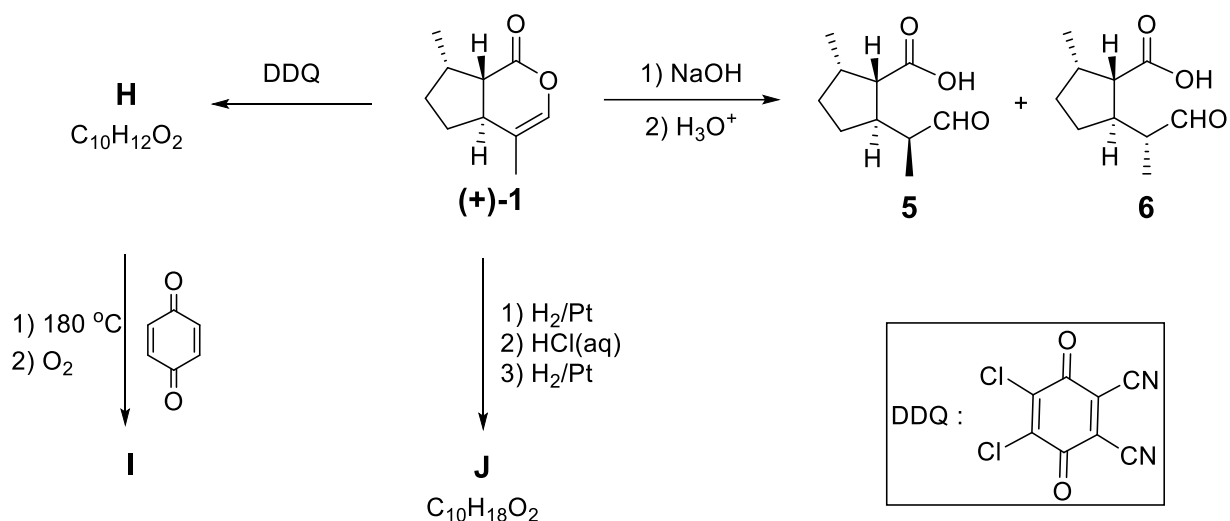
Total synthesis of nepetalactone:



1.1. The above scheme describes the total synthesis of nepetalactone. **Draw** structures of **A–G**, without stereochemical details.

Hints:

- Compound **A** has strong and sharp band at 3300 cm⁻¹ in the IR spectrum.
- **A**, **B**, and **F** are monocyclic, while **C**, **D**, **E**, and **G** are bicyclic compounds.
- **F** has one doublet at ~ 9.8 ppm in the ¹H-NMR spectrum.

Reactions of nepetalactone:

The above scheme includes a few reactions of one of the enantiopure nepetalactone **1** isomers. Three of the reaction products (**5**, **6**, and **J**) are used as insect repellents in industry.

1.2. For the relationship between **5** and **6**, which of the following is/are true? **Tick** the box next to the correct answer(s) on your answer sheets.

<input type="checkbox"/>	Enantiomers
<input type="checkbox"/>	Diastereomers
<input type="checkbox"/>	Identical
<input type="checkbox"/>	Stereoisomers

Reaction of **1** with DDQ gives highly conjugated compound **H**. Also, thermal reaction of compound **H** with *p*-quinone gives **I** with molar mass of 226.28 g/mol.

1.3. Draw the structures of **H**, **I**, and **J** indicating stereochemistry.

Hints:

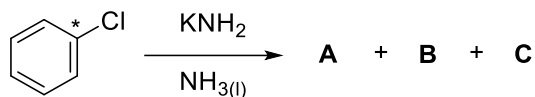
- During the formation of **I**, sequential pericyclic reactions and an oxidation reaction (due to the presence of O_2) take place, and a well-known gas forms during the reaction.
- **J** has a strong and very broad band between 3300 and 2500 cm^{-1} in the IR spectrum.

Problem 2 10% of the total	Question	2.1	2.2	2.3	2.4	2.5	2.6	2.7	Total
	Points	7	9	8	16	5	4	28	77

Problem 2. A Tale of a Reactive Intermediate

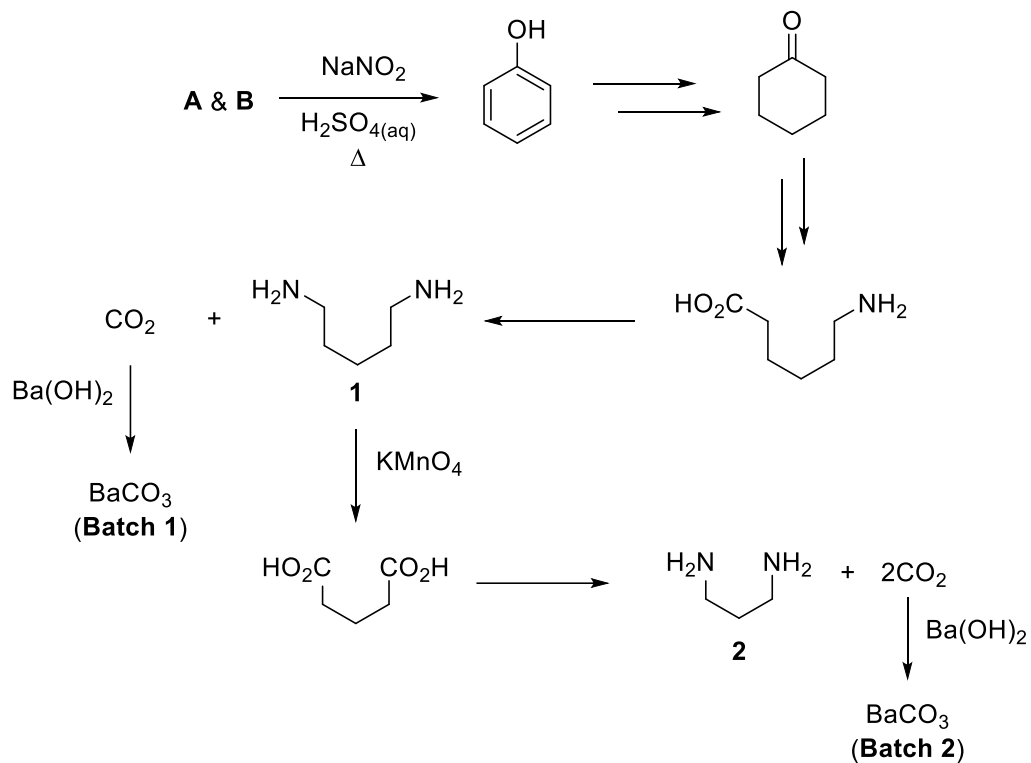
Arynes constitute a special class of reactive intermediates. The first experimental evidence for the structure of an aryne (benzyne) was demonstrated in 1953 via the elegant labeling experiments by John D. Roberts and coworkers.

In one such experiment, chlorobenzene, whose carbon at position 1 was labeled with radioactive ^{14}C , was reacted with KNH_2 in liquid NH_3 to give nearly equal amounts of isotopic isomers **A** and **B** along with the inorganic salt **C**. This reaction proceeds via the formation of aryne intermediate **D**.



2.1. Draw the structure of **A**, **B** and **D**, and provide the formula of **C**. Indicate the position(s) of ^{14}C -labeled carbon(s) with an asterisk (*) whenever applicable.”

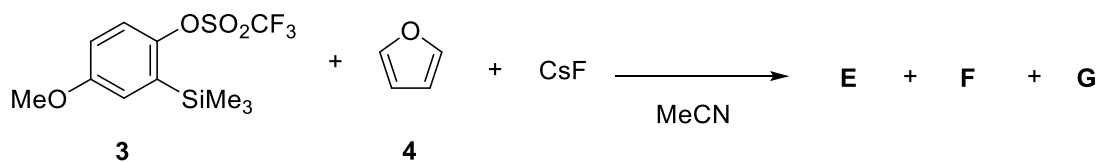
Analysis of the ^{14}C -labeled product(s) was achieved via degradation experiments (the ^{14}C -labeled carbons are not shown on the structures). Radioactivities of the intermediates and final products were examined.



2.2. **Tick** the appropriate boxes on the answer sheet for the intermediates and products that you expect to exhibit radioactivity.

Considering only A :	Considering only B :
<input type="checkbox"/> Compound 1	<input type="checkbox"/> Compound 1
<input type="checkbox"/> BaCO ₃ (Batch 1)	<input type="checkbox"/> BaCO ₃ (Batch 1)
<input type="checkbox"/> Compound 2	<input type="checkbox"/> Compound 2
<input type="checkbox"/> BaCO ₃ (Batch 2)	<input type="checkbox"/> BaCO ₃ (Batch 2)

With the aim of facilitating aryne formation, Kobayashi and co-workers developed a fluoride-induced aryne generation protocol. Using this method, benzene derivative **3** is reacted with furan (**4**) in the presence of CsF, resulting in the formation of **E**, **F**, and **G**.



- Combustion analysis of **E** revealed the following atom content: 75.8% carbon, 5.8% hydrogen, and 18.4% oxygen.
- **E** does not have a proton that is exchangeable with D₂O in ¹H-NMR spectroscopy.
- **F** is an ionic compound.

2.3. Determine the structures of **E**, **F**, and **G** (without stereochemical details).

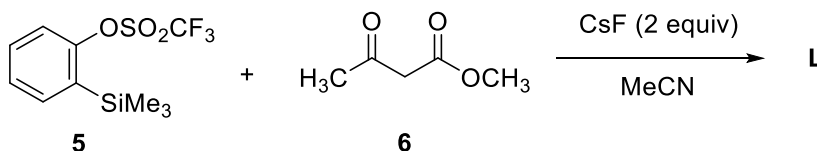
In the absence of a nucleophile or a trapping agent, arynes can undergo [2+2]-type cyclodimerization or [2+2+2]-type cyclotrimerization reactions under suitable conditions. The aryne derivative that is obtained when **3** is treated with one equivalent of CsF in MeCN can give, in principle, four different dimerization and trimerization products (**H–K**).

- **H** has two planes of symmetry.
- **I** is expected to exhibit 21 signals in its ¹³C-NMR spectrum.
- **I** and **J** both exhibit an *m/z* value of 318.1 in their mass spectra.

2.4. Determine the structures of **H–K**.

When **5** is reacted with β -ketoester **6** in the presence of 2 equivalents of CsF at 80 °C, **L** is obtained as the major product. The ¹H-NMR and ¹³C-NMR data for **L**, in CDCl₃, are as follows:

- ¹H-NMR: δ 7.79 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.47–7.33 (m, 2H), 7.25–7.20 (m, 1H), 3.91 (s, 2H), 3.66 (s, 3H), 2.56 (s, 3H) ppm.
- ¹³C-NMR: δ 201.3, 172.0, 137.1, 134.4, 132.8, 132.1, 130.1, 127.5, 51.9, 40.2, 28.8 ppm.



2.5. Determine the structure of **L**.

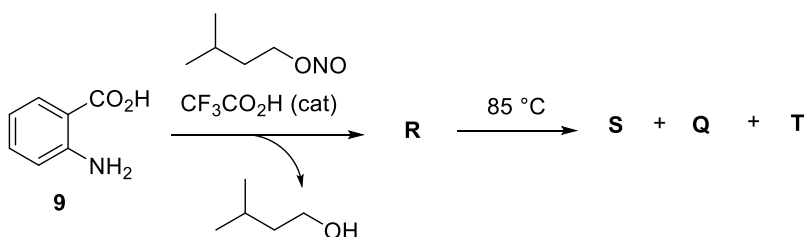
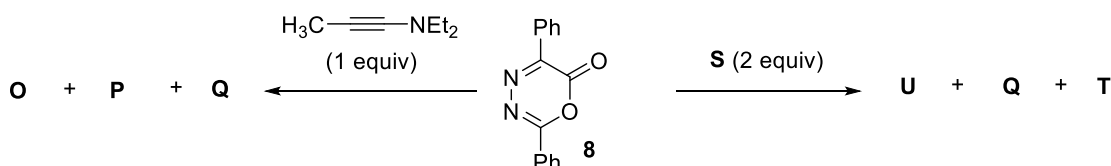
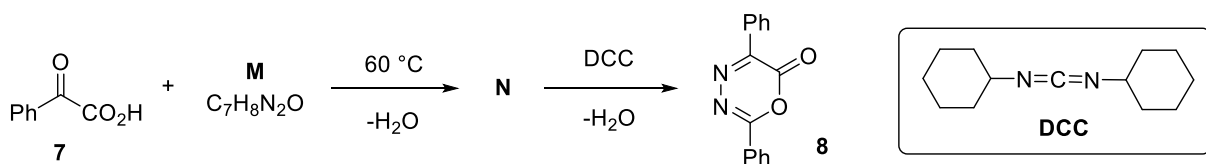
2.6. In the reaction shown in task **2.5**, which of the statement(s) in the answer sheet describe(s) the function of CsF?

- The *pK_a* values of HF and β -ketoester **6** in dimethyl sulfoxide (DMSO) are about 15 and 14, respectively.

- F⁻ hydrolyzes the trifluoromethanesulfonate (O₃SCF₃) group of **5**.
- F⁻ attacks the -SiMe₃ group of **5**.
- F⁻ acts as a base to deprotonate **6**.
- F⁻ acts as a nucleophile and attacks the ester group of **6**.

Diazapyrone derivative **8** was shown to be a useful reactant for the construction of a variety of cyclic frameworks. Its preparation from phenylglyoxylic acid (**7**) and its use in two different reactions are described below.

- **Q** and **T** are gases under ambient conditions.
- **O** and **P** are constitutional isomers.
- **Q** does not have any signals in its IR spectrum.
- Heating 1 mol of **R** at 85 °C generates 1 mol of reactive intermediate **S**.
- Reaction of **8** with two equivalents of **S** gives **U**, **Q**, and **T**.



Note:

equiv= equivalent

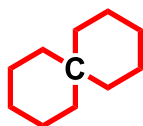
cat= catalyst

2.7. Determine the structures of **M–U**.

Problem 3 8% of the total	Question	3.1	3.2	3.3	3.4	3.5	3.6	3.7	Total
	Points	8	16	4	8	5	5	5	5

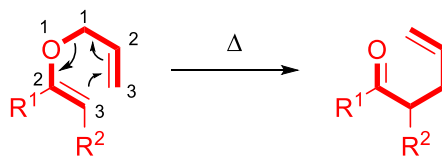
Problem 3. (\pm)-Coerulescine

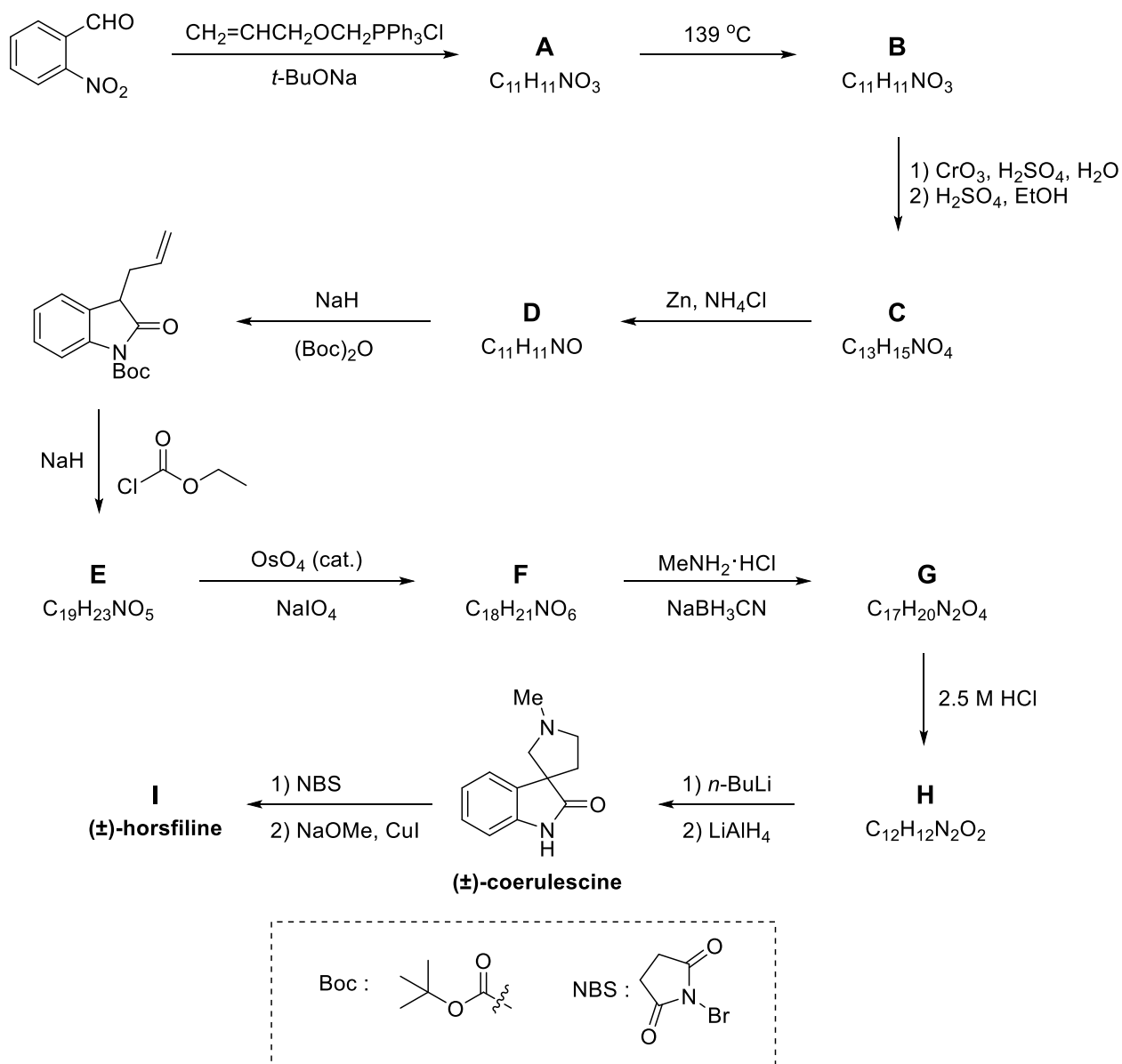
A spiro compound is typically an organic compound containing rings linked together by one common atom (spiroatom) as carbon atom with bold in figure below. The spiro[pyrrolidin-3,3'-oxindole] ring system is a structural framework incorporated in several cytostatic alkaloids and unnatural compounds. Coerulescine (**1**) and horsfiline are the simplest prototype members of this subfamily that can be synthesized by the route shown below.



Claisen rearrangement, which is a [3,3]-sigmatropic rearrangement, is a powerful carbon–carbon bond-forming reaction in which an allyl vinyl ether is converted thermally to an unsaturated carbonyl compound as shown in the Scheme below. When compound **A** is heated, it undergoes Claisen rearrangement to give carbonyl compound **B**.

For this entire task, your answers can be given without any stereochemical details.





3.1. Draw the structures of **A** and **B**.

- **A** is an inseparable mixture of *cis/trans* isomers.
- **B** has IR absorption at 1726 cm^{-1} .

3.2. Draw structures for **C**, **D**, **E**, and **F**.

- **D–F** have a bicyclic structure.

3.3. **Choose** the correct order of steps for the transformation of **F** to **G**.

- Imine formation, then reduction, then amidation

Amidation, then imine formation, then reduction

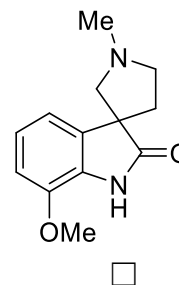
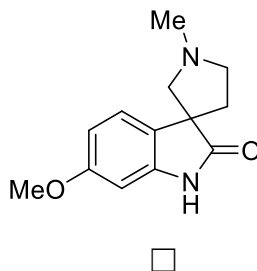
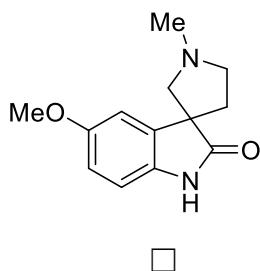
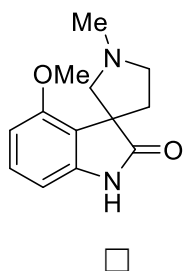
Reduction, then amidation, then imine formation

3.4. **Draw** structures for **G** and **H** (both spiro compounds).

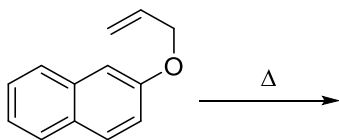
3.5. **Draw** the structure of the intermediate produced by treatment with *n*-BuLi in the step **H** → **coerulescine (1)**.

Coerulescine (1), on treatment with *N*-bromosuccinimide (NBS), gives the bromo derivative, which upon heating with sodium methoxide in the presence of cuprous iodide gives **horsfiline (I)** in 60% yield.

3.6. **Choose** the correct structure for compound **I** consistent with the following selected ¹H-NMR data: δ 7.05 (d, *J* = 1.4 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.72 (dd, *J* = 8.0, 1.4 Hz, 1H) ppm.



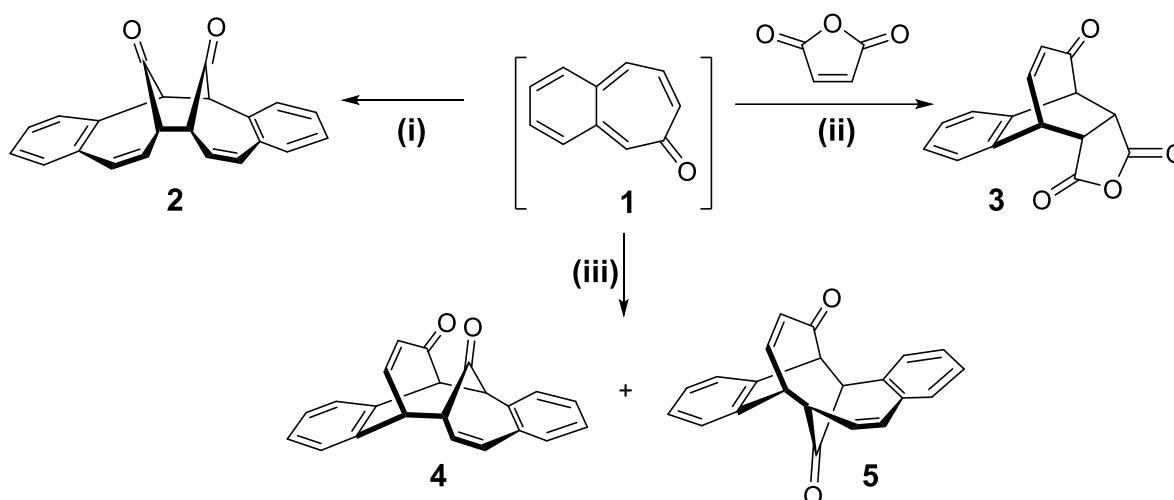
3.7. When the allyl ether of 2 naphthol is heated a sigmatropic rearrangement is initiated. **Write** the structure of major product isolated from this reaction.



Problem 4 10% of the total	Question	4.1	4.2	4.3	4.4	4.5	4.6	4.7	Total
	Points	12	6	6	16	9	9	8	

Problem 4. Symmetry Does Matter!

There are numerous reactions in organic chemistry that proceed through cyclic transition states and these are classified as pericyclic reactions. Woodward–Hoffmann rules, developed by Robert B. Woodward and Roald Hoffmann, are used to rationalize stereochemical aspects and the activation energy of pericyclic reactions.



Woodward–Hoffmann rules				
Number of electrons	Electrocyclic reactions		Cycloadditions	
	Thermal (Δ)	Photochemical ($h\nu$)	Thermal (Δ)	Photochemical ($h\nu$)
$4n$ ($n = 1, 2, \dots$)	Conrotatory (con)	Disrotatory	Disfavored	Favored
$4n+2$ ($n = 1, 2, \dots$)	Disrotatory (dis)	Conrotatory	Favored	Disfavored

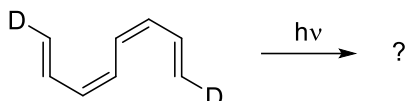
4.1. **Fill** in the table for reactions (i)–(iii) or products 2–5:

Reaction	Product	[? + ?] cycloaddition	Δ or $h\nu$
i	2		
ii	3		
iii	4		
	5		

There are three possible benzotropone isomers. Although two of the benzotropone isomers were isolated, 3,4-benzotropone (**1**) has not been isolated. Its instability is attributed to the *o*-quinoidal structure of **1** because it has no sextet electron system in the benzene ring.

4.2. Draw the structures of stable benzotropone isomers **A** (with 6 signals in its ¹³C-NMR) and **B** (with 11 signals in its ¹³C-NMR).

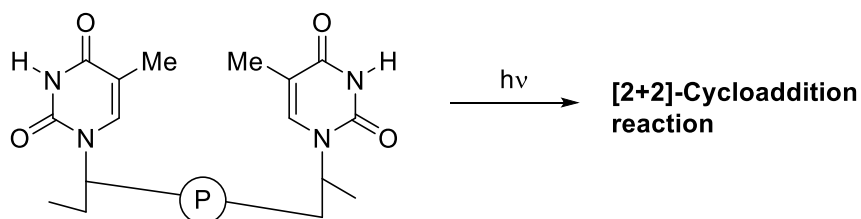
4.3. When the following tetraene is reacted under photochemical conditions, symmetry-allowed product(s) of three different ring sizes can form according to the Woodward–Hoffmann rules. **Tick** the correct answer in each row.



<input type="checkbox"/>		<input type="checkbox"/>	
<input type="checkbox"/>		<input type="checkbox"/>	
<input type="checkbox"/>		<input type="checkbox"/>	



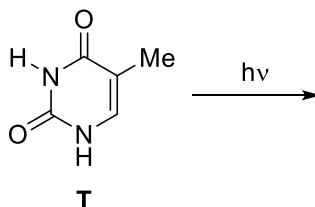
Prof. Dr. Aziz Sancar



The Nobel Prize in Chemistry 2015 was awarded jointly to the Turkish scientist Aziz Sancar, Swedish scientist Tomas Lindahl, and American scientist Paul Modrich for their “mechanistic studies of DNA repair”. Pyrimidine bases found in DNA may undergo a photochemical **[2+2]-cycloaddition reaction** (see above figure) with UV light that reaches a person’s skin, causing

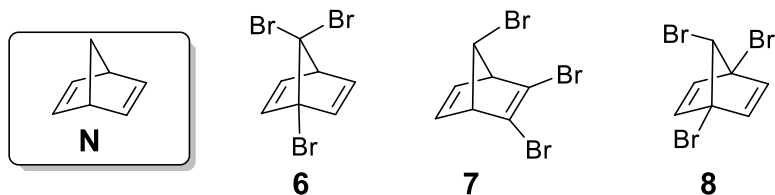
damage to DNA, which may ultimately lead to skin cancer. The research by Professor Aziz Sancar focused on the DNA repair mechanism for this type of damage.

Thymine (**T**) is one of the nucleobases that can undergo such a photochemical reaction with UV light. Let us assume that we have a solution of free thymine that was subjected to UV irradiation.



4.4. Considering stereochemistry, draw the structures of **all possible products** of this reaction between two free thymine (**T**) molecules. Circle the compound(s) which is/are chiral. Drawing only one enantiomer of an enantiomeric pair is sufficient. Please note that only C=C bonds participate in this reaction.

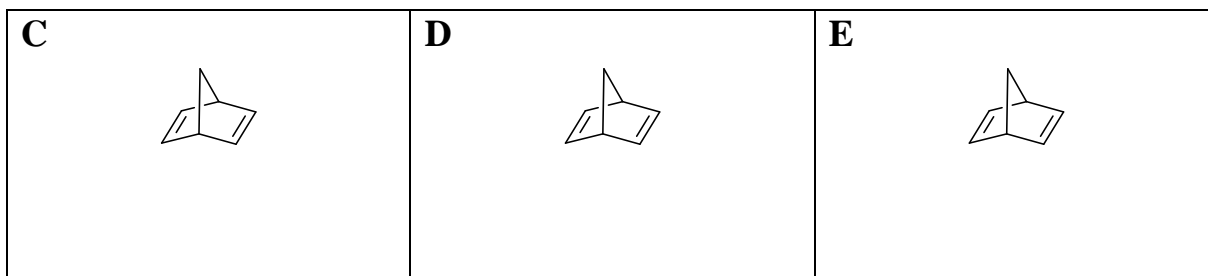
A broad range of halogenated derivatives of norbornadiene (**N**) are known in the literature. Tribromo-norbornadiene ($C_7H_5Br_3$) has six achiral isomers. Three of these isomers (**6**, **7**, and **8**) are given below.



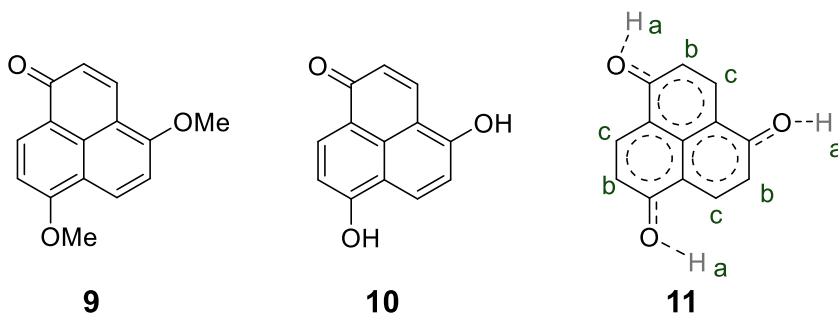
4.5. How many signals do you expect from the ^{13}C -NMR spectra of **6**, **7**, and **8**? Fill in the following boxes.

6 	7 	8
--------------	--------------	--------------

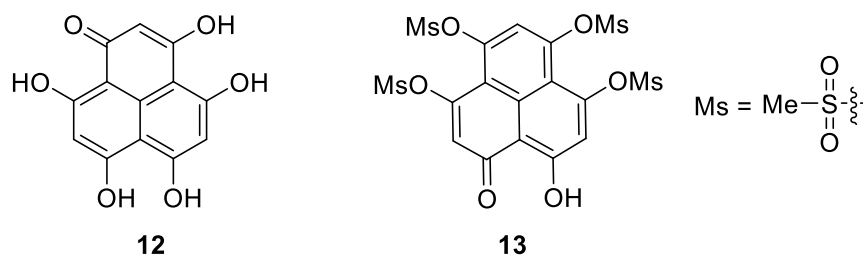
4.6. **Draw** structures of the remaining achiral tribromo-norbornadiene ($C_7H_5Br_3$) isomers (**C**, **D**, and **E**) in addition to **6–8** over the given figures in the boxes.



The NMR spectrum of ether **9** is complex. Two MeO– groups are different as are all the hydrogen atoms on the rings. However, diphenol **10** has a very simple NMR spectrum and there are only three types of protons (marked as a, b, and c). A reasonable average structure responsible for all resonance structures and its symmetry is shown as **11**.

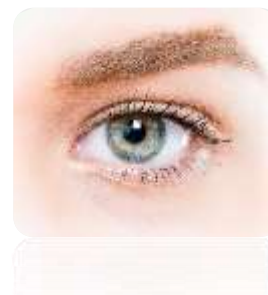
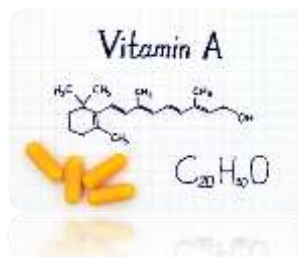


4.7. How many signals do you expect from the ^{13}C - and 1H -NMR spectra of **12** and **13**?



Problem 5 14% of the total	Question	5.1	5.2	5.3	5.4	5.5	5.6	5.7	5.8	Total
	Points	13	13	15	8	12	10	17	12	100

Problem 5. Konya, Carrot, Beta-Carotene, Vitamin-A, Immune System, Vision



Mevlana (Rumi) was a great mystic and Sufi poet who lived out his days in Konya in the 13th century. The indirect relevance of Konya to chemistry is that the city provides 65% of the country's carrot production, from which one of the essential vitamins (vitamin A) is obtained.

Carrot is an important source of β -carotene, which gives the vegetable its orange color. This molecule is a red-orange pigment naturally found in plants and fruits and is a provitamin A carotenoid. It is converted to vitamin A, which is essential for normal growth and development, the immune system, and vision function.

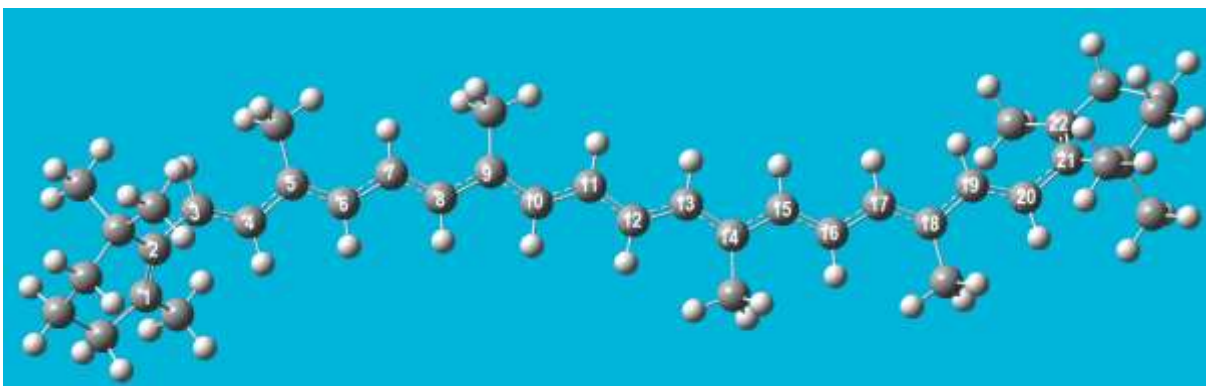


Figure 1. Ball and stick representation of the structure of β -carotene. The gray and white spheres represent the carbon and hydrogen atoms, respectively. The numbered carbon atoms belong to the linear conjugated π -segment of the molecule.

β -Carotene has an extended polyene chain of 22 carbon atoms. It is a conjugated π -system, having alternating single and double bonds. Its experimental maximum absorption wavelength (λ_{max}) is 455 nm. We assume that all the bonds between C_1 and C_{22} are conjugated bonds. There are 22 π -electrons in the molecule (Figure 1).

To a crude approximation, the electrons in the C-2p_z orbitals, which are perpendicular to the molecular plane, are assumed to move along the entire molecule, without interacting with each other. They are like independent particles confined in a molecule moving along the x-axis in one dimension. These characteristics of π-electrons make them eligible for being treated by the simplest model called the **particle in one-dimensional box** model.

The wave function and the energies of the quantized levels for an electron moving in a one-dimensional box with infinite potential walls are given as follows:

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad \text{Eq.1}$$

where n is the quantum number, n=1,2,3,4,... ∞, and L is the box length.

$$E_n = \frac{n^2 h^2}{8m_e L^2} \quad \text{Eq.2}$$

In two dimension, within the framework of independent particle approximation, the wavefunction is expressed as a product of one-dimensional wavefunctions, and the energy is expressed as a sum of one-dimensional energies. The energy levels of the two dimensional rectangular box is given as follows:

$$E_{n_x, n_y} = \left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right] \left\{ \frac{h^2}{8m_e} \right\} \quad \text{Eq. 3}$$

where n_x, n_y are the quantum numbers and they are positive integers. L_x, L_y are the dimensions of the box in the 2D model. They are positive numbers.

5.1. Which two of the sentences given below are correct? **Tick** only one answer which includes correct sentences in your answer sheet.

The β-carotene molecule is orange in color because

- i) it absorbs in the visible region of the electromagnetic spectrum.
- ii) HOMO →LUMO transition occurs by absorption of IR photon.
- iii) the spacing between the 22nd and the 23rd energy levels is equal to the energy of the IR photon at the orange wavelength.
- iv) it absorbs green/blue light and it transmits red/yellow color.
- v) it absorbs in the UV-Vis region since the molecule has no net dipole moment.

- | | | | |
|--|---------------------------------------|--------------------------------------|--|
| <input type="checkbox"/> a) i and ii | <input type="checkbox"/> b) i and iii | <input type="checkbox"/> c) i and iv | <input type="checkbox"/> d) i and v |
| <input type="checkbox"/> e) ii and iii | <input type="checkbox"/> f) ii and iv | <input type="checkbox"/> g) ii and v | <input type="checkbox"/> h) iii and iv |
| <input type="checkbox"/> j) iii and v | <input type="checkbox"/> k) iv and v | | |

Although it is highly unrealistic, let us assume that the conjugated segment of the molecule is linear and treated with the particle in a one-dimensional box model as shown in figure 2. In this case, the length of the box can be approximated as $L=1.40 \times n_C$ (in Å), where n_C is the number of carbon atoms in the conjugated segment.

Use this information to answer the questions 5.2–5.6.

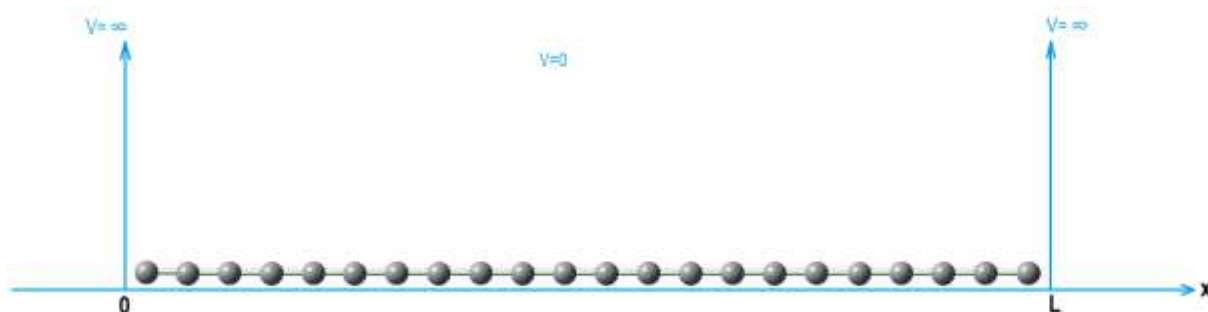


Figure 2. Schematic representation of the conjugated line segment made up carbon atoms of β -carotene in a one-dimensional box of length L .

- 5.2. **Calculate** the energies (in J) of the lowest two energy levels
- 5.3. **Draw** the wavefunctions of the lowest two energy levels with proper labelling the x-axis.
- 5.4. **Sketch** the energy level diagram up to $n = 4$ showing the relative spacing.
- 5.5. What is the total π -energy (in J) of the molecule?
- 5.6. **Calculate** the wavelength (in nm) at which the transition between the highest occupied and lowest unoccupied energy levels occurs.

Use the particle in a two-dimensional box model to answer questions 5.7–5.8.

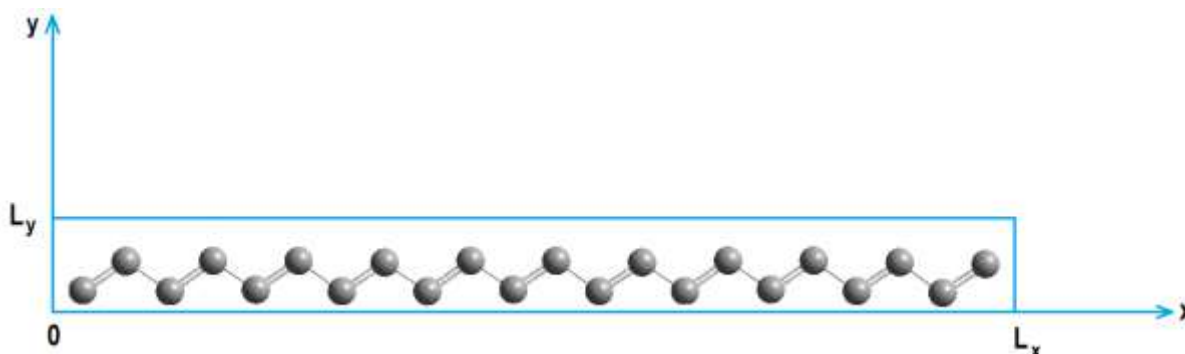


Figure 3. Schematic representation of the conjugated carbon atoms of β -carotene in a two-dimensional box.

Assume that the conjugated segment is made up of conjugated bonds that are all-*trans* to each other. The motion of the π -electrons is studied in the two-dimensional rectangular box with the dimensions $L_x = 26.0 \text{ \AA}$, $L_y = 3.0 \text{ \AA}$ (Figure 3).

5.7. Calculate the energies (in J) of the highest occupied and the lowest unoccupied energy levels and the wavelength (in nm) at which the transition between these energy levels occurs.

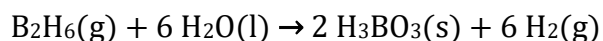
5.8. What should be the L_x value (in \AA) in order for the molecule to absorb light at the experimental $\lambda_{\text{max}}=455 \text{ nm}$ if L_y is kept constant at 3.0 \AA . (Assume that the quantum numbers for homo and lumo are the same as in the question 5.7.)

Problem 6 12% of the total	Question	6.1	6.2	6.3	6.4	6.5	6.6	6.7	6.8	Total
	Points	5	12	6	3	6	6	5	3	
	Question	6.9	6.10	6.11	6.12	6.13				
	Points	8	6	6	8	6				

Problem 6. Thermodynamics through an Interstellar Journey

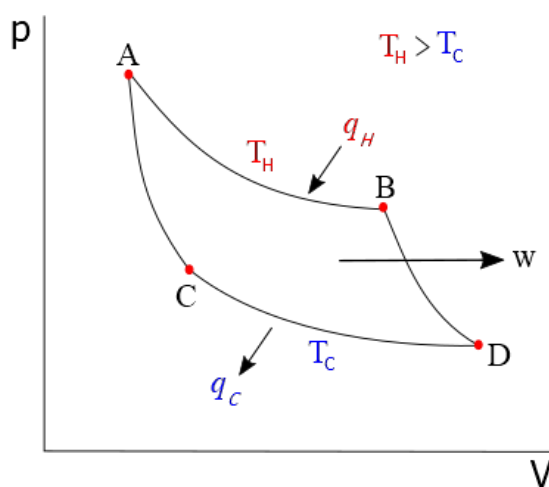
Part 1

In a hypothetical universe, an unknown amount of diborane participates in the following reaction:



Assume that in this hypothetical universe, $\text{H}_3\text{BO}_3(\text{s})$ obtained from this reaction was completely sublimed at 300 K. The necessary energy for sublimation was obtained through work released by **one cycle** of an ideal heat engine in which one mole of monoatomic perfect gas flows through the cycle described in the pressure (p) – volume (V) diagram below:

- A→B; isothermal reversible expansion receiving 250 J by heat transfer (q_H) at a temperature of 1000 K (T_H) from a hot source.
- B→D; reversible adiabatic expansion.
- D→C; isothermal reversible compression at a temperature of 300 K (T_C) releasing some amount of heat (q_C) to a cold sink.
- C→A; reversible adiabatic compression.

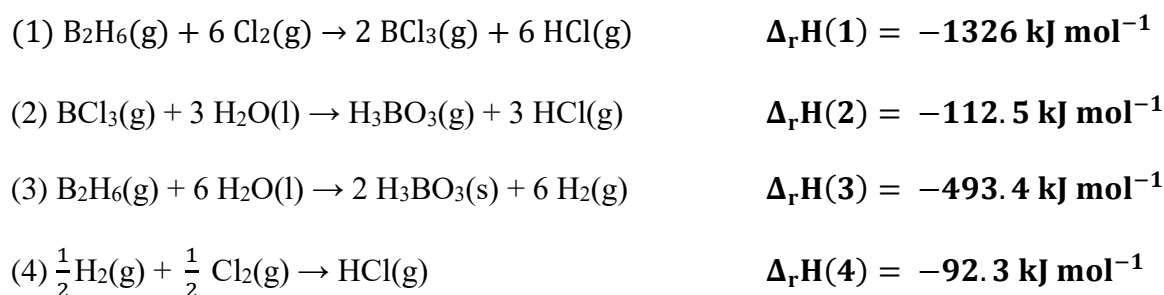


After heat transfers, the remaining energy is released as work (w). Also, q_H and q_C are related to T_C and T_H as follows:

$$\frac{|q_H|}{|q_C|} = \frac{T_H}{T_C}$$

The efficiency of the cycle can be found by work released by cycle (w) divided by heat absorbed by cycle (q_H).

You are provided with the change in enthalpies of the following reactions at 300 K.



6.1. Calculate the molar enthalpy of sublimation (in kJ mol^{-1}) for H_3BO_3 at 300 K.

6.2. Calculate the $\Delta_r U$ (internal energy) in terms of kJ mol^{-1} at 300 K for the reactions (2) and (4) given above (assume ideal gas behavior for each gaseous species in each reaction).

6.3. Calculate the amount of overall work produced by a heat engine ($|w|$) in terms of J and the amount of overall heat released to the cold sink ($|q_C|$) in terms of J.

6.4. Calculate the efficiency of the heat engine described above.

6.5. Calculate the entropy change (ΔS) for $A \rightarrow B$ and $D \rightarrow C$ processes in the heat engine in terms of J K^{-1} .

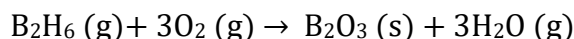
6.6. Calculate the Gibbs energy change (ΔG) in terms of J for $A \rightarrow B$ and $D \rightarrow C$ processes in the heat engine.

6.7. Calculate the ratio of pressure at point A to the pressure at point B in the cycle (standard pressure: 1 bar).

6.8. Calculate the amount of $\text{H}_2(\text{g})$ (in moles) produced according to the reaction given at the beginning of the task for one cycle of the engine.

Part 2

Interstellar journeys can be done by using diborane as rocket fuel. Combustion of diborane is shown below:



Combustion of diborane is experimented in a 100 L closed container at different temperatures and the equilibrium amounts were recorded.

	8930 K	9005 K
B₂H₆(g)	0.38 mol	0.49 mol
H₂O(g)	0.20 mol	0.20 mol

Partial pressure of $\text{O}_2(\text{g})$ was stabilized to 1 bar and kept constant at all conditions. Assume that in this hypothetical universe; $\Delta_r S^\circ$ and $\Delta_r H^\circ$ are independent of temperature, the standard molar entropy (S°) of $\text{B}_2\text{O}_3(\text{s})$ does not change with pressure, all the gas species behave as an ideal gas, and all species remain in the same phase, without any further decomposition before or after reaction, at all temperatures then:

6.9. Calculate K_p (pressure based equilibrium constant) at 8930 K and 9005 K.

6.10. Calculate $\Delta_r G^\circ$ of the reaction in terms of kJ mol^{-1} at 8930 K and 9005 K. (If you failed to find K_p , please use $K_p(8930 \text{ K}) = 2$, $K_p(9005 \text{ K}) = 0.5$)

6.11. Calculate $\Delta_r G^\circ$ (in terms of kJ mol^{-1}), $\Delta_r H^\circ$ (in terms of kJ mol^{-1}), and $\Delta_r S^\circ$ (in terms of $\text{J mol}^{-1}\text{K}^{-1}$) of the combustion reaction at 298 K. (If you failed to find K_p , please use $K_p(8930 \text{ K}) = 2$, $K_p(9005 \text{ K}) = 0.5$)

6.12. Tick the correct answer in the table by determining whether combustion reactions are favored or not at given T below under standard pressure (1 bar).

	favored	Unfavored
298 K	<input type="checkbox"/>	<input type="checkbox"/>
8930 K	<input type="checkbox"/>	<input type="checkbox"/>
9005 K	<input type="checkbox"/>	<input type="checkbox"/>
9100 K	<input type="checkbox"/>	<input type="checkbox"/>

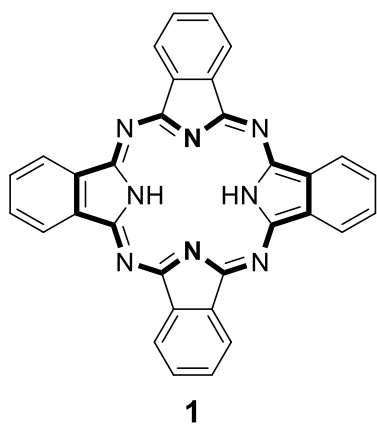
6.13. Calculate the $\Delta_f H$ (kJ mol^{-1}) and S° ($\text{kJ mol}^{-1} \text{K}^{-1}$) of $\text{H}_2\text{O}(\text{g})$ using the values given in the table below. ($\Delta_f H$ = enthalpy of formation, S° = standard entropy)

(If you fail to find $\Delta_r H^\circ$ and $\Delta_r S^\circ$ of the combustion, please use $\Delta H^\circ = 1000 \text{ kJ mol}^{-1}$, $\Delta S^\circ = 150 \text{ J K}^{-1} \text{ mol}^{-1}$)

	ΔH_f (298 K)	S° (298 K)
B_2H_6 (g)	$36.40 \text{ kJ mol}^{-1}$	$0.23 \text{ kJ mol}^{-1} \text{K}^{-1}$
O_2 (g)	0.00 kJ mol^{-1}	$0.16 \text{ kJ mol}^{-1} \text{K}^{-1}$
B_2O_3 (s)	$-1273 \text{ kJ mol}^{-1}$	$0.05 \text{ kJ mol}^{-1} \text{K}^{-1}$

Problem 7 12% of the total	Question	7.1	7.2	7.3	7.4	7.5	7.6	7.7	7.8	7.9	Total
	Points	4	8	6	8	8	14	19	12	6	85

Problem 7. Phthalocyanines

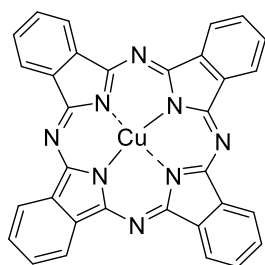


*Emeritus Professor Özer
Bekaroğlu*

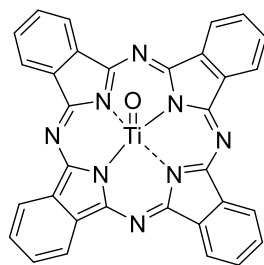
The term phthalocyanine (Pc) takes its origin from the Greek “naphtha”, which means rock oil, and “cyanine”, which means dark blue. Turkish scientist Özer Bekaroğlu can be regarded as the pioneer of Pc chemistry in Turkey.

Metal-free phthalocyanine (**1**, H₂Pc) is a large planar macrocyclic compound with the formula (C₈H₄N₂)₄H₂.

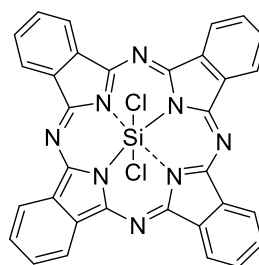
7.1. How many π -electrons are there in the bold region of the H₂Pc molecule in compound **1** shown above?



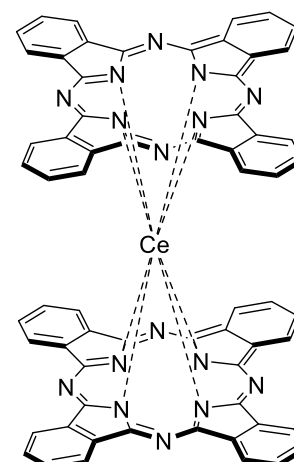
CuPc
2



TiOPc
3



SiCl₂Pc
4



Ce(Pc)₂
5

Pcs containing one or two metal ions are called metallo-phthalocyanines (MPcs) and they exhibit different geometries as given above.

7.2. **Complete** the table in your answer sheet by determining the coordination number of central ions in 2–5.

Central ion	Copper ion	Titanium ion	Silicon ion	Cerium ion
Coordination number				

7.3. **Complete** the table in your answer sheet by determining the oxidation number of each metal (Cu, Ti, and Ce) in 2, 3, and 5.

Metal in compounds	2	3	5
Oxidation number			

7.4. **Complete** the table in your answer sheet by determining the geometry of compounds 2–5.

Geometry	Compound
Octahedral	
Square prism	
Square pyramidal	
Square planar	

7.5. **Complete** the table in your answer sheet by determining the magnetic property of compounds 2–5.

- Use the letter "p" for paramagnetic property and letter "d" for a diamagnetic property.

Compound	Magnetic property
2	
3	
4	
5	

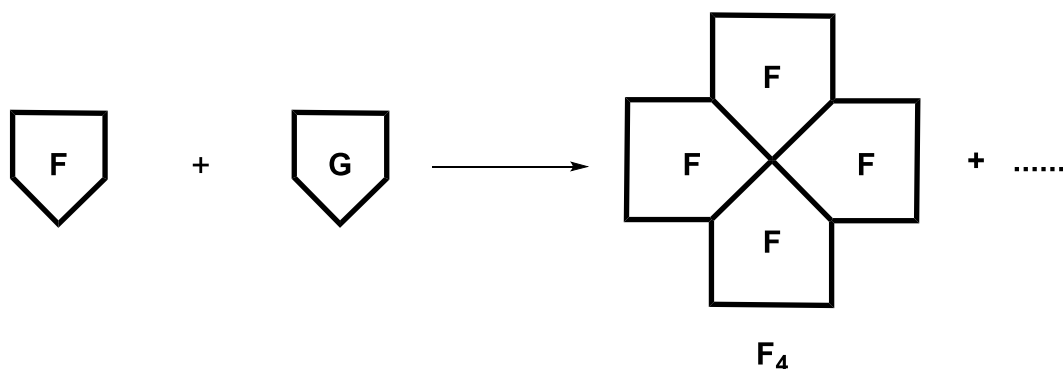
7.6. Write the ground-state electron configuration of the silicon (Si) ion in the compound **4** and **find** all the quantum numbers for the 2p electrons in its ground state.

Electron configuration:				
Quantum numbers for 2p electrons:	<i>n</i>	<i>l</i>	<i>m_l</i>	<i>m_s</i>

Metal-free phthalocyanine (**1**, H₂Pc) is commonly formed through the cyclotetramerization of phthalonitriles. On the other hand, Pcs having different substituents are called asymmetric, which can be prepared by the statistical cyclization of two different phthalonitriles. This method has no selectivity and the product is a mixture of all possible isomers.

7.7. Draw the possible products that may occur in the statistical cyclization method by using **F** and **G**. If there are any stereoisomers label as *cis*- or *trans*-.

- **F** and **G** represent two different symmetrical phthalonitriles.
- One of the products is **F₄** as given below.
- Draw other products similar to the format of **F₄**.



Pcs are used as photosensitizers in the photodynamic therapy (PDT) of cancer due to their strong absorption in the visible spectrum and high molar absorption coefficients. PDT consists of three essential components: **photosensitizer**, light, and oxygen. None of these is individually toxic, but together they initiate a photochemical reaction resulting in the generation of cytotoxic singlet oxygen (¹O₂) that can destroy cancer cells.

(multiplicity) $1\mathbf{O}_2$

- The multiplicity of an energy level is defined as $2S+1$
- If the two spins are parallel ($\uparrow\uparrow$), $S = 1$, and if the two spins are antiparallel ($\uparrow\downarrow$), $S = 0$.

7.8. Draw the molecule orbital (MO) diagram of the lowest energy singlet state of dioxygen ($^1\mathbf{O}_2$) and calculate bond order.

- There are no unpaired electrons in that state!

7.9. If the wavelength of the light needed to excite triplet oxygen into singlet oxygen is 1270 nm, **calculate** the energy (in kJ/mol) needed for this transition process.

Problem 8 14% of the total	Question	8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	Total
	Points	3	3	4	4	4	4	6	3	58
	Question	8.9	8.10	8.11	8.12	8.13	8.14	8.15	8.16	
	Points	2	3	2	4	4	4	2	2	
	Question	8.17								
	Points	4								

Problem 8. Boron Compounds and Hydrogen Storage



Sodium borohydride (NaBH_4) and ammonia borane (BNH_6) are the most studied chemical hydrogen storage materials. In this question, you will explore the chemistry of boron and the use of boron compounds as hydrogen storage materials.

Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot n\text{H}_2\text{O}$) is a boron mineral that is produced by ETI Mining Company in Turkey. NaBH_4 can be synthesized by the reduction of anhydrous borax with metallic sodium under high-pressure hydrogen gas in the presence of silicon dioxide (silica) at $700\text{ }^\circ\text{C}$, namely the Bayer process. In this process, all hydrogen is stored in NaBH_4 . On the other hand, it has been shown that ammonia borane (BNH_6) can be synthesized by the reaction of NaBH_4 and ammonium sulfate in dry tetrahydrofuran (THF) at $40\text{ }^\circ\text{C}$ (**Hint:** BNH_6 synthesis must be conducted in a well-ventilated fume-hood because flammable gas is generated as one of the by-products). While NaBH_4 is an ionic compound, ammonia borane is a Lewis acid–base adduct.

8.1. Write a balanced chemical equation for the synthesis of NaBH_4 from anhydrous borax.

8.2. Write a balanced chemical equation for the synthesis of ammonia borane from NaBH_4 .

8.3. Draw the molecular geometry of the BH_4^- ion and BNH_6 molecule.

8.4. Calculate the hydrogen content of NaBH_4 and BNH_6 as a percentage by mass (wt%).

The hydrogen stored in both compounds can be released via hydrolysis reactions in the presence of a suitable catalyst at room temperature. Upon the hydrolysis reactions, 4 and 3 moles of H_2 gas are released from the hydrolysis of 1 mole of $NaBH_4$ and BNH_6 , respectively, along with metaborate anion including B-O bonds.

8.5. Write the balanced chemical equations for the hydrolysis of $NaBH_4$ and BNH_6 .

One of the simplest stable borates is diboron trioxide (B_2O_3). Higher borates such as $B_3O_6^{3-}$ having cyclic structures containing B-O-bonds can be formed. Since B_2O_3 is an acidic compound, it is easily reacted with water to produce boric acid (H_3BO_3). On the other hand, the high temperature and high-pressure reaction of B_2O_3 with ammonia yields two-dimensional boron nitride, which consists of planar graphite-like sheets of alternating B and N atoms.

8.6. Write the balanced chemical equations for the synthesis of boric acid and boron nitride.

8.7. Draw the molecular structures of the $B_3O_6^{3-}$ ion, boric acid, and a single two-dimensional boron nitride sheet. **Hint:** show at least 10 B atoms in the boron nitride structure.

Furthermore, B-H compounds, called boranes, are an important class of boron compounds. The simplest stable borane is diborane (B_2H_6) and many of the higher boranes can be prepared by the pyrolysis of diborane. Diborane can be synthesized via metathesis of a boron halide and a hydride source.

8.8. Write a balanced chemical equation for the synthesis of diborane from the reaction of BF_3 and $LiBH_4$. **Hint:** both products are boron compounds.

8.9. Draw the molecular geometry of the diborane molecule. **Hint:** there is no B-B bond in the structure.

BH_3 (borane) is an unstable and highly reactive molecule. Therefore, it is not possible to isolate it as BH_3 under ordinary conditions. However, it can be stabilized via its reaction with carbon monoxide to yield borane carbonyl (BH_3CO) compound, which is an adduct of borane. The preparation of BH_3CO plays an important role in exploring the chemistry of boranes as it indicates the likely existence of the borane molecule.

8.10. Sketch the Lewis dot structure of $BH_3 - CO$ molecule by showing the formal charges.

8.11. Which of the statements given in your answer sheet is observed in the C – O bond of a CO molecule upon the bond formation between BH₃ and CO? **Tick** the correct box.

- It gets longer because there will be π -back donation from BH₃ to CO.
- It gets longer because CO donates π -bonding electrons to BH₃.
- No or slight change on it because CO donates its mainly non-bonding electrons to BH₃.
- It gets shorter because CO donates π^* anti-bonding electrons to BH₃.

Borazine consists of single and double bonded cyclic B – N units and hydrogen atoms attached to these atoms with the molecular formula B₃N₃H₆ and is isostructural to benzene. Borazine can be synthesized by using a two-step procedure including the synthesis of symmetrically trisubstituted chlorine derivatives of borazine (B₃N₃H₃Cl₃) from the reaction of ammonium chloride and boron trichloride, and then reduction of B₃N₃H₃Cl₃ with LiBH₄ in THF.

8.12. Write the balanced chemical equations for the two-step synthesis of borazine starting from ammonium chloride in THF (tetrahydrofuran). **Hint:** THF stabilizes one of the products by forming a Lewis acid-base adduct.

8.13. Draw the molecular structures of borazine and its symmetrically trisubstituted chlorine derivative.

Catalysts are substances that accelerate the rate of reactions by allowing them to proceed in a lower energy pathway. The catalytic activity of the catalysts is generally determined by the turnover frequency (TOF), which is calculated by dividing the molar amount of the product to the mole of active catalyst and the time (TOF = mole product/(mole catalyst x time)). A typical hydrolysis of BNH₆ was carried out in 10.0 mL of water by using 100.0 mM BNH₆ and 5.0 mg of CuPt/C catalyst (CuPt alloy nanoparticles supported on carbon black containing 8.2 wt% Pt atom). 67.25 mL of hydrogen gas was generated in 5 minutes.

8.14. Assuming the catalytic reaction is performed under standard conditions (1 atm and 273.15 K), **calculate** the TOF (min^{-1}) of the CuPt/C catalyst **in terms of only Pt atoms** in the hydrolysis of BNH₆ by considering the volume of the hydrogen gas generated.

As a result of detailed crystal analysis of a synthesized Cu_xPt_y alloy nanoparticles (the subscripts indicate molar percentages of the atoms in the alloy structure), it was determined that the face centered cubic (fcc) unit cell was formed by Pt atoms and the Pt atoms on the face of the fcc unit cell are supposed to be replaced with Cu atoms to form Cu_xPt_y displacement alloy nanoparticles. According to this information, answer the following questions.

- 8.15. Determine** the composition of the alloy nanoparticles by finding x and y in the Cu_xPt_y .
- 8.16. Sketch** the shape of the described crystal unit cell of Cu_xPt_y alloy nanoparticles by showing the position of all atoms on the unit cell.
- 8.17.** Another alloy has a Cu_2Pt_1 composition. Assume that this alloy also has a fcc unit cell with an edge length of 380 pm, but the Cu and Pt atoms are randomly distributed in the atomic positions. **Calculate** the density of this alloy in g/cm^3 .

Problem 9 12% of the total	Question	9.1	9.2	9.3	9.4	9.5	9.6	9.7	9.8	Total
	Points	5	5	8	16	5	6	25	30	100

Problem 9. Quantification of Heavy Metal Ions

For the quantitative analysis of heavy metal ions in a factory's wastewater pool, the following steps have been applied by an analyzer at 298 K:

Step 1) 10-mL samples of each were obtained from five different regions in a wastewater pool, mixed in a 100-mL beaker, and then stirred for 5 minutes using a magnetic stirrer.

Step 2) 10-mL of sample solution was taken from the 100-mL beaker and 142 mg of Na_2SO_4 was added while stirring, followed by transfer to a three-electrode cell as seen in Figure 1a. In this electrochemical cell, Pt wire, Ag/AgCl (3 M KCl), and Pt foil served as the working, reference, and counter electrodes, respectively.

Step 3) These electrodes were connected to a potentiostat and a constant potential of -0.50 V vs. Ag/AgCl for 14 minutes was applied as seen in Figure 1b (horizontal line). It is assumed that 14 min. is sufficient to complete the expected electrochemical reactions.

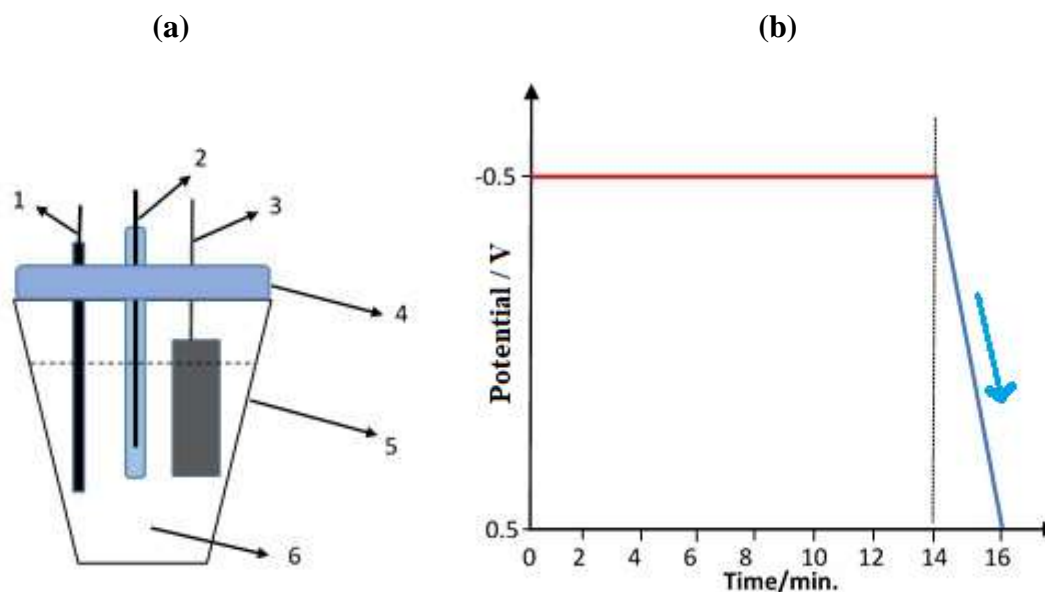


Figure 1. **a)** Electrochemical cell design; 1) Working electrode (Pt wire), 2) reference electrode (Ag/AgCl, 3M KCl), 3) counter electrode (Pt foil), 4) cell tap, 5) electrochemical cell, 6) 10-mL of sample solution. **b)** Potential change of working electrode as a function of time. y-axis: potential/V vs Ag/AgCl, x-axis: time/min.

Step 4) The electrodes were rinsed with distilled water, placed into another electrochemical cell including 10-mL of 0.1 M H₂SO₄ solution, and potential was scanned between -0.50 and +0.50 V as seen in Figure 1b (downward sloping line in 2 min.). Current vs. potential data for this step are presented in Figure 2a, which is like an excellent view of *Mount Ararat (Ağrı Dağı)*, the highest mountain in Turkey (Figure 2b).

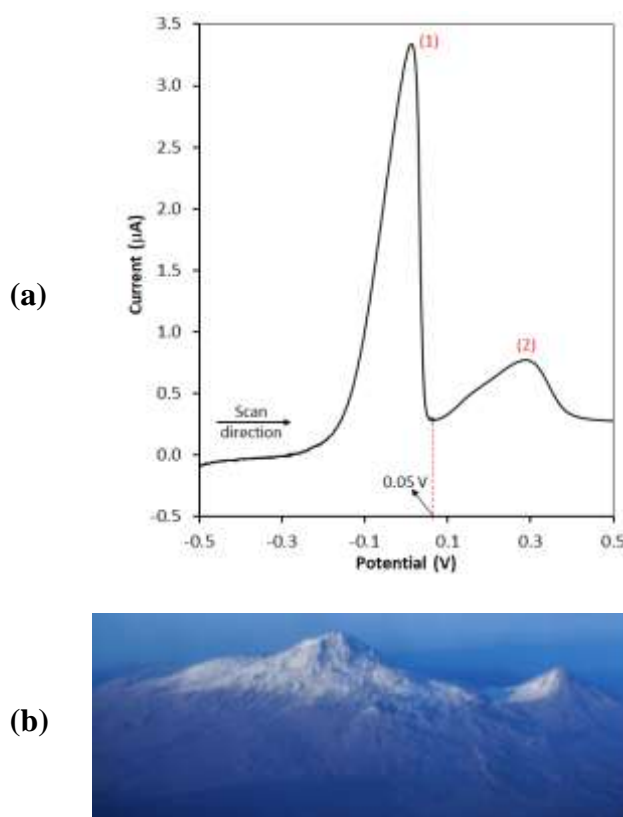


Figure 2. a) Potential scan of the working electrode as a function of current in 0.1 M H₂SO₄ solution after keeping it constant at a potential of -0.50 V in 10-mL of wastewater sample as seen in Figure 1b (horizontal line). y-axis: current/µA, x-axis: potential/V vs Ag/AgCl, b) A view of *Great and Little Ararat* peaks.

Step 5) Another 10-mL of the sample solution prepared in *step 1* was taken and the processes explained in *steps 2 and 3* were applied in that order. The electrodes were rinsed with distilled water and placed into 10-mL of 0.1 M H₂SO₄ solution. Then the potential of the working electrode was kept constant at +0.05 V for 14 minutes. It is assumed that 14 min. is sufficient to complete the expected electrochemical reactions.

Step 6) After *step 5* was performed, the solution in the electrochemical cell was placed in a suitable oven to evaporate at 150 °C until dry solid was obtained.

Step 7) 5-mL of ethylenediaminetetraacetic acid (EDTA, H₄Y) (Figure 3) solution was added to the solid obtained in *step 6* and it was shaken to dissolve. It is known that 1-mL of EDTA solution is equivalent to 3.85 mg/mL BaCO₃. Then, pH of the solution was adjusted to 10.0. Excess EDTA was titrated with standard 0.0010 M Ni(NO₃)₂ solution and it was observed that 95.60 mL of Ni(NO₃)₂ solution was consumed up to the endpoint.

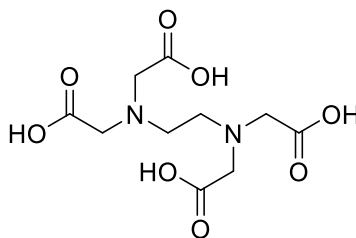


Figure 3. Chemical structure of EDTA (H₄Y).

- In water saturated with H₂S, equilibrium concentration of [H₂S] is 0.1 M.
- $K_{sp}(\text{NiS}) = 4.0 \times 10^{-20}$; $K_{sp}(\text{CuS}) = 1.0 \times 10^{-36}$
- $K_{a1}(\text{H}_2\text{S}) = 9.6 \times 10^{-8}$; $K_{a2}(\text{H}_2\text{S}) = 1.3 \times 10^{-14}$
-

Reaction	E°/V (at 298 K)
$2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$	-0.83
$\text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni}(s)$	-0.24
$2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g)$	0.00
$\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)$	+0.34
$\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$	+0.80
$\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}(l)$	+1.23

9.1. Which of the following can be considered for peak 1 and peak 2 in Figure 2a, respectively?

Tick the correct box on the answer sheet.

- Peak 1: electrochemical reduction of Ni / Peak 2: electrochemical reduction of Cu

Peak 1: electrochemical reduction of Cu / Peak 2: electrochemical reduction of Ni

Peak 1: electrochemical reduction of Ni / Peak 2: electrochemical oxidation of Cu

Peak 1: electrochemical oxidation of Ni / Peak 2: electrochemical oxidation of Cu

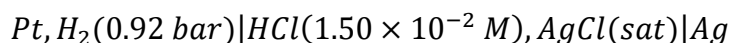
Peak 1: electrochemical oxidation of Cu / Peak 2: electrochemical oxidation of Ni

9.2. Which of the statement is expected, if the potential is applied as -1.2 V instead of -0.5 V at the first step (horizontal line) in Figure 1b? **Tick** the correct box on the answer sheet.

- NO evolution
- NO_2 evolution
- Nitrogen evolution
- Oxygen evolution
- Hydrogen evolution

9.3. **Calculate** the scan rate of data presented in Figure 2a as mV/s at 298 K.

The potential of the following cell is measured as 0.437 V.



9.4. **Calculate** the standard electrode potential value (V) of half-cell of $\text{AgCl}(s) + e^- \rightarrow \text{Ag}(s) + \text{Cl}^-(aq)$ at 298 K. *Note:* You must show all works.

9.5. Which of the statements is the main purpose of *step 5* in this analysis? **Tick** the correct box on the answer sheet.

- Modification of Pt wire with Ni–Cu alloy film
- Modification of Pt wire with Ni film
- Electrochemical stripping of both Cu and Ni from Cu–Ni-modified Pt wire to the solution
- Electrochemical stripping of Cu from Cu–Ni-modified Pt wire to the solution
- Electrochemical stripping of Ni from Cu–Ni-modified Pt wire to the solution

9.6. **Write** net ionic equations for the complexation and the back titration reaction of *step 7* on the answer sheet

9.7. **Calculate** Ni^{2+} concentration as *mg/L* in the wastewater of the factory. *Note:* You must show all works.

9.8. **Calculate** the minimum pH value for starting the precipitation of Ni^{2+} ions in the solution obtained in *step 5* by passing H_2S gas into the solution until saturation. If you cannot solve question 9.7, use 20 *mg/L* Ni^{2+} sample for this question. *Note:* You must show all works.

The End

