

IChO 2012

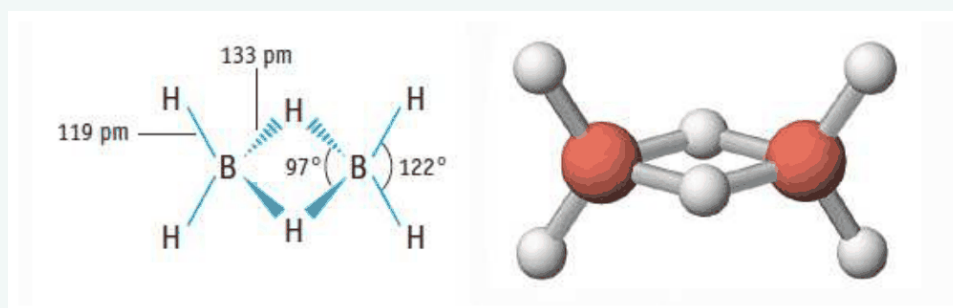
Theory problems and solutions · Washington, D.C., United States · 8 theory problems with complete solutions

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Problem 1: Boron hydrides and other boron compounds

A. Boron Hydrides and Other Boron Compounds

Boron hydride chemistry was first developed by Alfred Stock (1876 – 1946). More than 20 neutral molecular boron hydrides with the general formula B_xH_y have been characterized. The simplest boron hydride is B_2H_6 , diborane.



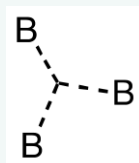
1.1 Using the data below derive the molecular formulae for two other members of this series of boron hydrides, **A** and **B**.

Substance	State (25 °C, 1 bar)	Mass Percent of Boron	Molar mass (g mol^{-1})
A	Liquid	83.1	65.1
B	Solid	88.5	122.2

William Lipscomb received the Nobel Prize in Chemistry in 1976 for “studies on the structures of boron hydrides illuminating the problems of chemical bonding.” Lipscomb recognized that, in all boron hydrides, each B atom has a normal 2-electron bond to at least one H atom ($B-H$). However, additional bonds of several types occur, and he developed a scheme for describing the structure of a borane by giving it a *styx* number where:

s = number of $B-H-B$ bridges in the molecule,

t = the number of 3-center BBB bonds in the molecule,



y = the number of two-center $B-B$ bonds in the molecule,

x = the number of BH_2 groups in the molecule.

The *styx* number for B_2H_6 is 0002.

1.2 Propose a structure for tetraborane, B_4H_{10} , with a styx number of 4012.

1.3 A boron-based compound is composed of boron, carbon, chlorine, and oxygen. Spectral measurements indicate that the molecule has two types of B atoms, with tetrahedral and trigonal planar geometry, in a 1 : 3 ratio, respectively. These spectra are also consistent with a CO triple bond. The molecular formula of the compound is B_4CCl_6O . Suggest a structure for its molecule.

B. Thermochemistry of Boron Compounds

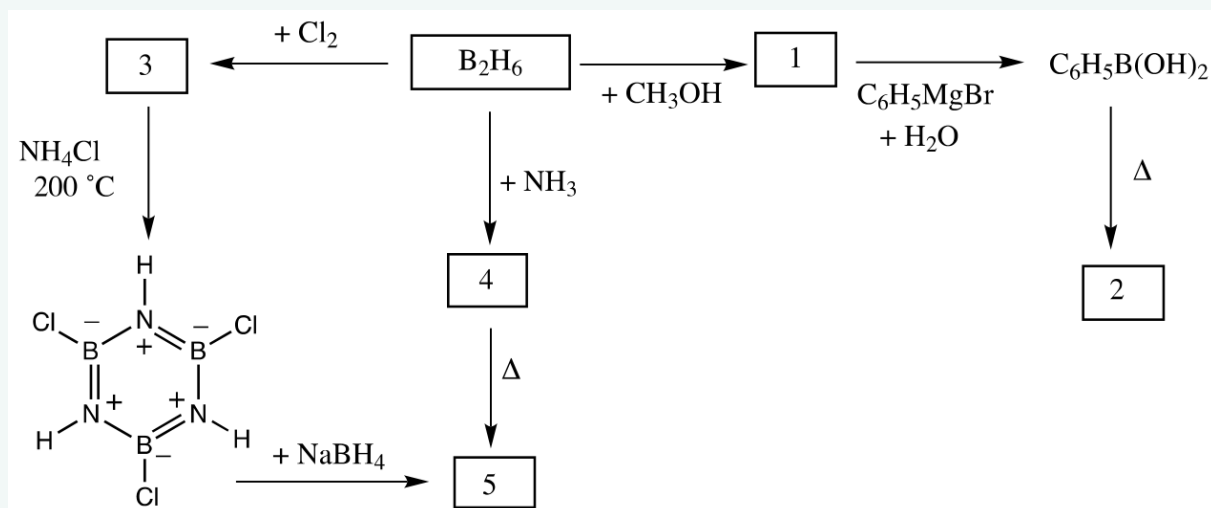
1.4 Estimate the B-B single bond dissociation enthalpy in B_2Cl_4 (g) using the following information:

Bond	Bond dissociation enthalpy (kJ mol^{-1})
B–Cl	443
Cl–Cl	242

Compound	$\Delta_f H^\circ$ (kJ mol^{-1})
BCl_3 (g)	–403
B_2Cl_4 (g)	–489

C. Chemistry of Diborane

1.5 Give the structure for each numbered compound in the scheme below. Each numbered compound is a boron-containing compound.



NOTES:

- The boiling point of compound **5** is 55 °C.
- Excess reagents used in all reactions.
- The freezing point depression for 0.312 g of compound **2** in 25.0 g of benzene, is 0.205 °C. The freezing point depression constant for benzene is $5.12\text{ kg K mol}^{-1}$.

Official English text of the problem.

Answers

Ordinary SMILES cannot directly encode a three-centre two-electron bond. For the explicitly specified borane connectivities below, **extended connectivity SMILES** use ~ for contacts belonging to such bonds. These strings require the accompanying bonding description. Part 1.1 determines molecular

formulae, not unique cage connectivities, so assigning structural SMILES there would require additional information.

- **1.1:** **A** is pentaborane(11), $\boxed{\text{B}_5\text{H}_{11}}$; **B** is decaborane(14), $\boxed{\text{B}_{10}\text{H}_{14}}$.
- **1.2:** Tetraborane(10), B_4H_{10} , has a folded, butterfly-shaped boron framework: two BH hinge atoms joined by one ordinary B–B bond, two BH_2 wing-tip atoms, and four hydrogen bridges connecting the hinge atoms to the wing tips. Extended connectivity SMILES: $[\text{BH}]12\sim[\text{H}]\sim[\text{BH}2]\sim[\text{H}]\sim[\text{BH}]1\sim[\text{H}]\sim[\text{BH}2]\sim[\text{H}]\sim2$.
- **1.3:** The carbon monoxide adduct of tris(dichloroboryl)borane, $\boxed{(\text{Cl}_2\text{B})_3\text{B} \leftarrow \text{CO}}$, with carbon bonded to the central boron and a $\text{C}\equiv\text{O}$ bond. SMILES: $\text{ClB}(\text{Cl})[\text{B}-](\text{B}(\text{Cl})\text{Cl})(\text{B}(\text{Cl})\text{Cl})\text{C}\#[\text{O}+]$.
- **1.4:** $\boxed{D(\text{B}-\text{B}) \approx 327 \text{ kJ mol}^{-1}}$.
- **1.5:** The numbered compounds are:

Number	Identification and structure	SMILES
1	Trimethyl borate, $\text{B}(\text{OCH}_3)_3$	<chem>COB(OC)OC</chem>
2	Triphenylboroxine, $(\text{C}_6\text{H}_5\text{BO})_3$: a six-membered alternating B–O ring, with one phenyl group on each boron	<chem>c1ccccc1B1OB(c2ccccc2)OB(c2ccccc2)O1</chem>
3	Boron trichloride, BCl_3	<chem>ClB(Cl)Cl</chem>
4	Diammoniate of diborane, $[\text{BH}_2(\text{NH}_3)_2]^+[\text{BH}_4]^-$, also called diammineboronium borohydride; see the condition-dependent alternative below	<chem>[BH2-]([NH3+])[NH3+].[BH4-]</chem>
5	Borazine, $\text{B}_3\text{N}_3\text{H}_6$: a planar alternating B–N ring with one hydrogen on every ring atom	<chem>[BH-]1=[NH+][BH-]=[NH+][BH-]=[NH+]1</chem>

For **4**, molecular **ammonia–borane**, NH_3BH_3 , SMILES $[\text{NH}3+][\text{BH}3-]$, is another possible product of diborane and ammonia under different conditions. The supplied scheme does not specify those conditions; both routes to **5** are balanced below.

Solution

1.1 — Molecular formulae

For a borane B_xH_y of molar mass M and boron mass fraction w_{B} ,

$$x = \frac{w_{\text{B}}M}{M_{\text{B}}}, \quad y = \frac{(1 - w_{\text{B}})M}{M_{\text{H}}}.$$

Using the conventional atomic molar masses $M_{\text{B}} = 10.81 \text{ g mol}^{-1}$ and $M_{\text{H}} = 1.008 \text{ g mol}^{-1}$:

For **A**,

$$x = \frac{0.831(65.1)}{10.81} = 5.00, \quad y = \frac{0.169(65.1)}{1.008} = 10.9 \approx 11.$$

Thus,

$$\boxed{\text{A: B}_5\text{H}_{11}, \text{pentaborane(11).}}$$

For **B**,

$$x = \frac{0.885(122.2)}{10.81} = 10.0, \quad y = \frac{0.115(122.2)}{1.008} = 13.9 \approx 14.$$

Thus,



The approximately integral atom counts identify the formulae despite the limited precision of the tabulated data.

1.2 — Tetraborane with styx number 4012

The four digits require:

$$s = 4, \quad t = 0, \quad y = 1, \quad x = 2.$$

Label the boron atoms B_1, B_2, B_3, B_4 . A precise description of the required drawing is:

- Join B_1 and B_2 by an ordinary two-centre, two-electron bond. These are the **hinge atoms**, each carrying one terminal hydrogen.
- Place B_3 and B_4 at the two wing tips of a folded butterfly framework. Each carries two terminal hydrogens.
- Add one hydrogen bridge on each of the four connections B_1-B_3 , B_2-B_3 , B_1-B_4 , and B_2-B_4 .
- Include no three-centre BBB bonds.

Each bridge is a single three-centre, two-electron B–H–B bond. The butterfly is folded about the central B_1-B_2 bond; the connectivity string does not specify this conformation.

The hydrogen count is

$$2(1) + 2(2) + 4 = 10.$$

The structure therefore has four bridges, zero BBB bonds, one ordinary B–B bond, and two terminal BH₂ groups: exactly **4012**.

An electron-count check gives

$$3(4) + 10 = 22$$

valence electrons, accounted for by six terminal B–H bonds, four hydrogen-bridge bonds, and one B–B bond:

$$6(2) + 4(2) + 1(2) = 22.$$

1.3 — Structure of B₄CCl₆O

Four boron atoms in a tetrahedral-to-trigonal-planar ratio of 1 : 3 require one four-coordinate boron and three three-coordinate borons.

Place one boron at the centre, bonded to three peripheral borons. Attach two chlorine atoms to each peripheral boron. Each peripheral boron then has three bonds—two B–Cl bonds and one B–B bond—and is trigonal planar.

The remaining carbon monoxide unit coordinates through **carbon** to the central boron. This supplies the central boron's fourth bond and gives approximately tetrahedral coordination:



Carbon monoxide is named carbon monoxide, SMILES [C-]#[O+]. Its carbon lone pair supplies the donor–acceptor bond.

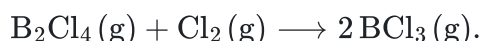
In an ordinary covalent Lewis representation of the adduct, the central boron carries formal charge -1 , oxygen carries $+1$, and carbon has one B–C bond plus a C–O triple bond. This is the representation encoded by

C1B(Cl)[B-](B(Cl)Cl)(B(Cl)Cl)C#[O+].

It has the required composition, three trigonal-planar peripheral borons, one tetrahedral central boron, and a retained C–O triple bond.

1.4 — B–B bond dissociation enthalpy

Consider the balanced reaction



Here B_2Cl_4 is tetrachlorodiborane(4), with structure $\text{Cl}_2\text{B}-\text{BCl}_2$, SMILES C1B(Cl)B(Cl)Cl.

Because chlorine gas is an element in its standard state,

$$\Delta_f H^\circ(\text{Cl}_2(\text{g})) = 0.$$

Hence

$$\begin{aligned}\Delta_r H^\circ &= 2\Delta_f H^\circ(\text{BCl}_3(\text{g})) - \Delta_f H^\circ(\text{B}_2\text{Cl}_4(\text{g})) \\ &= 2(-403) - (-489) \\ &= -317 \text{ kJ mol}^{-1}.\end{aligned}$$

In the net bond accounting, one B–B bond and one Cl–Cl bond are broken, and two additional B–Cl bonds are formed:

$$\Delta_r H^\circ \approx D(\text{B}-\text{B}) + D(\text{Cl}-\text{Cl}) - 2D(\text{B}-\text{Cl}).$$

Therefore,

$$-317 = D(\text{B}-\text{B}) + 242 - 2(443),$$

so

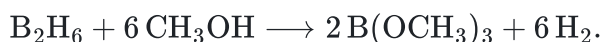
$$\boxed{D(\text{B}-\text{B}) \approx 327 \text{ kJ mol}^{-1}}.$$

This is an estimate because it treats the supplied B–Cl bond enthalpy as transferable between the compounds.

1.5 — Identification of the numbered compounds

Compound 1: trimethyl borate

Methanol replaces the hydridic hydrogens of diborane with methoxy groups, releasing hydrogen. With excess methanol, the balanced reaction is



Thus **1** is trimethyl borate, COB(OC)OC. Its boron is trigonal planar.

Reaction with phenylmagnesium bromide, followed by hydrolysis, gives the phenylboronic acid shown in the scheme. Phenylboronic acid has SMILES OB(O)c1ccccc1.

A balanced overall equation, representing the magnesium-containing hydrolysis product as magnesium bromide hydroxide, is



The phenyl group becomes bonded directly to boron, while hydrolysis replaces the remaining methoxy-derived ligands with hydroxyl groups.

Compound 2: triphenylboroxine

Heating phenylboronic acid causes condensation through B–O–B linkages. The freezing-point measurement determines the size of the product.

For a neutral, nondissociating solute,

$$\Delta T_f = K_f m.$$

Consequently,

$$m = \frac{0.205 \text{ K}}{5.12 \text{ kg K mol}^{-1}} = 0.0400 \text{ mol kg}^{-1}.$$

The solvent mass is 0.0250 kg, giving

$$n_2 = (0.0400 \text{ mol kg}^{-1})(0.0250 \text{ kg}) = 1.00 \times 10^{-3} \text{ mol}.$$

Using unrounded intermediate values,

$$M_2 = \frac{0.312 \text{ g}}{n_2} = 311.7 \text{ g mol}^{-1} \approx 312 \text{ g mol}^{-1}.$$

Loss of one water molecule per phenylboronic acid unit leaves the repeat composition $\text{C}_6\text{H}_5\text{BO}$. Its molar mass is approximately

$$M(\text{C}_6\text{H}_5\text{BO}) = 6(12.01) + 5(1.008) + 10.81 + 16.00 = 103.91 \text{ g mol}^{-1}.$$

Thus the number of repeat units is

$$\frac{311.7}{103.91} = 3.00.$$

Therefore **2** is the cyclic trimer, **triphenylboroxine**:



The balanced condensation is

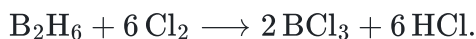


Draw a six-membered, approximately planar ring with alternating boron and oxygen atoms, placing one phenyl substituent on each boron. Each boron is trigonal planar. Its SMILES is

c1ccccc1B1OB(c2ccccc2)OB(c2ccccc2)O1.

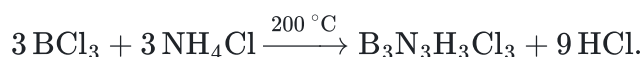
Compound 3: boron trichloride

Excess chlorine converts diborane to boron trichloride:

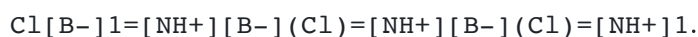


Thus **3** is BCl_3 , c1B(c1)c1, with trigonal-planar geometry.

Its reaction with ammonium chloride at 200°C produces the B-trichloroborazine drawn in the scheme:



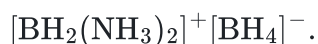
B-Trichloroborazine has an alternating B–N six-membered ring, with chlorine on each boron and hydrogen on each nitrogen. A charge-separated resonance-form SMILES matching the type of drawing in the question is



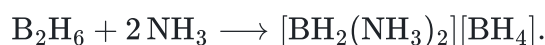
The formal charges and alternating double bonds describe a Lewis resonance form; they do not imply isolated ions.

Compound 4: the ammonia adduct

A conventional product of the diborane–ammonia reaction is **diammoniate of diborane**, the salt



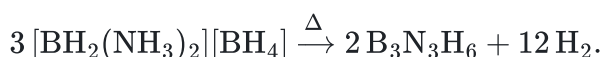
Its formation is balanced as



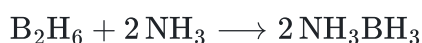
The cation is **diammineboronium**, $[\text{BH}_2-] ([\text{NH}_3+]) [\text{NH}_3+]$, with two terminal hydrogens and two ammonia ligands arranged approximately tetrahedrally around boron. The anion is **borohydride**, $[\text{BH}_4-]$, also tetrahedral.

The covalent SMILES representation places formal positive charges on the coordinated nitrogen atoms and a negative charge on the cation's boron; their sum is the required +1 cation charge.

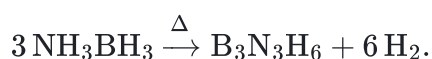
On heating, the balanced overall conversion to borazine is



The ammonia-reaction conditions are unspecified. A molecular alternative is **ammonia–borane**, $\text{H}_3\text{N} \longrightarrow \text{BH}_3$, $[\text{NH}_3+][\text{BH}_3-]$, in which nitrogen donates its lone pair to boron. Both atoms have approximately tetrahedral coordination. Its corresponding reactions are



and

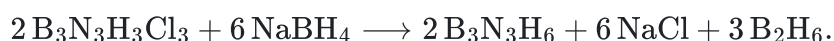


Both formulations therefore give the same overall diborane/ammonia-to-borazine stoichiometry.

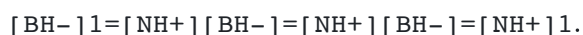
Compound 5: borazine

Sodium borohydride replaces the three B–Cl substituents of B-trichloroborazine with B–H groups. The ring product is therefore **borazine**, $\text{B}_3\text{N}_3\text{H}_6$, consistent with the stated boiling point of 55 °C.

A balanced equation, with the borane byproduct represented as diborane, is



Draw a planar six-membered ring with alternating B and N atoms and one hydrogen attached to every ring atom. Each ring atom is approximately trigonal planar. Nitrogen-to-boron electron donation produces delocalized bonding; a charge-separated resonance-form SMILES is



For completeness, the other species used in these equations have the following names and SMILES. Ionic salts are represented by disconnected ionic components; the Grignard representation omits solvent coordination and aggregation.

Species	Name	SMILES
B_2H_6	Diborane(6), with two three-centre hydrogen bridges	Extended connectivity: $[\text{BH}_2]1\sim[\text{H}]\sim[\text{BH}_2]\sim[\text{H}]1$
CH_3OH	Methanol	CO
H_2	Molecular hydrogen	$[\text{H}][\text{H}]$
H_2O	Water	O
$\text{C}_6\text{H}_5\text{MgBr}$	Phenylmagnesium bromide	c1ccccc1[Mg]Br
$\text{Mg}(\text{OH})\text{Br}$	Magnesium bromide hydroxide	$[\text{Mg}+2].[\text{OH}-].[\text{Br}-]$

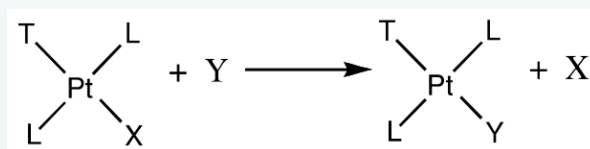
Species	Name	SMILES
C ₆ H ₆	Benzene	c1ccccc1
Cl ₂	Chlorine	ClCl
HCl	Hydrogen chloride	[H]Cl
NH ₃	Ammonia	N
NH ₄ Cl	Ammonium chloride	[NH4+] . [Cl-]
NaBH ₄	Sodium borohydride	[Na+] . [BH4-]
NaCl	Sodium chloride	[Na+] . [Cl-]

The solution was checked against the official solution.

Problem 2: Platinum(II) compounds, isomers and the trans effect

A. Platinum(II) Compounds, Isomers, and the *Trans* Effect.

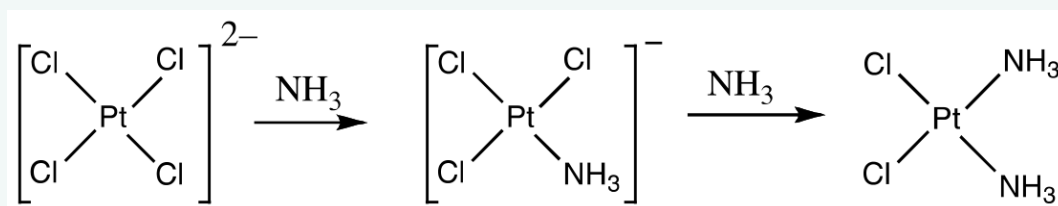
Platinum and other Group 10 metals form square planar complexes and the mechanisms of their reactions have been studied extensively. For example, it is known that substitution reactions of these complexes proceed with retention of stereochemistry.



It is also known that the rate of substitution of ligand X by Y depends on the nature of the ligand *trans* to X, that is, on ligand T. This is known as the ***trans effect***. When T is one of the molecules or ions in the following list, the rate of substitution at the trans position decreases from left to right.



The preparations of *cis*- and *trans*-Pt(NH₃)₂Cl₂ depend on the *trans* effect. The preparation of the *cis* isomer, a cancer chemotherapy agent commonly called cisplatin, involves the reaction of K₂PtCl₄ with ammonia.

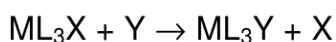


2.1 Draw all possible stereoisomers for square planar platinum(II) compounds with the formula Pt(py)(NH₃)BrCl (where py = pyridine, C₅H₅N).

2.2 Write reaction schemes including intermediate(s), if any, to show the preparation in aqueous solution for each of the stereoisomers of [Pt(NH₃)(NO₂)Cl₂]⁻ using, as reagents, PtCl₄²⁻, NH₃, and NO₂⁻. The reactions are controlled kinetically by the *trans* effect.

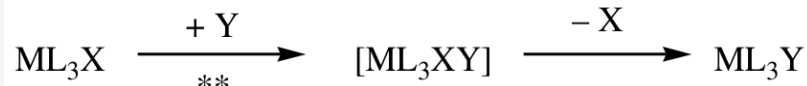
B. Kinetic Studies of Substitution Reactions of Square Planar Complexes

Substitutions of the ligand X by Y in square planar complexes



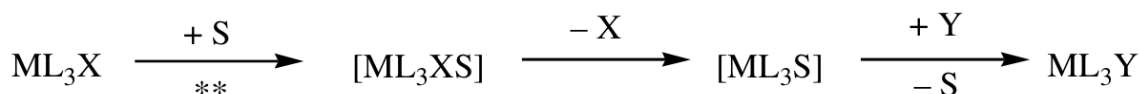
can occur in either or both of two ways:

i) *Direct substitution*: The incoming ligand Y attaches to the central metal, forming a five-coordinate complex, which then rapidly eliminates a ligand, X, to give the product, ML_3Y .



** = rate determining step, rate constant = k_Y

ii) *Solvent-assisted substitution*: A solvent molecule S attaches to the central metal to give ML_3XS , which eliminates the X to give ML_3S . Y rapidly displaces S to give ML_3Y .



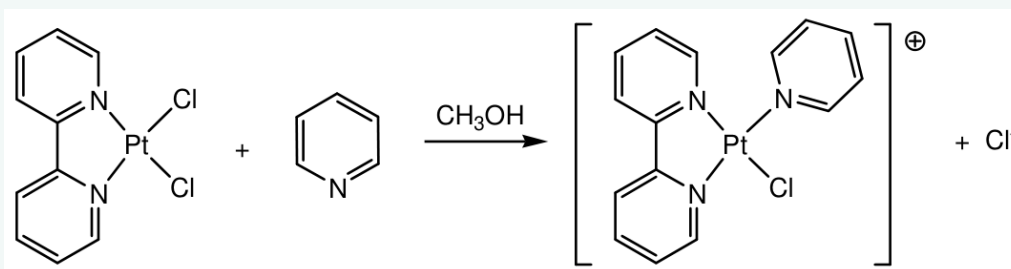
** = rate determining step, k_S = rate constant

The overall rate law for such substitutions is

$$\text{Rate} = k_s[\text{ML}_3\text{X}] + k_Y[\text{Y}][\text{ML}_3\text{X}]$$

When $[\text{Y}] \gg [\text{ML}_3\text{X}]$, then $\text{Rate} = k_{\text{obs}}[\text{ML}_3\text{X}]$.

The values of k_s and k_Y depend on the reactants and solvent involved. One example is the displacement of the Cl^- ligand in a square planar platinum(II) complex, ML_2X_2 , by pyridine ($\text{C}_5\text{H}_5\text{N}$). (The ML_3X scheme above applies to ML_2X_2 .)



Data for reaction at 25°C in methanol where $[\text{pyridine}] \gg$ the concentration of the platinum complex, are given in the table below.

Concentration of pyridine (mol dm^{-3})	k_{obs} (s^{-1})
0.122	$7.20 \cdot 10^{-4}$
0.061	$3.45 \cdot 10^{-4}$
0.030	$1.75 \cdot 10^{-4}$

2.3 Calculate the values of k_s and k_Y . Give the proper unit for each constant.

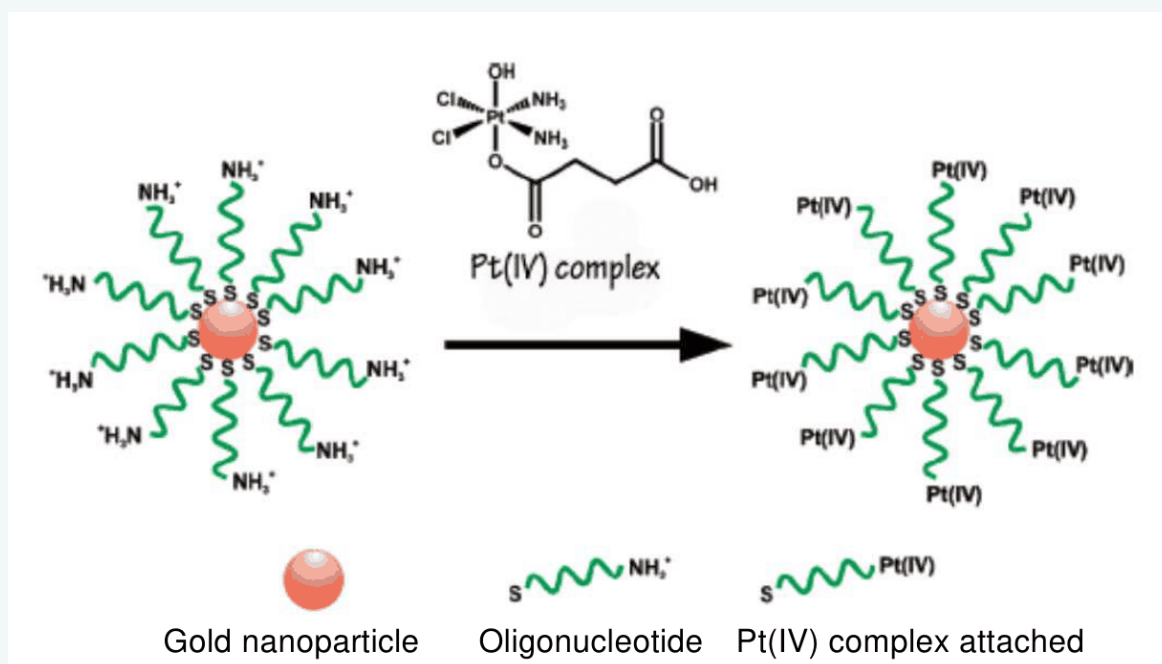
(A grid is given if you wish to use it.)

2.4 When $[\text{pyridine}] = 0.10 \text{ mol dm}^{-3}$, which of the following is true? (Tick the box next to the correct answer.)

- Most pyridine product is formed by the solvent-assisted (k_s) substitution pathway.
- Most pyridine product is formed by the direct substitution (k_Y) pathway
- Comparable amounts of product are formed by the two pathways.
- No conclusions may be drawn regarding the relative amounts of product produced by the two pathways.

C. A chemotherapy agent

In an effort to better target cisplatin to cancer cells, Professor Lippard's group at MIT attached a platinum(IV) complex to oligonucleotides bound to gold nanoparticles.



2.5 Experiments showed that the diameter of a gold nanoparticle was 13 nm. Attached to this nanoparticle are 90 oligonucleotide groups, with 98 % of them being bound to a Pt(IV) complex. Suppose that the reaction vessel used for treating cells with the Pt(IV) nanoparticle reagent had a volume of 1.0 cm^3 and the concentration of the solution was $1.0 \cdot 10^{-6} \text{ mol dm}^{-3}$ in Pt. Calculate the mass of platinum and that of gold used in this experiment.

(The density of gold = 19.3 g cm^{-3} , the volume of a sphere = $(4/3)\pi r^3 = 4.18879 r^3$.)

Official English text of the problem.

Answers

The coordination SMILES below use dative bonds and @SP descriptors for square-planar stereochemistry. The ligand positions are also specified in words in the solution.

- **2.1:** There are **three stereoisomers** of **amminebromidochlorido(pyridine)platinum(II)**:

I — pyridine trans to ammonia: [NH3]->[Pt@SP3+2](<-[Cl-])(<-[Br-])<-n1cccc1

II — pyridine trans to bromido: [NH3]->[Pt@SP2+2](<-[Cl-])(<-[Br-])<-n1cccc1

III — pyridine trans to chlorido: [NH3]->[Pt@SP1+2](<-[Cl-])(<-[Br-])<-n1cccc1

- **2.2:** There are **two stereoisomers**:

cis-Amminedichlorido(nitro)platinate(II), obtained by adding ammonia first, then nitrite: [NH3]->[Pt@SP1+2](<-[Cl-])(<-[Cl-])<-N(=O)[O-]

trans-Amminedichlorido(nitro)platinate(II), obtained by adding nitrite first, then ammonia: [NH3]->[Pt@SP3+2](<-[Cl-])(<-[Cl-])<-N(=O)[O-]

- **2.3:** $k_s \approx 0 \text{ s}^{-1}$, $k_Y \approx 5.9 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

- **2.4:** Tick the **second box**: most product is formed by the **direct substitution pathway**.

- **2.5:** To two significant figures,

$$m(\text{Pt}) = 2.0 \times 10^{-7} \text{ g} = 0.20 \mu\text{g}$$

$$m(\text{Au}) = 1.5 \times 10^{-4} \text{ g} = 0.15 \text{ mg}.$$

Solution

The simple molecular and ionic species used below are:

Name	Formula	SMILES
Ammonia	<chem>NH3</chem>	<chem>[NH3]</chem>
Pyridine	<chem>C5H5N</chem>	<chem>n1cccc1</chem>
Bromide ion	<chem>Br^-</chem>	<chem>[Br-]</chem>
Chloride ion	<chem>Cl^-</chem>	<chem>[Cl-]</chem>
Nitrite ion	<chem>NO2^-</chem>	<chem>O=N[O-]</chem>

For the complexes containing nitrite, the structural SMILES represent **N-bound nitro coordination**. All platinum(II) complexes considered here have square-planar coordination. The SMILES encode connectivity and the indicated stereochemistry; they do not depict the electron flow during substitution.

2.1 — All square-planar stereoisomers

Fix pyridine at one position. The ligand opposite it can be ammonia, bromido, or chlorido, giving three possibilities. Once this opposite ligand is chosen, exchanging the remaining two positions gives a superposable arrangement after rotation in three-dimensional space.

Thus there are exactly **three geometrical isomers**, with these pairs of opposite ligands:

Isomer	First trans pair	Second trans pair
I	Pyridine–ammonia	Bromido–chlorido
II	Pyridine–bromido	Ammonia–chlorido
III	Pyridine–chlorido	Ammonia–bromido

To draw them precisely, put platinum at the centre of a cross and pyridine above it. Place the other ligands as follows:

Isomer	Below platinum	Left of platinum	Right of platinum
I	<chem>NH3</chem>	<chem>Br</chem>	<chem>Cl</chem>
II	<chem>Br</chem>	<chem>NH3</chem>	<chem>Cl</chem>

Isomer	Below platinum	Left of platinum	Right of platinum
III	Cl	NH ₃	Br

The corresponding names and stereochemical SMILES are given in Answers 2.1. These ideal square-planar arrangements do not generate additional enantiomeric pairs.

2.2 — Preparation of both stereoisomers

The relevant trans-effect order is



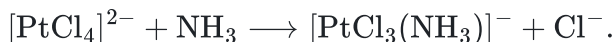
The starting ion and the two monosubstituted intermediates are:

Name	Formula	SMILES
Tetrachloridoplatinate(II) ion	$[\text{PtCl}_4]^{2-}$	<chem>[Cl-]>[Pt+2](<-[Cl-])(<-[Cl-])<-[Cl-])</chem>
Amminetrichloridoplatinate(II) ion	$[\text{PtCl}_3(\text{NH}_3)]^-$	<chem>[NH3]>[Pt+2](<-[Cl-])(<-[Cl-])<-[Cl-])</chem>
Trichlorido(nitro)platinate(II) ion	$[\text{PtCl}_3(\text{NO}_2)]^{2-}$	<chem>O=N([O-])>[Pt+2](<-[Cl-])(<-[Cl-])<-[Cl-])</chem>

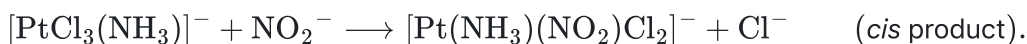
Each has square-planar geometry; three identical chlorido ligands mean that no distinct geometrical isomers need to be specified for these intermediates.

Preparation of the cis isomer: ammonia first

First replace one chlorido ligand with ammonia:



Then introduce nitrite:



In the intermediate, one chlorido ligand is trans to ammonia, while the other two are trans to each other. Because chloride has a stronger trans effect than ammonia, nitrite preferentially replaces a chlorido ligand **trans to another chlorido ligand**.

Consequently, the incoming nitro ligand is **cis to ammonia**, and the two remaining chlorido ligands are also cis.

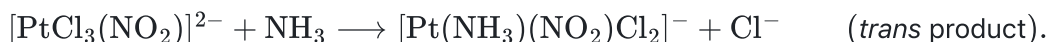
A precise drawing of the product has ammonia above platinum, nitro to the right, and chlorido ligands below and to the left. Its trans pairs are ammonia–chlorido and nitro–chlorido.

Preparation of the trans isomer: nitrite first

First introduce nitrite:



Then introduce ammonia:



The nitro ligand has a stronger trans effect than chloride. Ammonia therefore preferentially replaces the chlorido ligand **trans to nitro**.

The resulting ammonia and nitro ligands are opposite each other, as are the two remaining chlorido ligands. Draw ammonia above platinum, nitro below it, and the chlorido ligands to the left and right.

All four substitution equations conserve both atoms and charge.

2.3 — Determination of the rate constants

From the supplied rate law,

$$\text{Rate} = (k_s + k_Y[\text{pyridine}])[\text{platinum complex}],$$

so

$$k_{\text{obs}} = k_s + k_Y[\text{pyridine}].$$

Therefore, a plot of k_{obs} against pyridine concentration has:

- intercept k_s , with units s^{-1} ;
- slope k_Y , with units $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$.

The three values of $k_{\text{obs}}/[\text{pyridine}]$ are

$$5.902 \times 10^{-3}, \quad 5.656 \times 10^{-3}, \quad 5.833 \times 10^{-3} \quad \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}.$$

They are approximately constant, so the plotted line passes approximately through the origin.

The data are not exactly collinear: an unconstrained least-squares fit gives an intercept of $-9.47 \times 10^{-6} \text{s}^{-1}$, which cannot be a physical rate constant. Constraining both rate constants to be nonnegative gives the best fit at $k_s = 0$. The corresponding slope is

$$k_Y = \frac{\sum_i [\text{pyridine}]_i k_{\text{obs},i}}{\sum_i [\text{pyridine}]_i^2} = 5.8516 \times 10^{-3} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}.$$

Thus the appropriate approximate results are

$$k_s \approx 0 \text{ s}^{-1}, \quad k_Y \approx 5.9 \times 10^{-3} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}.$$

Here k_s is the effective first-order constant in the given rate law, which already incorporates the constant solvent concentration.

2.4 — Dominant substitution pathway

At $[\text{pyridine}] = 0.10 \text{ mol dm}^{-3}$, the direct pathway contributes

$$k_Y[\text{pyridine}] \approx (5.9 \times 10^{-3} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}) (0.10 \text{ mol dm}^{-3}) = 5.9 \times 10^{-4} \text{ s}^{-1}.$$

This greatly exceeds the approximately zero solvent-assisted contribution.

Equivalently, the fraction formed through direct substitution is

$$f_{\text{direct}} = \frac{k_Y[\text{pyridine}]}{k_s + k_Y[\text{pyridine}]} \approx 1.$$

Therefore, **most pyridine product is formed by direct substitution: the second box is correct.**

2.5 — Masses of platinum and gold

Use the standard constants

$$M(\text{Pt}) = 195.08 \text{ g mol}^{-1}, \quad N_A = 6.022 \times 10^{23} \text{ mol}^{-1},$$

which are not printed in the problem.

The solution volume is

$$1.0 \text{ cm}^3 = 1.0 \times 10^{-3} \text{ dm}^3.$$

Thus the amount of platinum is

$$n(\text{Pt}) = (1.0 \times 10^{-6} \text{ mol dm}^{-3}) (1.0 \times 10^{-3} \text{ dm}^3) = 1.0 \times 10^{-9} \text{ mol}.$$

Its mass is

$$m(\text{Pt}) = n(\text{Pt})M(\text{Pt}) = 1.9508 \times 10^{-7} \text{ g},$$

or, to two significant figures,

$$m(\text{Pt}) = 2.0 \times 10^{-7} \text{ g} = 0.20 \mu\text{g}.$$

Each nanoparticle carries, on average,

$$90(0.98) = 88.2$$

platinum complexes, each containing one platinum atom. Therefore, the number of gold nanoparticles is

$$N_{\text{particles}} = \frac{n(\text{Pt})N_{\text{A}}}{88.2} = \frac{(1.0 \times 10^{-9})(6.022 \times 10^{23})}{88.2} = 6.83 \times 10^{12}.$$

The radius of one particle is

$$r = \frac{13}{2} \text{ nm} = 6.5 \times 10^{-7} \text{ cm}.$$

Using the given sphere-volume expression,

$$V_{\text{particle}} = 4.18879r^3 = 4.18879(6.5 \times 10^{-7} \text{ cm})^3 = 1.15035 \times 10^{-18} \text{ cm}^3.$$

The gold mass per particle is

$$m_{\text{particle}} = \rho V_{\text{particle}} = (19.3 \text{ g cm}^{-3})(1.15035 \times 10^{-18} \text{ cm}^3) = 2.22017 \times 10^{-17} \text{ g}.$$

Consequently,

$$m(\text{Au}) = N_{\text{particles}}m_{\text{particle}} = 1.5159 \times 10^{-4} \text{ g},$$

giving

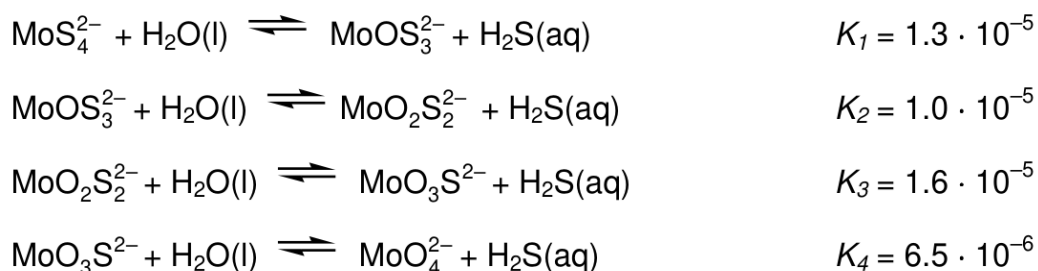
$$m(\text{Au}) = 1.5 \times 10^{-4} \text{ g} = 0.15 \text{ mg}.$$

The solution was checked against the official solution.

Problem 3: Thiomolybdate ions

Thiomolybdate ions are derived from molybdate ions, MoO_4^{2-} , by replacing oxygen atoms with sulfur atoms. In nature, thiomolybdate ions are found in such places as the deep waters of the Black Sea, where biological sulfate reduction generates H_2S . The molybdate to thiomolybdate transformation leads to rapid loss of dissolved Mo from seawater to underlying sediments, depleting the ocean in Mo, a trace element essential for life.

The following equilibria control the relative concentrations of molybdate and thiomolybdate ions in dilute aqueous solution:



3.1 If at equilibrium the concentrations of MoO_4^{2-} and $\text{H}_2\text{S}(\text{aq})$ are equal to $1 \cdot 10^{-7}$ and $1 \cdot 10^{-6}$, respectively, what would be the equilibrium concentration of MoS_4^{2-} ?

Solutions containing $\text{MoO}_2\text{S}_2^{2-}$, MoOS_3^{2-} and MoS_4^{2-} display absorption peaks in the visible wavelength range at 395 and 468 nm. The other ions, as well as H_2S , absorb negligibly in the visible wavelength range. The molar absorptivities (ϵ) at these two wavelengths are given in the following table:

	ϵ at 468 nm $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$	ϵ at 395 nm $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$
MoS_4^{2-}	11870	120
MoOS_3^{2-}	0	9030
$\text{MoO}_2\text{S}_2^{2-}$	0	3230

3.2 A solution not at equilibrium contains a mixture of MoS_4^{2-} , MoOS_3^{2-} and $\text{MoO}_2\text{S}_2^{2-}$ and no other Mo-containing species. The total concentration of all species containing Mo is $6.0 \cdot 10^{-6} \text{ mol dm}^{-3}$. In a 10.0 cm absorption cell, the absorbance of the solution at 468 nm is 0.365 and that at 395 nm is 0.213. Calculate the concentrations of all three Mo-containing anions in this mixture.

A solution with initial concentration of MoS_4^{2-} equal to $2.0 \cdot 10^{-7} \text{ mol dm}^{-3}$ hydrolyzes in a closed system. The H_2S product accumulates until equilibrium is reached. When calculating the final equilibrium concentrations of $\text{H}_2\text{S}(\text{aq})$, and all five Mo-containing anions (that is, MoO_4^{2-} , $\text{MoO}_3\text{S}^{2-}$, $\text{MoO}_2\text{S}_2^{2-}$, MoOS_3^{2-} and MoS_4^{2-}) ignore the possibility that H_2S might ionize to HS^- under certain pH conditions.

3.3 Write the six independent equations that determine the system.

3.4 Calculate the above mentioned six concentrations making reasonable approximations, giving your answers to two significant figures.

Official English text of the problem.

Answers

- **3.1**

$$[\text{MoS}_4^{2-}] = 7.4 \times 10^{-12} \text{ mol dm}^{-3}$$

- **3.2** To two significant figures:

$$\begin{aligned} &= 3.1 \times 10^{-6} \text{ mol dm}^{-3}, \\ [\text{MoOS}_3^{2-}] &= 2.0 \times 10^{-6} \text{ mol dm}^{-3}, \\ [\text{MoO}_2\text{S}_2^{2-}] &= 9.5 \times 10^{-7} \text{ mol dm}^{-3}. \end{aligned}$$

- **3.3** Let $h = [\text{H}_2\text{S}(\text{aq})]$, and let x_0, x_1, x_2, x_3, x_4 denote the concentrations of MoO_4^{2-} , $\text{MoO}_3\text{S}^{2-}$, $\text{MoO}_2\text{S}_2^{2-}$, MoOS_3^{2-} , and MoS_4^{2-} , respectively. With $C = 2.0 \times 10^{-7} \text{ mol dm}^{-3}$, the six equations are

$$\begin{aligned} \frac{x_3 h}{x_4} &= K_1, & \frac{x_2 h}{x_3} &= K_2, \\ \frac{x_1 h}{x_2} &= K_3, & \frac{x_0 h}{x_1} &= K_4, \\ x_0 + x_1 + x_2 + x_3 + x_4 &= C, \\ h + x_1 + 2x_2 + 3x_3 + 4x_4 &= 4C. \end{aligned}$$

- **3.4**

$$\begin{aligned} &= 7.8 \times 10^{-7} \text{ mol dm}^{-3}, \\ [\text{MoO}_4^{2-}] &= 1.8 \times 10^{-7} \text{ mol dm}^{-3}, \\ [\text{MoO}_3\text{S}^{2-}] &= 2.1 \times 10^{-8} \text{ mol dm}^{-3}, \\ [\text{MoO}_2\text{S}_2^{2-}] &= 1.0 \times 10^{-9} \text{ mol dm}^{-3}, \\ [\text{MoOS}_3^{2-}] &= 8.0 \times 10^{-11} \text{ mol dm}^{-3}, \\ [\text{MoS}_4^{2-}] &= 4.8 \times 10^{-12} \text{ mol dm}^{-3}. \end{aligned}$$

Solution

The species and notation used throughout are:

Concentration	Ion	SMILES
x_0	Molybdate, MoO_4^{2-}	[O-][Mo](=O)(=O)[O-]
x_1	Monothiomolybdate, $\text{MoO}_3\text{S}^{2-}$	[O-][Mo](=O)(=S)[O-]
x_2	Dithiomolybdate, $\text{MoO}_2\text{S}_2^{2-}$	[S-][Mo](=O)(=O)[S-]
x_3	Trithiomolybdate, MoOS_3^{2-}	[S-][Mo](=O)(=S)[S-]
x_4	Tetrathiomolybdate, MoS_4^{2-}	[S-][Mo](=S)(=S)[S-]

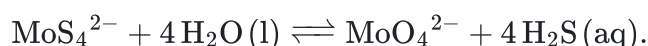
These SMILES give formal Lewis representations; the placement of localized bonds and charges is not unique because of resonance. The four oxygen/sulfur ligands have approximately tetrahedral coordination around molybdenum(VI), which these SMILES do not explicitly specify.

Water, H_2O , has SMILES o; hydrogen sulfide, H_2S , has SMILES s; and hydrosulfide, HS^- , has SMILES [SH-]. Hydrosulfide formation is excluded as instructed.

The given equilibrium constants are used in their dilute-solution concentration form, with liquid water omitted from the expressions.

3.1

Adding the four hydrolysis reactions cancels the intermediate ions:



The equilibrium constant for this overall reaction is the product of the four constants:

$$K_1 K_2 K_3 K_4 = (1.3 \times 10^{-5})(1.0 \times 10^{-5})(1.6 \times 10^{-5})(6.5 \times 10^{-6}) = 1.352 \times 10^{-20}.$$

Consequently,

$$K_1 K_2 K_3 K_4 = \frac{[\text{MoO}_4^{2-}][\text{H}_2\text{S}]^4}{[\text{MoS}_4^{2-}]}.$$

Rearranging and substituting the specified concentrations gives

$$[\text{MoS}_4^{2-}] = \frac{(1 \times 10^{-7})(1 \times 10^{-6})^4}{1.352 \times 10^{-20}} = 7.396 \times 10^{-12} \text{ mol dm}^{-3}.$$

Thus,

$$\boxed{[\text{MoS}_4^{2-}] \approx 7.4 \times 10^{-12} \text{ mol dm}^{-3}}.$$

3.2

For a mixture, the Beer–Lambert law is

$$A_\lambda = l \sum_i \varepsilon_{i,\lambda} c_i.$$

At 468 nm, only tetrathiomolybdate absorbs appreciably. Hence,

$$0.365 = (10.0)(11870)x_4,$$

so

$$x_4 = 3.0749789 \times 10^{-6} \text{ mol dm}^{-3}.$$

The molybdenum balance gives

$$x_3 + x_2 = 6.0 \times 10^{-6} - x_4.$$

At 395 nm, all three species contribute:

$$0.213 = 10.0(120x_4 + 9030x_3 + 3230x_2).$$

Substituting $x_2 = 6.0 \times 10^{-6} - x_4 - x_3$,

$$x_3 = \frac{0.213/10.0 - 120x_4 - 3230(6.0 \times 10^{-6} - x_4)}{9030 - 3230} = 1.9798594 \times 10^{-6} \text{ mol dm}^{-3}.$$

Therefore,

$$x_2 = 6.0 \times 10^{-6} - x_4 - x_3 = 9.4516167 \times 10^{-7} \text{ mol dm}^{-3}.$$

Rounded to two significant figures, these are 3.1×10^{-6} , 2.0×10^{-6} , and $9.5 \times 10^{-7} \text{ mol dm}^{-3}$, respectively. No equilibrium relations are used because this mixture is explicitly not at equilibrium.

3.3

There are six unknown concentrations: $x_0, x_1, x_2, x_3, x_4, h$.

The four equilibrium relations are

$$K_1 = \frac{x_3 h}{x_4} = 1.3 \times 10^{-5},$$

$$K_2 = \frac{x_2 h}{x_3} = 1.0 \times 10^{-5},$$

$$K_3 = \frac{x_1 h}{x_2} = 1.6 \times 10^{-5},$$

$$K_4 = \frac{x_0 h}{x_1} = 6.5 \times 10^{-6}.$$

Each anion contains one molybdenum atom, so conservation of molybdenum gives

$$\boxed{x_0 + x_1 + x_2 + x_3 + x_4 = C = 2.0 \times 10^{-7} \text{ mol dm}^{-3}}.$$

Initially, every molybdenum atom is associated with four sulfur atoms. At equilibrium, sulfur is distributed between the anions and dissolved hydrogen sulfide. Thus,

$$h + x_1 + 2x_2 + 3x_3 + 4x_4 = 4C = 8.0 \times 10^{-7} \text{ mol dm}^{-3}.$$

These are the required six independent equations. Combining the two elemental balances also gives the useful equivalent relation

$$h = 4x_0 + 3x_1 + 2x_2 + x_3.$$

The coefficients count the number of hydrogen sulfide molecules released when one initial tetrathiomolybdate ion reaches each hydrolysis state.

3.4

The sulfur balance bounds the hydrogen sulfide concentration:

$$0 < h \leq 4C = 8.0 \times 10^{-7} \text{ mol dm}^{-3}.$$

The equilibrium relations give the successive concentration ratios

$$\frac{x_1}{x_0} = \frac{h}{K_4}, \quad \frac{x_2}{x_1} = \frac{h}{K_3}, \quad \frac{x_3}{x_2} = \frac{h}{K_2}, \quad \frac{x_4}{x_3} = \frac{h}{K_1}.$$

Even at the upper bound for h , these ratios are only approximately 0.12, 0.050, 0.080, and 0.062. Molybdate therefore predominates, and nearly complete hydrolysis provides a reasonable first approximation:

$$h^{(0)} = 4C = 8.0 \times 10^{-7} \text{ mol dm}^{-3}.$$

To obtain reliable two-significant-figure results for the minor species, refine this approximation using both balances. Express every molybdenum concentration in terms of x_0 and h :

$$\begin{aligned} x_1 &= x_0 \frac{h}{K_4}, \\ x_2 &= x_0 \frac{h^2}{K_3 K_4}, \\ x_3 &= x_0 \frac{h^3}{K_2 K_3 K_4}, \\ x_4 &= x_0 \frac{h^4}{K_1 K_2 K_3 K_4}. \end{aligned}$$

The molybdenum balance then gives

$$x_0 = \frac{C}{1 + \frac{h}{K_4} + \frac{h^2}{K_3 K_4} + \frac{h^3}{K_2 K_3 K_4} + \frac{h^4}{K_1 K_2 K_3 K_4}}.$$

For each estimate of h , calculate these concentrations and update h from

$$h_{\text{new}} = 4C - x_1 - 2x_2 - 3x_3 - 4x_4.$$

Successive approximations are

$$\begin{aligned} h^{(0)} &= 8.0000000 \times 10^{-7}, \\ h^{(1)} &= 7.7574998 \times 10^{-7}, \\ h^{(2)} &= 7.7647978 \times 10^{-7}, \\ h^{(3)} &= 7.7645781 \times 10^{-7}, \end{aligned} \quad \text{mol dm}^{-3}.$$

The concentrations have stabilized sufficiently for the requested rounding:

Species	Value before final rounding (mol dm^{-3})	Two significant figures (mol dm^{-3})
$\text{H}_2\text{S}(\text{aq})$	7.7646×10^{-7}	7.8×10^{-7}
MoO_4^{2-}	1.7766×10^{-7}	1.8×10^{-7}
$\text{MoO}_3\text{S}^{2-}$	2.1223×10^{-8}	2.1×10^{-8}
$\text{MoO}_2\text{S}_2^{2-}$	1.0299×10^{-9}	1.0×10^{-9}
MoOS_3^{2-}	7.9968×10^{-11}	8.0×10^{-11}
MoS_4^{2-}	4.7763×10^{-12}	4.8×10^{-12}

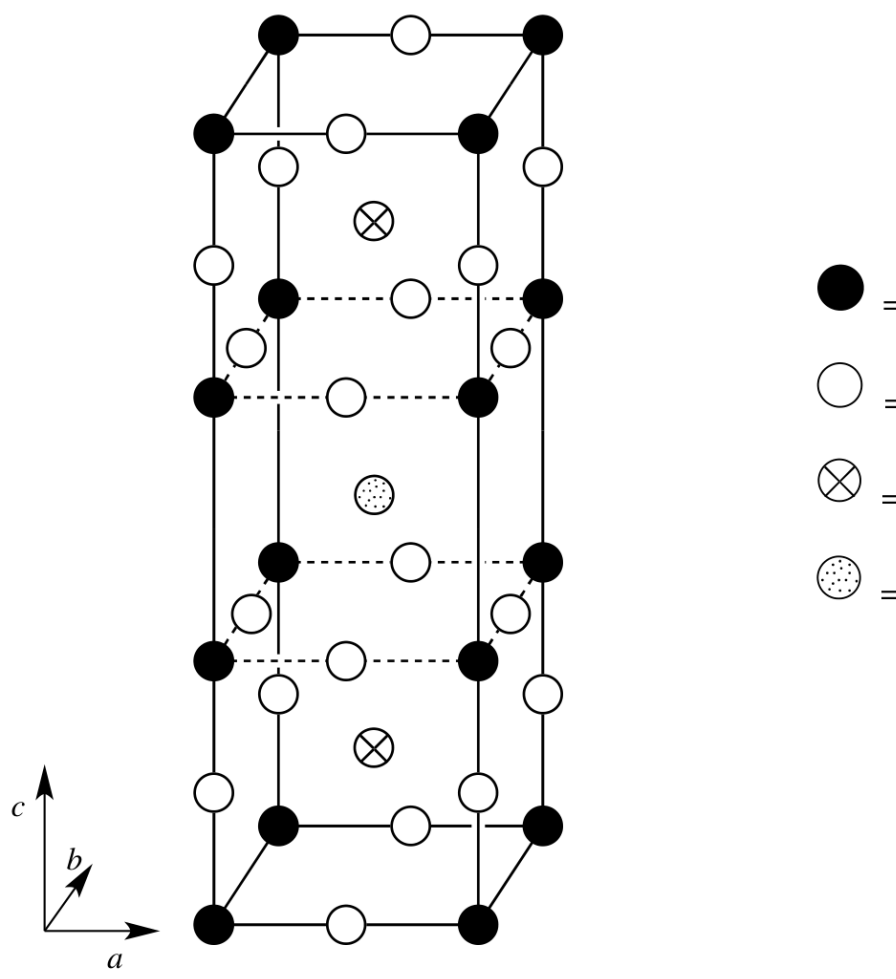
Using unrounded values, the molybdenum concentrations sum to $2.0 \times 10^{-7} \text{ mol dm}^{-3}$, and the total sulfur concentration is $8.0 \times 10^{-7} \text{ mol dm}^{-3}$, as required.

The solution was checked against the official solution.

Problem 4: The superconductor YBCO

In the 1980's a class of ceramic materials was discovered that exhibits superconductivity at the unusually high temperature of 90 K. One such material contains yttrium, barium, copper and oxygen and is called "YBCO". It has a nominal composition of $\text{YBa}_2\text{Cu}_3\text{O}_7$, but its actual composition is variable according to the formula $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($0 < \delta < 0.5$).

4.1 One unit cell of the idealized crystal structure of YBCO is shown below. Identify which circles correspond to which elements in the structure.



The true structure is actually orthorhombic ($a \neq b \neq c$), but it is approximately tetragonal, with $a \approx b \approx (c/3)$.

4.2 A sample of YBCO with $\delta = 0.25$ was subjected to X-ray diffraction using $\text{CuK}\alpha$ radiation ($\lambda = 154.2 \text{ pm}$). The lowest-angle diffraction peak was observed at $2\theta = 7.450^\circ$. Assuming that $a = b = (c/3)$, calculate the values of a and c .

4.3 Estimate the density of this sample of YBCO (with $\delta = 0.25$) in g cm^{-3} . If you were unable to calculate the values for a and c from part 4.2, then use $a = 500 \text{ pm}$ and $c = 1500 \text{ pm}$.

When YBCO is dissolved in aqueous HCl ($c = 1.0 \text{ mol dm}^{-3}$) bubbles of gas are observed (identified as O_2 by gas chromatography). After boiling for 10 min to expel the dissolved gases, the solution reacts with excess KI solution, turning yellow-brown. This solution can be titrated with thiosulfate solution to a starch endpoint. If YBCO is added under Ar directly to a solution in which concentrations of both KI and HCl are equal to 1.0 mol dm^{-3} , the solution turns yellow-brown but no gas evolution is observed.

4.4 Write a balanced net ionic equation for the reaction when solid $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ dissolves in aqueous HCl with evolution of O_2 .

4.5 Write a balanced net ionic equation for the reaction when the solution from 4.4 reacts with excess KI in acidic solution after the dissolved oxygen is expelled.

4.6 Write a balanced net ionic equation for the reaction when the solution from 4.5 is titrated with thiosulfate ($\text{S}_2\text{O}_3^{2-}$).

4.7 Write a balanced net ionic equation for the reaction when solid $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ dissolves in aqueous HCl containing excess KI in an Ar atmosphere.

Two identical samples of YBCO with an unknown value of δ were prepared. The first sample was dissolved in 5 cm^3 of aqueous HCl ($c = 1.0\text{ mol dm}^{-3}$), evolving O_2 . After boiling to expel gases, cooling, and addition of 10 cm^3 of KI solution ($c = 0.7\text{ mol dm}^{-3}$) under Ar , titration with thiosulfate to the starch endpoint required $1.542 \cdot 10^{-4}\text{ mol}$ thiosulfate. The second sample of YBCO was added under Ar directly to 7 cm^3 of a solution in which $c(\text{KI}) = 1.0\text{ mol dm}^{-3}$ and $c(\text{HCl}) = 0.7\text{ mol dm}^{-3}$. Titration of this solution required $1.696 \cdot 10^{-4}\text{ mol}$ thiosulfate to reach the endpoint.

4.8 Calculate the amount of substance of Cu (in mol) in each of these samples of YBCO.

4.9 Calculate the value of δ for these samples of YBCO.

Official English text of the problem.

Answers

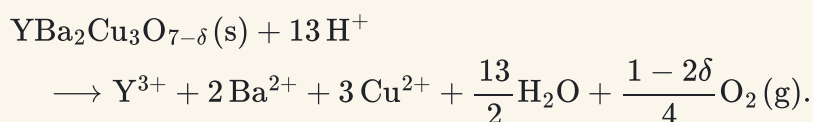
Iodine in excess iodide is represented as triiodide, I_3^- . Names and SMILES for the reaction species are provided in the Solution.

- **4.1** Filled black circles: **copper**; empty circles: **oxygen**; crossed circles: **barium**; dotted circle: **yttrium**.

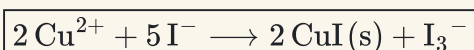
- **4.2** $a = b = 395.6\text{ pm}, \quad c = 1.187 \times 10^3\text{ pm}.$

- **4.3** $\rho = 5.92\text{ g cm}^{-3}.$

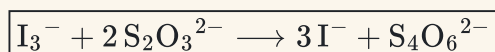
- **4.4**



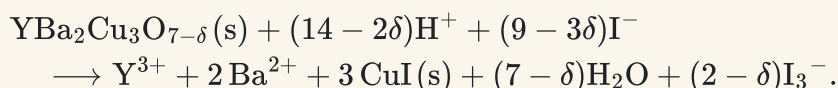
- **4.5**



- **4.6**



- **4.7**



- **4.8** $n(\text{Cu}) = 1.542 \times 10^{-4}\text{ mol}$ in **each** sample.

- **4.9** $\delta \approx 0.350.$

Solution

4.1 — Identifying the atoms

An atom at a unit-cell corner contributes $1/8$ to that cell; one on an edge contributes $1/4$; one on a face contributes $1/2$; and one inside contributes 1.

Circle type	Positions in the drawing	Effective number per cell	Element
Filled black	8 corners and 8 other positions on vertical edges	$8/8 + 8/4 = 3$	Copper, Cu
Empty	12 edge positions and 8 face positions	$12/4 + 8/2 = 7$	Oxygen, O
Crossed	2 interior positions	2	Barium, Ba
Dotted	1 interior position	1	Yttrium, Y

These counts give exactly one nominal formula unit of $\text{YBa}_2\text{Cu}_3\text{O}_7$ per unit cell, so $Z = 1$. Oxygen vacancies change the oxygen content to $7 - \delta$.

YBCO is an extended crystal, so no discrete molecular SMILES represents its structure. The figure specifies its periodic arrangement.

4.2 — Lattice parameters

For a tetragonal lattice,

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}.$$

Because $c = 3a$, the largest interplanar spacing is $d_{001} = c$. It produces the lowest-angle reflection.

Bragg's law for this reflection is

$$\lambda = 2c \sin \theta, \quad \theta = \frac{7.450^\circ}{2} = 3.725^\circ.$$

Thus

$$c = \frac{154.2 \text{ pm}}{2 \sin 3.725^\circ} = 1186.743 \text{ pm},$$

and

$$a = b = \frac{c}{3} = 395.581 \text{ pm}.$$

Therefore,

$$\boxed{a = b = 395.6 \text{ pm}, \quad c = 1187 \text{ pm}}.$$

4.3 — Density

For $\delta = 0.25$, the composition is $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$. Using standard atomic molar masses in g mol^{-1} ,

$$\begin{aligned} M &= 88.91 + 2(137.33) + 3(63.55) + 6.75(16.00) \\ &= 662.22 \text{ g mol}^{-1}. \end{aligned}$$

Since $1 \text{ pm} = 10^{-10} \text{ cm}$, the cell volume, retaining unrounded lattice parameters, is

$$V = a^2 c = 1.8570673 \times 10^{-22} \text{ cm}^3.$$

With one formula unit per cell,

$$\rho = \frac{ZM}{N_A V} = \frac{662.22}{(6.02214076 \times 10^{23})(1.8570673 \times 10^{-22})} \text{ g cm}^{-3}.$$

Hence

$$\boxed{\rho = 5.92 \text{ g cm}^{-3}}.$$

Species names and SMILES for parts 4.4–4.9

The following representations apply to every occurrence of these species in the equations.

Species	Name	SMILES
H^+	Proton	[H+]
Y^{3+}	Yttrium(III) ion	[Y+3]
Ba^{2+}	Barium(II) ion	[Ba+2]
Cu^{2+}	Copper(II) ion	[Cu+2]
Cu^+	Copper(I) ion	[Cu+]
I^-	Iodide ion	[I-]
I_2	Molecular iodine	II
I_3^-	Triiodide ion	I [I-] I
H_2O	Water	O
O_2	Dioxygen	O=O
CuI	Copper(I) iodide, ionic formula unit	[Cu+] . [I-]
$\text{S}_2\text{O}_3^{2-}$	Thiosulfate ion	[O-] S(=O) (=O) [S-]
$\text{S}_4\text{O}_6^{2-}$	Tetrathionate ion	[O-] S(=O) (=O) SSS(=O) (=O) [O-]

Triiodide is linear; its SMILES is a formal connectivity representation and does not describe its three-centre bonding. The copper(I) iodide representation does not encode the extended solid lattice. The sulfur oxyanion SMILES show individual resonance representations.

4.4 — Dissolution in acid with oxygen evolution

Using formal oxidation states +3 for yttrium, +2 for barium and −2 for oxygen, charge neutrality gives

$$3 + 2(2) + 3\bar{v}_{\text{Cu}} - 2(7 - \delta) = 0.$$

Consequently,

$$3\bar{v}_{\text{Cu}} = 7 - 2\delta.$$

After dissolution in acid, the three copper atoms are present as copper(II), with total oxidation number 6. Their reduction therefore consumes

$$(7 - 2\delta) - 6 = 1 - 2\delta$$

electrons per formula unit.

Oxidation of lattice oxygen from oxidation state −2 to dioxygen supplies four electrons per molecule of O_2 . Thus the oxygen yield is

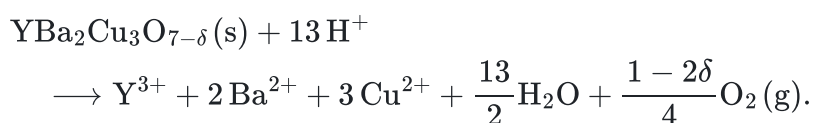
$$\frac{1 - 2\delta}{4}$$

molecules per formula unit.

The dissolved cations have total charge

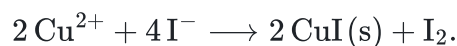
$$3 + 2(2) + 3(2) = 13,$$

so 13 protons are required. Balancing hydrogen and oxygen gives

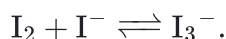


4.5 — Reaction of dissolved copper with iodide

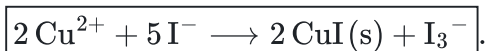
Copper(II) oxidizes iodide to iodine while being reduced to copper(I), which precipitates as copper(I) iodide:



In excess iodide,



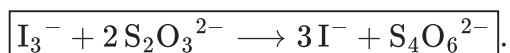
Adding these equations gives



Thus two moles of copper produce one mole of triiodide. Removing dissolved oxygen beforehand prevents it from producing additional iodine.

4.6 — Titration with thiosulfate

Thiosulfate reduces triiodide to iodide and is oxidized to tetrathionate:



One mole of triiodide therefore consumes two moles of thiosulfate.

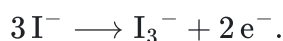
4.7 — Direct dissolution in acid containing iodide

Here iodide supplies the electrons needed to reduce all copper to copper(I). The total copper oxidation number decreases from $7 - 2\delta$ to 3, requiring

$$(7 - 2\delta) - 3 = 4 - 2\delta$$

electrons per formula unit.

Formation of one triiodide ion releases two electrons:



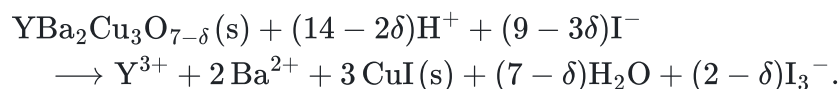
Therefore, each formula unit produces

$$\frac{4 - 2\delta}{2} = 2 - \delta$$

triiodide ions. Three additional iodide ions enter the three formula units of copper(I) iodide, so the total iodide requirement is

$$3 + 3(2 - \delta) = 9 - 3\delta.$$

All $7 - \delta$ oxygen atoms become water, requiring $14 - 2\delta$ protons. The balanced equation is



Iodide oxidation accounts for the electron transfer, consistent with the absence of oxygen evolution.

4.8 — Amount of copper

In the first procedure, all copper becomes copper(II) before iodide is added. Combining the stoichiometries of 4.5 and 4.6,



Hence the mole ratio of copper to thiosulfate is 1 : 1:

$$n(\text{Cu}) = 1.542 \times 10^{-4} \text{ mol}.$$

The samples are identical, so

$$n(\text{Cu}) = 1.542 \times 10^{-4} \text{ mol in each sample}.$$

The corresponding amount of YBCO formula units in each sample is

$$n_0 = \frac{n(\text{Cu})}{3} = \frac{1.542 \times 10^{-4}}{3} = 5.140 \times 10^{-5} \text{ mol.}$$

4.9 — Oxygen deficiency

The direct-dissolution procedure produces $2 - \delta$ moles of triiodide per mole of YBCO. Each mole of triiodide consumes two moles of thiosulfate, giving

$$n_{\text{thio},2} = (4 - 2\delta)n_0.$$

Therefore,

$$1.696 \times 10^{-4} = (4 - 2\delta)(5.140 \times 10^{-5}),$$

and

$$\begin{aligned} \delta &= \frac{1}{2} \left(4 - \frac{1.696 \times 10^{-4}}{5.140 \times 10^{-5}} \right) \\ &= 0.3501945 \dots \end{aligned}$$

Thus

$$\boxed{\delta \approx 0.350}.$$

This lies within the stated range $0 < \delta < 0.5$. The supplied acid and iodide are in excess: each procedure requires less than 7×10^{-4} mol of protons and 4.1×10^{-4} mol of iodide, compared with the supplied $4.9\text{--}5.0 \times 10^{-3}$ mol of acid and 7.0×10^{-3} mol of iodide.

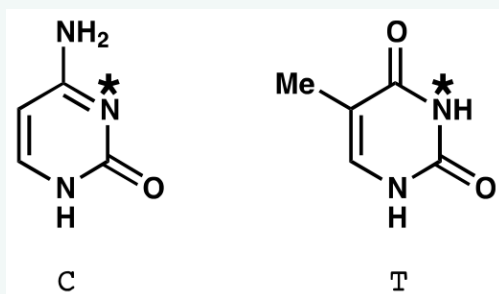
The solution was checked against the official solution.

Problem 5: Chemical modification of DNA

Deoxyribonucleic Acid (DNA) is one of the fundamental molecules of life. This question will consider ways that DNA's molecular structure may be modified, both naturally and in ways devised by humankind.

Consider the pyrimidine bases, cytosine (C) and thymine (T). The N-3 atom (indicated by *) of one of these bases is a common nucleophilic site in single strand DNA alkylation, while the other is not.

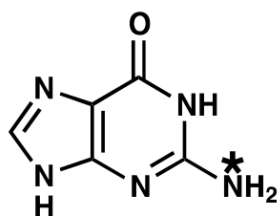
5.1 Select (circle) which base, C or T, has the more nucleophilic N-3 atom.



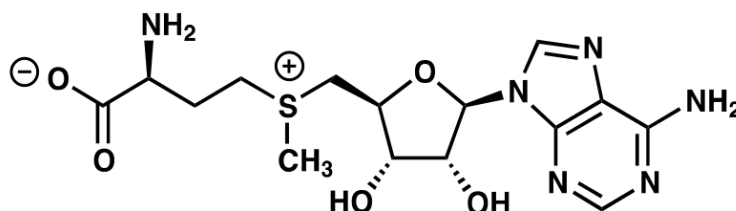
5.2. Draw two complementary resonance structures of the molecule you select to justify your answer.

One common modification of DNA in nature is methylation of the indicated (*) position of guanine (G) by S-adenosyl methionine (SAM).

5.3 Draw the structures of both of the products of the reaction between guanine and SAM.

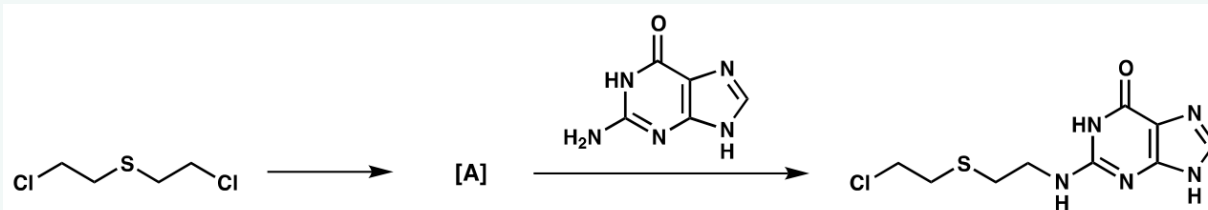


G



SAM

One of the earliest man-made DNA alkylating agents was mustard gas. Mustard gas acts by first undergoing an intramolecular reaction to form intermediate A which directly alkylates DNA, to give a nucleic acid product such as that shown in the part above.

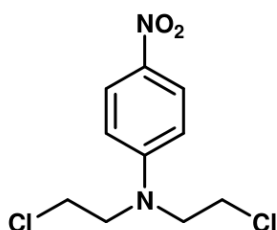


5.4 Draw the structure for reactive intermediate A.

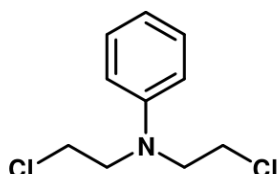
The nitrogen mustards react via an analogous pathway to the sulfur mustard of previous part. The reactivity of the compound may be modified depending on the third substituent on the nitrogen atom. The reactivity of nitrogen mustards increases with increasing nucleophilicity of the central nitrogen atom.

5.5 Select the most and least reactive from each of following groups of nitrogen mustards.

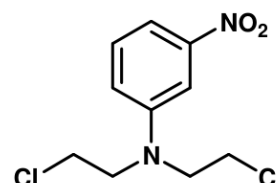
a)



I

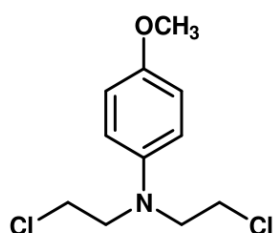


II

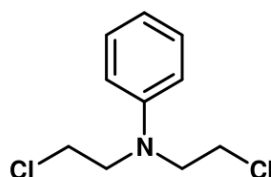


III

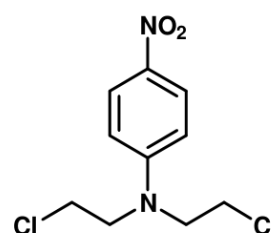
b)



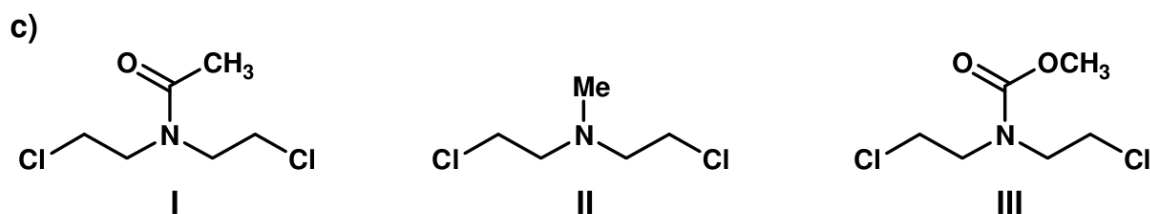
I



II

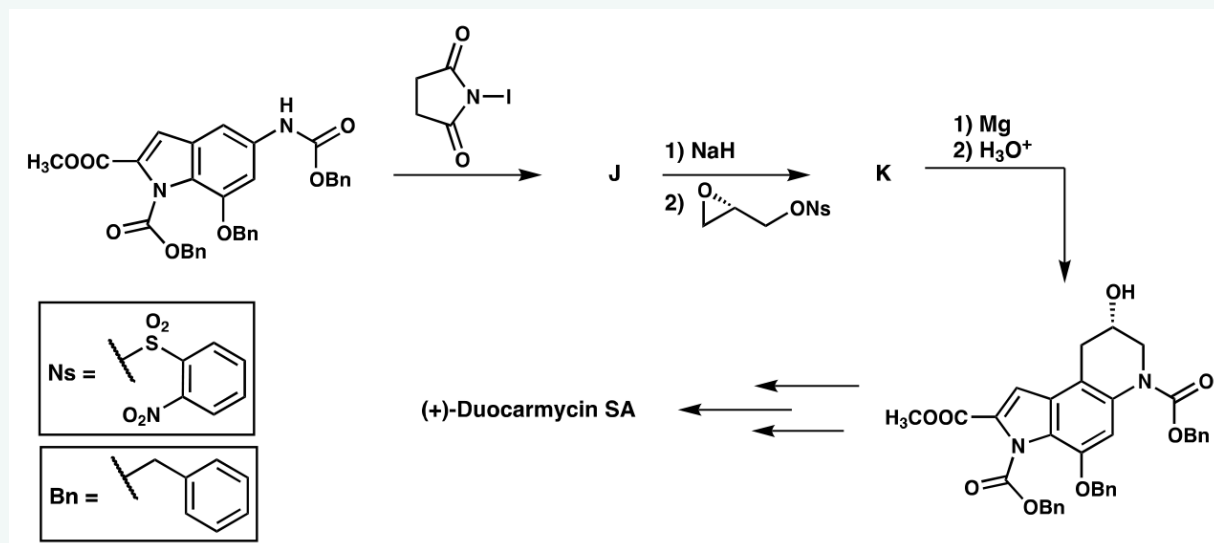


III



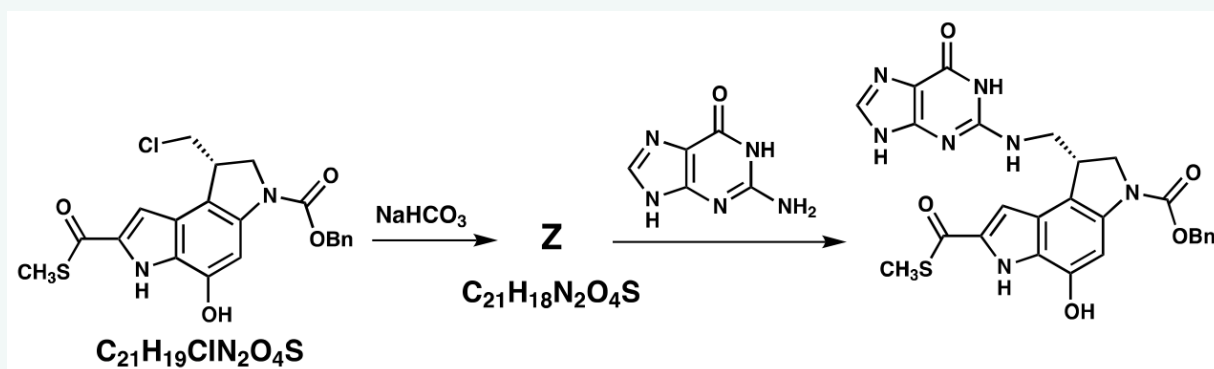
Some classes of natural products act as DNA alkylators, and in this way, they have the potential to serve as cancer therapies due to their antitumor activity. One such class is the duocarmycins. Shown below are steps from an asymmetric total synthesis of the natural product.

5.6 Draw the structures of isolable compounds J and K in the following scheme:



Related small molecules were synthesized to study the way in which the duocarmycins work. One such example is the thioester shown below.

5.7 Draw the structure of reactive intermediate Z.



Official English text of the problem.

Answers

- 5.1 — C, cytosine: NC1=NC(=O)NC=C1 .
- 5.2 — Two charge-separated resonance contributors of cytosine, supplementary to its neutral structure above:

1. Exocyclic amino nitrogen positive; N-3 negative: [NH2+]=C1[N-]C(=O)NC=C1.
2. Ring N-1 positive; N-3 negative: NC1=CC=[NH+]C(=O)[N-]1.

- **5.3 — The products are:**

***N*²-Methylguanine:** CNc1nc2[nH]cnc2c(=O)[nH]1.

S-Adenosyl-L-homocysteine (SAH), shown as its zwitterion: Nc1ncnc2c1ncn2[C@@H]1O[C@H](CSCC[C@H]([NH3+])C(=O)[O-])[C@@H](O)[C@H]1O.

- **5.4 — A is the 1-(2-chloroethyl)thiiran-1-ium ion**, a three-membered cyclic sulfonium ion: ClCC[S+]1CC1. Its counterion is chloride, [Cl-].
- **5.5 — Reactivity selections:**

Group	Most reactive	Least reactive
a	II: N,N-bis(2-chloroethyl)aniline, <chem>ClCCN(CCCl)c1ccccc1</chem>	I: N,N-bis(2-chloroethyl)-4-nitroaniline, <chem>ClCCN(CCCl)c1ccc([N+](=O)[O-])cc1</chem>
b	I: N,N-bis(2-chloroethyl)-4-methoxyaniline, <chem>COc1ccc(N(CCCl)CCl)cc1</chem>	III: N,N-bis(2-chloroethyl)-4-nitroaniline, <chem>ClCCN(CCCl)c1ccc([N+](=O)[O-])cc1</chem>
c	II: mechlorethamine, <chem>CN(CCCl)CCCl</chem>	I: N,N-bis(2-chloroethyl)acetamide, <chem>CC(=O)N(CCCl)CCCl</chem>

- **5.6 — J and K:**

J: methyl 7-benzyloxy-1-(benzyloxycarbonyl)-5-[(benzyloxycarbonyl)amino]-4-iodo-1H-indole-2-carboxylate. It is the starting compound with iodine replacing hydrogen at indole C-4.

COC(=O)c1cc2c(I)c(NC(=O)OCc3ccccc3)cc(OCc3ccccc3)c2n1C(=O)OCc1ccccc1

K: the 5-carbamate **N-[(2R)-oxiran-2-ylmethyl] derivative of J**. The aryl iodine and epoxide are both retained.

COC(=O)c1cc2c(I)c(N(C[C@@H]3CO3)C(=O)OCc3ccccc3)cc(OCc3ccccc3)c2n1C(=O)OCc1ccccc1

- **5.7 — Z:** the cyclopropane-fused cyclohexadienone thioester obtained by cyclization of the depicted seco precursor, with formula $C_{21}H_{18}N_2O_4S$.

CSC(=O)c1cc2c([nH]1)C(=O)C=C1N(C(=O)OCc3ccccc3)C[C@H]3C[C@@]213

In **Z**, the pre-existing methine stereocenter is *S*, and the newly tetrahedral carbon shared by the cyclopropane and cyclohexadienone rings is *R*.

Solution

5.1

Cytosine has the more nucleophilic N-3 atom.

In the neutral cytosine structure, N-3 is an imine-like nitrogen: its lone pair is available for bonding to an electrophile. Electron donation from the amino group and through the ring further supports electron density at this position.

In thymine, CC1=CNC(=O)NC1=O, N-3 is an imide nitrogen situated between two carbonyl groups. Its lone pair is strongly delocalized into those carbonyl groups and is consequently much less available for alkylation.

5.2

The two charge-separated contributors listed in the Answers can be obtained from neutral cytosine without moving any atoms or protons.

For the first contributor:

- Donate the exocyclic amino nitrogen's lone pair into its bond to C-4.
- Move the C-4=N-3 π -electron pair onto N-3.

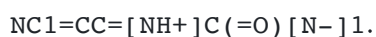
The exocyclic nitrogen becomes positively charged, and N-3 becomes negatively charged:



For the second contributor:

- Donate the N-1 lone pair to form N-1=C-6.
- Shift the C-6=C-5 electrons to form C-5=C-4.
- Shift the C-4=N-3 electrons onto N-3.

This gives:

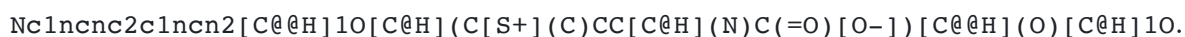


Both contributors place additional electron density at N-3. They are resonance contributors of the same molecule, not separate species or tautomers.

5.3

The marked atom is guanine's **exocyclic amino nitrogen at C-2**, not a ring nitrogen.

Guanine is Nc1nc2[nH]cnc2c(=O)[nH]1. SAM, in the protonation state drawn in the question, is:

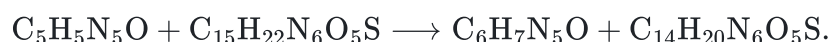


The guanine amino nitrogen attacks the methyl carbon attached to positively charged sulfur in an S_N2 displacement. The methyl-sulfur bond breaks, leaving a neutral thioether sulfur. Subsequent proton transfer gives N^2 -methylguanine and SAH.

To draw the products:

- Replace guanine's exocyclic $-\text{NH}_2$ group by $-\text{NHCH}_3$.
- Remove the sulfur-bound methyl group from SAM, leaving the adenosyl-sulfur-homocysteine linkage intact.
- Preserve all amino-acid and ribose stereochemistry.

With SAH represented as the zwitterion given in the Answers, the balanced equation is



This representation accounts for the proton lost from guanine's nitrogen: the SAH amino group is $-\text{NH}_3^+$, while its carboxylate remains negatively charged.

5.4

Sulfur mustard, or bis(2-chloroethyl) sulfide, is C1CCSCCC1.

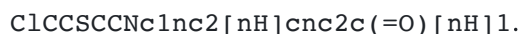
A sulfur lone pair attacks the terminal carbon of one of its own chloroethyl groups. Chloride leaves, forming a three-membered ring consisting of sulfur and the two carbon atoms of that arm. Sulfur now has three carbon-sulfur bonds and carries a positive charge.

Thus A is C1CC[S+](Cl)CC1, and its formation is balanced as



For the requested drawing, make a triangle with S^+ at one vertex and CH_2 at each of the other two vertices. Attach the remaining $-\text{CH}_2\text{CH}_2\text{Cl}$ arm to sulfur.

Guanine can attack a ring carbon, opening the strained ring. After deprotonation, this gives the depicted N^2 -{2-[(2-chloroethyl)sulfanyl]ethyl}guanine:



The overall substitution is



Hydrogen chloride has SMILES [H]Cl.

5.5

The central nitrogen must use its lone pair for intramolecular displacement of chloride. Substituents that make this lone pair more available increase reactivity; substituents that withdraw or delocalize it decrease reactivity.

(a) The order is



II has no nitro substituent. In III, the meta nitro group withdraws mainly through its inductive effect. In I, the para nitro group additionally allows strong resonance withdrawal through the aromatic ring, reducing the availability of the mustard nitrogen lone pair.

The meta compound III is **N,N-bis(2-chloroethyl)-3-nitroaniline**, C1CCN(CCC1)c1cccc([N+](=O)[O-])c1.

Therefore **II is most reactive and I least reactive**.

(b) The order is



The para methoxy group in I donates electron density by resonance, increasing nitrogen nucleophilicity. The unsubstituted compound II is intermediate. The para nitro group in III strongly withdraws electron density.

Therefore **I is most reactive and III least reactive**.

(c) The order is



II is a tertiary alkylamine, so its nitrogen lone pair is readily available.

I is an amide: the nitrogen lone pair is strongly delocalized into the adjacent carbonyl group. III is **methyl N,N-bis(2-chloroethyl)carbamate**, COC(=O)N(CCC1)CCC1. In III, the methoxy oxygen also donates into the carbonyl system, reducing the carbonyl's resonance withdrawal from nitrogen relative to I.

Therefore **II is most reactive and I least reactive**.

5.6

Use ordinary indole numbering: the methyl ester is at C-2, the protected amino group at C-5, and the benzyloxy group at C-7. Here **Cbz** denotes benzyloxycarbonyl, represented as the substituent *C(=O)OCc1ccccc1, where $*$ is the attachment point.

Formation of J. N-Iodosuccinimide, O=C1CCC(=O)N1I, effects electrophilic aromatic iodination.

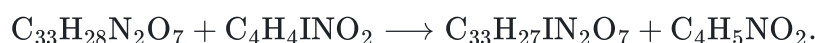
C-4 is ortho to the protected amino substituent and para to the benzyloxy substituent. It is also less crowded than C-6, which lies between those substituents. Iodination at C-4 supplies the aryl iodide required for the later ring closure.

Thus, to draw J, copy the starting structure and replace its C-4 hydrogen by iodine.

For reference, the uniodinated starting indole is:

COC(=O)c1cc2cc(NC(=O)OCc3ccccc3)cc(OCc3ccccc3)c2n1C(=O)OCc1ccccc1.

The other iodination product is **succinimide**, O=C1CCC(=O)N1. The balanced equation is

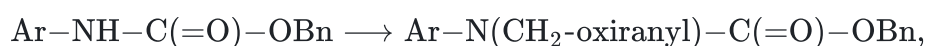


Formation of K. Sodium hydride removes the proton from the exocyclic carbamate nitrogen, releasing hydrogen. The resulting nitrogen nucleophile displaces the nosylate group from the primary carbon of the glycidyl reagent.

The reagent is **(S)-oxiran-2-ylmethyl 2-nitrobenzenesulfonate**, or **(S)-glycidyl nosylate**:

O=[N+]([O-])c1ccccc1S(=O)(=O)OC[C@H]1CO1.

The epoxide remains intact. Thus the change from J to K is precisely



with the complete connectivity and stereochemistry specified by K's SMILES in the Answers.

The displaced group forms **sodium 2-nitrobenzenesulfonate**:

[Na+].[O-]S(=O)(=O)c1ccccc1[N+](=O)[O-].

The balanced overall alkylation is



The substitution occurs at the primary carbon bearing the sulfonate, so there is no inversion at the epoxide stereocenter. Its descriptor changes from *S* in the reagent to *R* in K because replacing the oxygen-containing substituent by a nitrogen-containing substituent changes the CIP priorities.

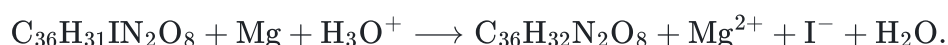
Consistency with the final cyclization. Magnesium inserts into the aryl carbon–iodine bond. The resulting carbon nucleophile attacks the less substituted epoxide carbon intramolecularly, opening the epoxide and forming a six-membered ring fused across indole C-4 and C-5. Acid workup protonates the alkoxide.

The resulting ***S*-configured cyclic secondary alcohol**, as drawn in the question, is:

COC(=O)c1cc2c(n1C(=O)OCc1ccccc1)c(OCc1ccccc1)cc1c2C[C@H](O)CN1C(=O)OCc1ccccc1.

The bond between the stereocenter and oxygen is retained throughout ring opening. Its *S* descriptor in the alcohol again reflects the changed CIP priorities.

A balanced net ionic equation for this sequence is



The small species used here are sodium hydride, [Na+].[H-]; hydrogen, [H][H]; magnesium, [Mg]; hydronium, [OH3+]; magnesium(II), [Mg+2]; iodide, [I-]; and water, O.

5.7

The starting **chloromethyl phenol, or seco thioester precursor**, is:

CSC(=O)c1cc2c([NH]1)c(O)cc1c2[C@H](Cl)CN1C(=O)OCc1ccccc1.

Use the underlying indole numbering to describe the changes. The phenolic oxygen is attached at C-7, and C-4 is para to it. Let the existing stereogenic carbon bearing the chloromethyl substituent be C^* .

Bicarbonate removes the phenolic proton. Electron donation from oxygen through the aromatic ring permits intramolecular carbon alkylation at C-4:

1. The original phenolic C-7–O bond becomes a carbonyl bond.
2. C-4 forms a new bond to the terminal carbon of the chloromethyl substituent.
3. Chloride leaves.
4. The existing C-4– C^* and C^* –methylene bonds, together with the new bond, form a cyclopropane.

Consequently, **Z is a cyclopropane-fused cyclohexadienone**, not an oxygen-cyclized ether.

To draw Z precisely:

- Replace the phenolic –OH by =O.
- Remove chlorine.
- Join the carbon that formerly bore chlorine to C-4.
- Make C-4 tetrahedral.
- In a Kekulé representation, place the cyclohexadienone double bonds at C-5=C-6 and C-3a=C-7a.
- Preserve the pre-existing stereochemistry and use the *S*, *R* configuration encoded in Z's SMILES.

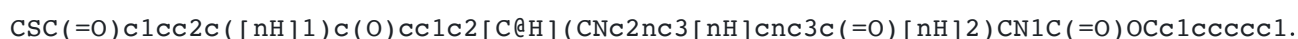
The net cyclization is



This gives exactly the molecular formula printed for Z: $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$.

The additional small species are sodium hydrogen carbonate, $[\text{Na}^+] \cdot \text{O}=\text{C}(\text{O}) [\text{O}^-]$; sodium chloride, $[\text{Na}^+] \cdot [\text{Cl}^-]$; and carbon dioxide, $\text{O}=\text{C}=\text{O}$.

Finally, guanine's exocyclic amino nitrogen attacks the less substituted cyclopropane carbon—the carbon originally bearing chlorine. Cleavage of its bond to C-4 allows the six-membered ring to regain aromaticity. Proton transfer restores the phenolic hydroxyl group and gives the depicted ***N*²-guanine adduct of the seco thioester**:



This addition is balanced without a separate coproduct:

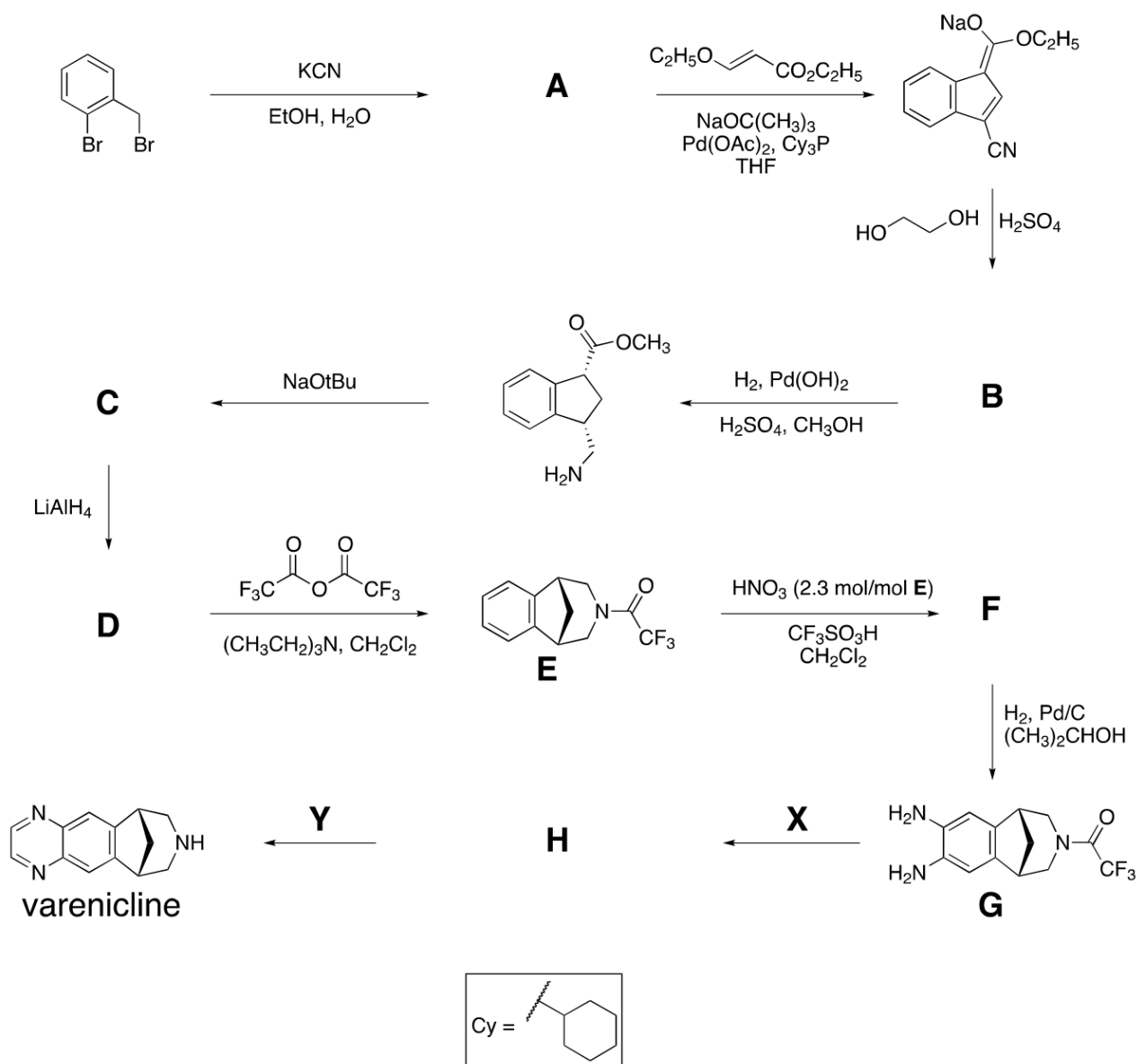


Cyclopropane strain relief and restoration of aromaticity explain why Z is the reactive alkylating intermediate.

The answers were checked against the official answers published by the organisers.

Problem 6: Synthesis of varenicline

Varenicline has been developed as an oral treatment for smoking addiction and can be synthesized by the route shown below. All compounds indicated by a letter (**A – H**) are uncharged, isolable species.

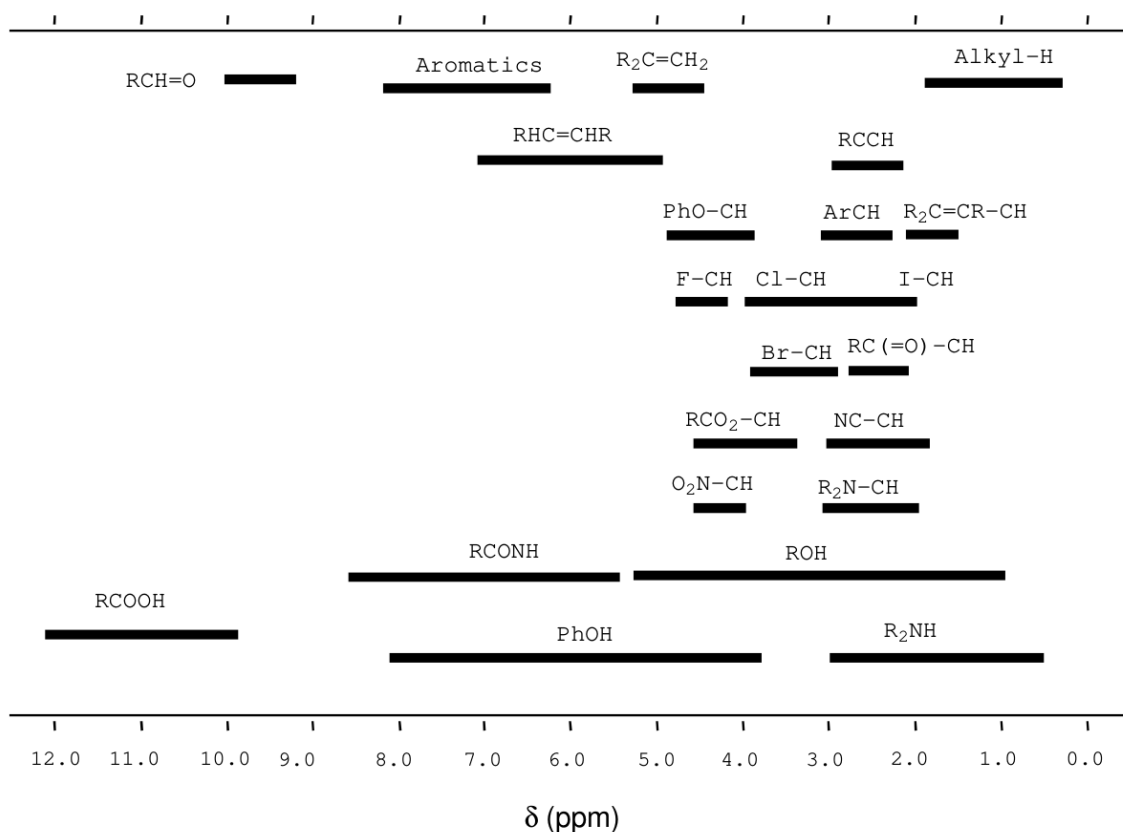


6.1 Suggest a structure for compound **A**.

6.2 Suggest a structure for compound **B** consistent with the following ^1H -NMR data:

δ 7.75 (singlet, 1H), 7.74 (doublet, 1H, $J = 7.9$ Hz), 7.50 (doublet, 1H, $J = 7.1$ Hz), 7.22 (multiplet, 2 nonequivalent H), 4.97 (triplet, 2H, $J = 7.8$ Hz), 4.85 (triplet, 2H, $J = 7.8$ Hz).

¹H NMR Chemical Shift Ranges*



6.3 Suggest a structure for compounds **C**, **D**, and **F**.

6.4 Suggest reagents **X** and **Y** to convert compound **G** into *varenicline*, and provide the isolable intermediate **H** along this route.

Official English text of the problem.

Answers

- **6.1 — A:** 2-(2-Bromophenyl)acetonitrile, N#CCc1ccccc1Br.
- **6.2 — B:** 3-(1,3-Dioxolan-2-ylidene)-3H-indene-1-carbonitrile, a cyclic ketene acetal: N#CC1=CC(=C2OCCO2)c2ccccc21.
- **6.3:**
- **C:** The **bridged lactam**, namely the **2-oxo derivative of D**: O=C1NC[C@H]2C[C@@H]1c1ccccc12.
- **D:** 2,3,4,5-Tetrahydro-1H-1,5-methano-3-benzazepine: c1ccc2c(c1)[C@H]1CNC[C@@H]2C1.
- **F:** 7,8-Dinitro-N-trifluoroacetyl-D, with adjacent nitro groups at the positions occupied by the amino groups in **G**: O=C(C(F)(F)F)N1C[C@H]2C[C@@H](C1)c1cc([N+](=O)[O-])c([N+](=O)[O-])cc12.
- **6.4:**
- **X:** Glyoxal (ethanedial), O=CC=O, for example aqueous glyoxal in ethanol.

- **H: N-Trifluoroacetylvarenicline:** O=C(C(F)(F)F)N1C[C@H]2C[C@@H](C1)c1cc3nccnc3cc12.
- **Y: Aqueous sodium hydroxide,** $[\text{Na}^+] \cdot [\text{OH}^-]$, with warming, to hydrolyse the trifluoroacetamide and isolate varenicline as its free base.

The stereochemical SMILES specify the required cis bridge arrangement. For the chiral amino ester and C, one enantiomer is represented; the achiral synthesis gives racemic material at these stages.

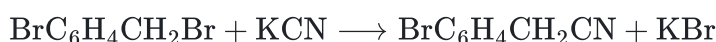
Solution

The equations below describe net transformations, with neutral organic products understood to be isolated after workup. Common species appearing in the balances are water O, methanol CO, ethanol CCO, molecular hydrogen $[\text{H}] [\text{H}]$, and the proton $[\text{H}^+]$.

6.1 — Identification of A

The starting material is **1-bromo-2-(bromomethyl)benzene**, BrCc1ccccc1Br.

Potassium cyanide, $[\text{K}^+] \cdot [\text{C}^-] \# \text{N}$, supplies a carbon nucleophile that substitutes the **benzylic** bromide by an $\text{S}_{\text{N}}2$ reaction. The unactivated aromatic carbon–bromine bond remains available for the subsequent palladium-mediated reaction.



The two substituents on the benzene ring remain ortho. Thus A is **2-(2-bromophenyl)acetonitrile**, with molecular formula $\text{C}_8\text{H}_6\text{BrN}$. The salt byproduct is potassium bromide, $[\text{K}^+] \cdot [\text{Br}^-]$.

6.2 — Identification of B

The intermediate drawn immediately before B is the **sodium enolate of ethyl 3-cyano-1H-indene-1-carboxylate**:

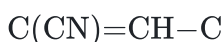


Treatment with **ethylene glycol (ethane-1,2-diol)**, OCCO, and acid incorporates both glycol oxygen atoms into a five-membered dioxolane ring. Its acetal carbon retains an **exocyclic double bond to the indene skeleton**, giving the cyclic ketene acetal B.

Omitting the sodium counterion, the balanced condensation is



To sketch B precisely, draw the benzene-fused five-membered carbocycle with the sequence



between its two benzene fusion atoms. The final carbon in this sequence has an exocyclic double bond to the carbon of a $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}^-$ ring.

The NMR data account for every hydrogen:

Observed signal	Assignment in B
$\delta 7.75$, singlet, 1H	The five-membered ring's vinylic CH; neither adjacent ring carbon bears hydrogen
$\delta 7.74$, doublet, 1H, and 7.50 , doublet, 1H	Two benzene-ring hydrogens, each with a dominant ortho coupling
$\delta 7.22$, multiplet, 2 nonequivalent H	The remaining two benzene-ring hydrogens

Observed signal	Assignment in B
δ 4.97 and 4.85, triplets, 2H each	The two distinct OCH_2 groups of the dioxolane ring

The two glycol methylene groups occupy different environments relative to the unsymmetrical indene fragment. Each couples to the two hydrogens of the neighboring methylene group, consistent with the matching $J = 7.8$ Hz triplets.

The total integration is

$$1 + 1 + 1 + 2 + 2 + 2 = 9 \text{ hydrogens,}$$

consistent with $\text{C}_{13}\text{H}_9\text{NO}_2$.

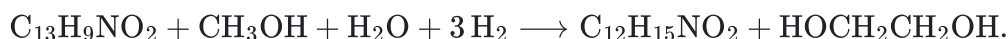
6.3 — Identification of C, D, and F

Formation of the amino ester shown before C. Acidic methanol converts B's cyclic ketene acetal into a methyl ester. Hydrogenation reduces the remaining carbocyclic double bond and converts the nitrile into an aminomethyl group.

The displayed product is **methyl cis-3-(aminomethyl)indane-1-carboxylate**:

COC(=O)[C@H]1C[C@H](CN)C2CCCC21

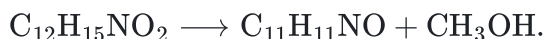
The net balance is



One equivalent of hydrogen reduces the ring double bond, and two equivalents reduce the nitrile.

C: intramolecular lactam formation. The ester and aminomethyl substituents are **cis**, as indicated by their dashed bonds in the problem. This places them suitably for cyclization.

Sodium tert-butoxide, CC(C)(C)[O-].[Na+], promotes intramolecular aminolysis of the methyl ester. The amino nitrogen bonds to the ester carbonyl carbon, and methanol is eliminated:



C therefore contains a six-membered lactam ring. To draw it, retain the indane skeleton and connect its two substituted benzylic carbons through



The existing one-carbon bridge between those benzylic carbons remains intact. This gives the bridged lactam specified in the Answers.

D: reduction of the lactam. Lithium aluminium hydride, [Li+].[AlH4-], reduces the amide carbonyl to a methylene group while preserving the carbon–nitrogen framework:



Here $[\text{H}]$ denotes a formal reducing hydrogen equivalent supplied by the reduction and workup.

Thus the bridge



becomes



giving the secondary amine D.

F: aromatic dinitration. The next displayed compound, E, is **N-trifluoroacetyl-D**:

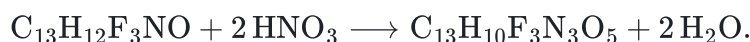
O=C(C(F)(F)F)N1C[C@H]2C[C@H](C1)C3CCCC32

Its subsequent hydrogenation product, **G**, is **7,8-diamino-N-trifluoroacetyl-D**:



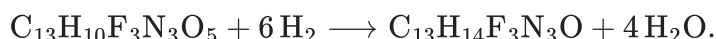
Catalytic hydrogenation converts aromatic nitro groups into amino groups. Consequently, **F** must contain **two adjacent nitro groups at exactly the aromatic positions bearing amino groups in G**: positions 7 and 8 of the benzazepine parent.

The nitration with nitric acid, $\text{O}=[\text{N}^+](\text{O}^-)\text{O}$, has the balance



The supplied 2.3 mol of nitric acid per mole of **E** is consistent with this two-equivalent requirement.

Reduction of **F** then gives the depicted **G**:

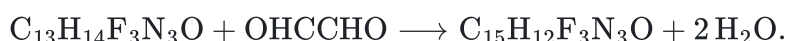


For the drawing of **F**, retain **E**'s entire bridged framework and its *N*-trifluoroacetyl group, and place NO_2 groups on the two adjacent aromatic carbons opposite the fused saturated ring.

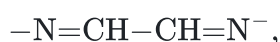
6.4 — Reagents X and Y, and intermediate H

X: construct the quinoxaline ring with glyoxal.

G contains an **ortho aromatic diamine**. Each amino group condenses with one aldehyde group of glyoxal, producing two imine bonds and eliminating two water molecules:



The two nitrogen atoms and glyoxal's two carbon atoms complete the new six-membered aromatic ring. In a drawing, the two adjacent amino substituents become the ring path



whose ends remain attached to the adjacent benzene carbons.

The bridged nitrogen retains its trifluoroacetyl protecting group, so the isolable product **H** is **N-trifluoroacetylvarenicline**.

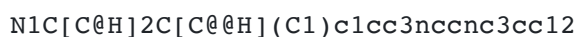
Y: remove the trifluoroacetyl group.

Aqueous sodium hydroxide hydrolyses the activated trifluoroacetamide, restoring the secondary amine:



The coproduct is **sodium trifluoroacetate**, $\text{O}=\text{C}(\text{O}^-)\text{C}(\text{F})(\text{F})\text{F} \cdot [\text{Na}^+]$.

The resulting **varenicline** is



and has molecular formula $\text{C}_{13}\text{H}_{13}\text{N}_3$, consistent with the final structure in the problem.

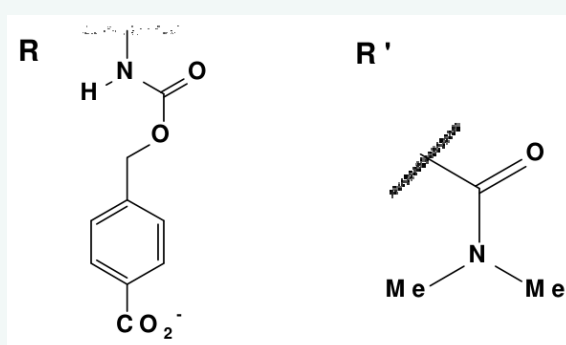
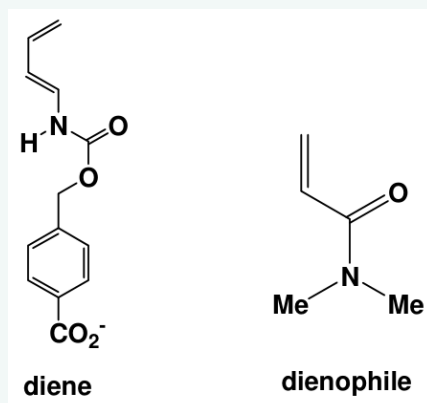
The answers were checked against the official answers published by the organisers.

Problem 7: An artificial enzyme for a Diels–Alder reaction

An artificial enzyme was designed to bind the two substrate molecules shown below (diene and dienophile) and catalyze a Diels–Alder reaction between them.

a. There are eight potential products from a Diels–Alder reaction involving these two molecules in the reaction without any enzyme.

7.1 Draw the structures of any two of the potential products that are **regioisomers** of each other, in the boxes that are given below. Use wedges ($\blacktriangleleft$) and dashes ($\cdots$) to show the stereochemistry of each product in your drawings. Use **R** and **R'** shown below to represent the substituents in the molecules that are not directly involved in the reaction.



7.2 Draw the structures of any two of the potential products that are **enantiomers** of each other, in the boxes that are given below. Use wedges ($\blacktriangleleft$) and dashes ($\cdots$) to show the stereochemistry of each product in your drawings. Use **R** and **R'** as in part (7.1).

7.3 Draw the structures of any two of the potential products that are **diastereomers** of each other, in the boxes that are given below. Use wedges ($\blacktriangleleft$) and dashes ($\cdots$) to show the stereochemistry of each product in your drawings. Use **R** and **R'** as in part (7.1).

b. The rate and regioselectivity of a Diels-Alder reaction depend on the degree of electronic complementarity between the two reactants. The structures of the diene and the dienophile from part **a** are given below.

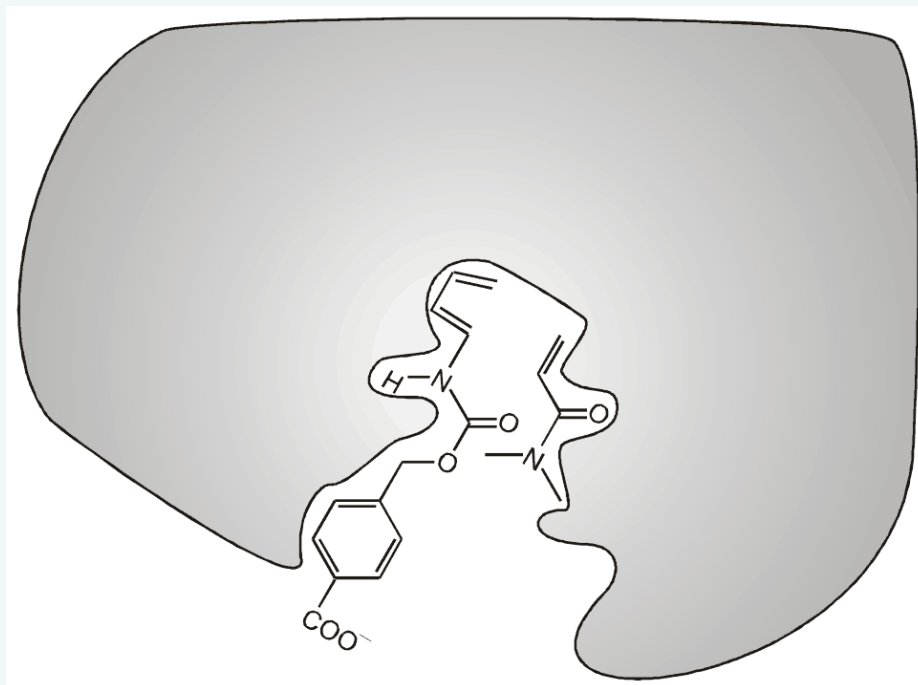
7.4 Circle the carbon atom in the diene that has increased electron density and therefore can act as an electron donor during the reaction. Draw one resonance structure of the diene in the box to support your answer. Indicate all non-zero formal charges on the atoms in the resonance structure that you draw.

7.5 Circle the carbon atom in the dienophile that has decreased electron density and therefore can act as an electron acceptor during the reaction. Draw one resonance structure of the dienophile in the box to support your answer. Indicate all non-zero formal charges on the atoms in the resonance structure that you draw.

7.6 Based on your assignments in parts (7.4) and (7.5), predict the regiochemistry of the uncatalyzed Diels-Alder reaction of the diene and dienophile by drawing the major product. You need not show the stereochemistry of the product in your drawing.

c. The figure below shows the Diels-Alder reactants as they are bound before they enter the transition state for product formation in the active site of the artificial enzyme. The gray area represents a cross-section through the enzyme. The dienophile is **below** the cross-section plane whereas the diene is **above** the cross-section plane, when the two molecules are bound in the active site that is shown.

7.7 Draw the structure of the product of the enzyme-catalyzed reaction in the box given below. Show the stereochemistry of the product in your drawing and use **R** and **R'** as you did for question a.



d. Consider the following statements about enzymes (artificial or natural). For each statement, indicate whether that statement is True or False (draw a circle around "True" or "False").

7.8 Enzymes bind more tightly to the transition state than to the reactants or products of the reaction.

True False

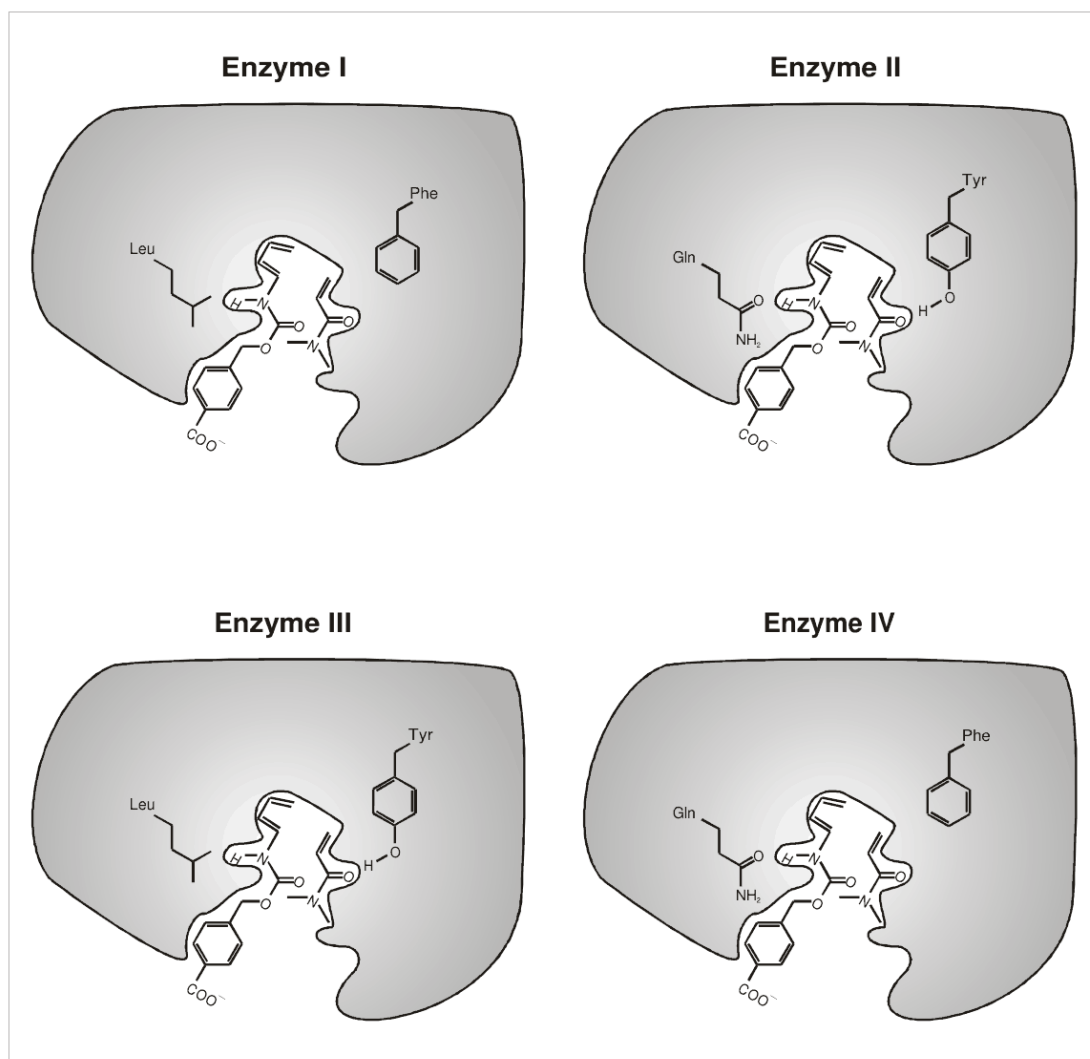
7.9 Enzymes alter the equilibrium constant of the reaction to favour the product.

True False

7.10 Enzymatic catalysis always increases the entropy of activation of the reaction compared to the uncatalyzed reaction.

True False

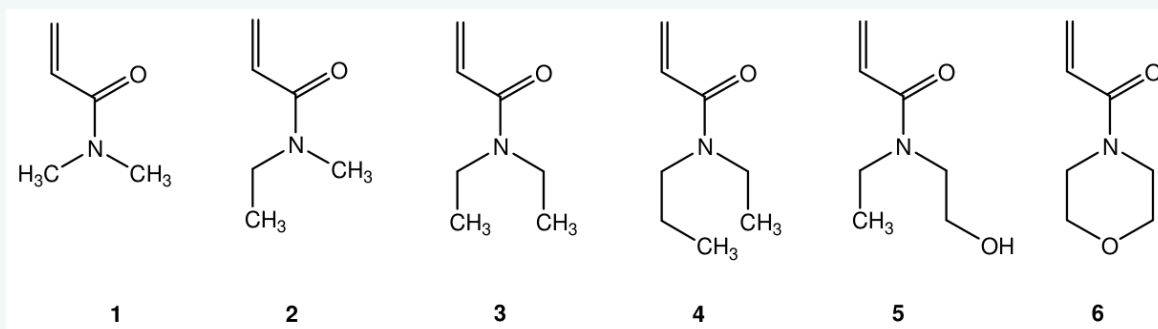
e. Modified versions of the artificial enzymes with different catalytic activities were prepared (enzymes I, II, III, and IV, shown in the figure below).



Two amino acid residues that differ among the different enzymes are shown. Assume that the enzyme functional groups shown are located in close proximity to the matching fragments of the reagents when they form the transition state in the enzyme active site.

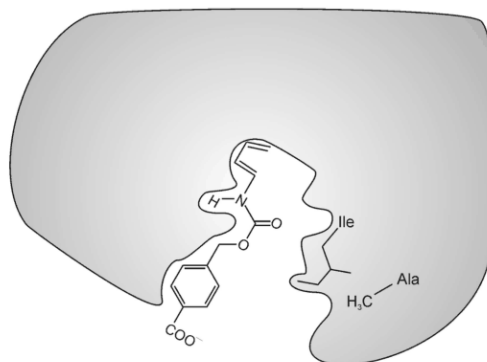
7.11 Of these four enzymes which one would cause the greatest increase in the rate of the Diels-Alder reaction compared to the uncatalyzed reaction?

f. The substrate specificity of the artificial enzymes **V** and **VI** (see below) was tested by using the dienophile reactants **1 - 6**, shown below.

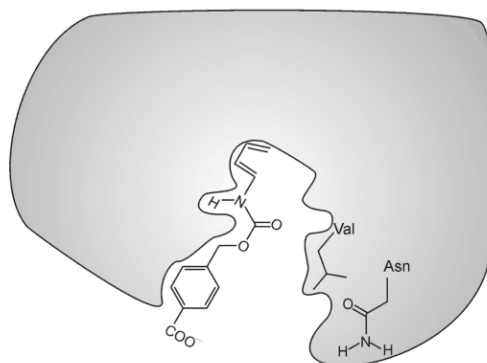


7.12 Dienophile **#1** reacted most rapidly in the reaction catalyzed by artificial **enzyme V** (see below). However, artificial **enzyme VI** catalyzed the reaction most rapidly with a different dienophile. Of the six dienophiles shown above, which one would react most rapidly in the Diels-Alder reaction catalyzed by **enzyme VI**?

Enzyme V



Enzyme VI



Official English text of the problem.

Answers

The substituents retain their definitions from the problem:

- ***R***: [(4-carboxylatobenzyl)oxycarbonyl]amino, fragment SMILES [*]NC(=O)OCc1ccc(C(=O)[O-])cc1.
- ***R'***: ***N,N***-dimethylcarbamoyl, fragment SMILES [*]C(=O)N(C)C.

Here [*] denotes attachment to the rest of the structure. Product names below use these fully specified substituents; all product SMILES expand them explicitly. Number the cyclohexene ring with its double bond at C1=C2 and *R* at C3.

- **7.1:** One suitable pair of regioisomers is:

A: cis-(3*R*,4*S*)-3-*R*-4-*R'*-cyclohex-1-ene:



B: cis-(3*S*,5*S*)-3-*R*-5-*R'*-cyclohex-1-ene:



- **7.2:** **A** and its enantiomer **$\bar{A}$** , cis-(3*S*,4*R*)-3-*R*-4-*R'*-cyclohex-1-ene:
C1=C[C@H](NC(=O)OCc2ccc(C(=O)[O-])cc2)[C@H](C(=O)N(C)C)CC1
- **7.3:** **A** and **T**, trans-(3*R*,4*R*)-3-*R*-4-*R'*-cyclohex-1-ene:
C1=C[C@@H](NC(=O)OCc2ccc(C(=O)[O-])cc2)[C@H](C(=O)N(C)C)CC1

- **7.4:** Circle the diene's **terminal CH₂ carbon farthest from nitrogen**. A supporting charge-separated resonance contributor of the diene is:
[CH2-]C=CC=[NH+]C(=O)OCc1ccc(C(=O)[O-])cc1
- **7.5:** Circle the dienophile's **terminal CH₂ carbon**, the carbon β to its carbonyl. A supporting charge-separated resonance contributor of N,N-dimethylprop-2-enamide is:
[CH2+]C=C([O-])N(C)C
- **7.6:** The major connectivity is **3-*R*-4-*R'*-cyclohex-1-ene**, with adjacent substituents; stereochemistry is unspecified:
C1=CC(NC(=O)OCc2ccc(C(=O)[O-])cc2)C(C(=O)N(C)C)CC1
- **7.7:** **T**, trans-(3*R*,4*R*)-3-*R*-4-*R'*-cyclohex-1-ene:
C1=C[C@H](NC(=O)OCc2ccc(C(=O)[O-])cc2)[C@H](C(=O)N(C)C)CC1
- **7.8: True.**
- **7.9: False.**
- **7.10: False.**
- **7.11: Enzyme II.**
- **7.12: Dienophile 5**, N-ethyl-N-(2-hydroxyethyl)prop-2-enamide:
C=CC(=O)N(CC)CCO

Solution

The starting diene is **(4-carboxylatobenzyl) N-[(1*E*)-buta-1,3-dien-1-yl]carbamate**, C=C/C=C/NC(=O)OCc1ccc(C(=O)[O-])cc1. The dienophile is **N,N-dimethylprop-2-enamide**, also called N,N-dimethylacrylamide, C=CC(=O)N(C)C.

Label the diene carbons D1–D4, starting at the end bonded to nitrogen. Thus its backbone is *R*–D1=D2–D3=D4. Label the dienophile's carbonyl-adjacent alkene carbon α , and its terminal alkene carbon β .

Cycloaddition forms two carbon–carbon single bonds, leaves D2=D3 as the ring double bond, and eliminates no atoms. Its balanced molecular equation is



For all product drawing instructions below, draw the hexagon with **C1 upper left, C2 left, C3 lower left, C4 lower right, C5 right, and C6 upper right**. Put the double bond between C1 and C2. A solid wedge points toward the viewer; a hashed wedge points away.

7.1 — Regioisomers

There are two possible orientations for joining the unsymmetrical reactants:

New bonds	Positions of substituents in the product
D1– α and D4– β	<i>R</i> at C3 and <i>R'</i> at C4
D1– β and D4– α	<i>R</i> at C3 and <i>R'</i> at C5

These give different connectivities and therefore regioisomers.

Draw **A** with *R* at C3 and *R'* at C4, both on **hashed wedges**. Draw **B** with *R* at C3 and *R'* at C5, again both on **hashed wedges**. At each stereocenter, the implicit hydrogen points toward the viewer.

In full, the first product's structural name is **(3R,4S)-3-[[4-carboxylatobenzyl]oxycarbonyl]amino}-4-(N,N-dimethylcarbamoyle)cyclohex-1-ene**; the second is the corresponding **(3S,5S)-5-(N,N-dimethylcarbamoyle)** regioisomer. Their full SMILES are given in the answers.

Each connectivity has two stereogenic centers and four configurations. There is no meso form, so the total number is

$$2 \text{ connectivities} \times 4 \text{ stereoisomers} = 8.$$

7.2 — Enantiomers

Enantiomers have identical connectivity and opposite configurations at every stereogenic center.

Use **A**, with both substituents on hashed wedges, and **$\bar{A}$** , with both substituents on solid wedges:

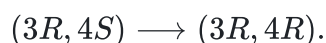


These structures are nonsuperimposable mirror images. The implicit hydrogen at each center is opposite its displayed substituent.

7.3 — Diastereomers

Use **A** and **T**. Both have *R* at C3 and *R'* at C4.

Keep the C3–*R* bond on a hashed wedge in both drawings. Change only the C4–*R'* bond from a hashed wedge in **A** to a solid wedge in **T**:



Thus **A** is cis and **T** is trans. They have the same connectivity but are not mirror images, so they are diastereomers.

7.4 — Electron-rich carbon of the diene

The nitrogen lone pair can donate into the conjugated diene. Draw the supporting resonance contributor by making these changes simultaneously:

1. Convert the N–D1 bond into an N=D1 double bond.
2. Move the D1=D2 π electrons to form D2=D3.
3. Move the D3=D4 π electrons onto D4.

The resulting bond sequence is N=D1–D2=D3–D4. Nitrogen has formal charge +1, and terminal D4 has formal charge –1.

The complete resonance contributor is:

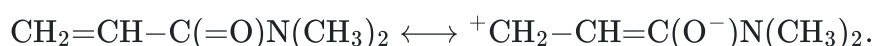


The pre-existing carboxylate oxygen must also retain its formal charge –1. Thus the complete structure contains **three nonzero formal charges**, and its net charge remains –1.

This contributor identifies **D4, the terminal carbon remote from nitrogen**, as the electron-rich reacting terminus.

7.5 — Electron-poor carbon of the dienophile

Conjugation with the carbonyl withdraws electron density from the terminal alkene carbon:



To draw this contributor, move the alkene π electrons toward the bond between the α carbon and the carbonyl carbon, and move the carbonyl π electrons onto oxygen.

The resulting contributor, $[\text{CH}_2^+]\text{C}=\text{C}([\text{O}^-])\text{N}(\text{C})\text{C}$, has formal charge +1 on the terminal β carbon and -1 on oxygen. Its overall charge is zero.

Therefore, circle the **terminal β -CH₂ carbon**.

7.6 — Uncatalyzed regioselectivity

The electron-rich diene terminus D4 preferentially bonds to the electron-poor dienophile terminus β . Ring closure then makes the second bond between D1 and α .

Since R is attached to D1 and R' to α , the two substituents become **adjacent**.

Draw a cyclohex-1-ene ring with R at C3 and R' at C4, using ordinary bonds without specifying stereochemistry. This is the constitutional product named and encoded in answer 7.6.

7.7 — Product selected by the enzyme

The binding diagram aligns D1 with α and D4 with β , giving the same adjacent-substituent connectivity.

The specified depth ordering also fixes the reacting faces: the dienophile approaches the diene from **below** its plane. Preserving the substituent orientations shown in the figure gives, in the product drawing convention defined above:

- C3- R : **hashed wedge**, away from the viewer.
- C4- R' : **solid wedge**, toward the viewer.

Consequently, the substituents are **trans**, and the product is **T**, trans-(3*R*,4*R*)-3- R -4- R' -cyclohex-1-ene.

The CIP priorities are:

At C3: N of R > C4 path > C2 path > H,

At C4: carbonyl C of R' > C3 path > C5 path > H.

These priorities give the stated (3*R*,4*R*) configuration and the stereochemical SMILES in answer 7.7.

7.8 — Transition-state binding

True. Preferential stabilization of the transition state relative to the reactants lowers the activation free energy. This is the basis of the transition-state binding description of enzyme catalysis.

7.9 — Equilibrium constant

False. An enzyme changes reaction rates, but it does not change the standard reaction Gibbs energy or the equilibrium constant:

$$K = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right).$$

It accelerates equilibration in both directions without shifting the equilibrium composition.

7.10 — Activation entropy

False. Catalysis requires a lower activation free energy, not necessarily a larger activation entropy:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger.$$

Preorganization can reduce an entropic penalty, but favorable enthalpic interactions can also account for acceleration. There is no requirement that $\Delta S^\ddagger$ always increase.

7.11 — Most effective enzyme

Enzyme II supplies both complementary hydrogen-bonding interactions.

Its **glutamine residue**, side-chain fragment $[*]CCC(=O)N$, presents a carbonyl oxygen that accepts a hydrogen bond from the diene's N–H group. This interaction supports the nitrogen's electron-donating role and stabilizes the developing positive character represented by the diene resonance contributor.

Its **tyrosine residue**, side-chain fragment $[*]Cc1ccc(O)cc1$, donates a hydrogen bond from its phenolic O–H group to the dienophile's carbonyl oxygen. This interaction increases dienophile polarization and stabilizes developing negative character on oxygen.

Here the side-chain wildcard denotes attachment to the protein backbone.

Enzyme II therefore combines activation of both reaction partners. Enzyme III supplies the tyrosine interaction, enzyme IV supplies the glutamine interaction, and enzyme I supplies neither of these two polar contacts.

7.12 — Substrate preferred by enzyme VI

The preferred substrate is **dienophile 5**, N-ethyl-N-(2-hydroxyethyl)prop-2-enamide, $C=CC(=O)N(CC)CCO$.

Two changes in the binding pocket explain this choice:

- **Isoleucine → valine**: the side-chain fragments change from $[*]C(C)CC$ to $[*]C(C)C$. The smaller valine side chain provides additional space for a larger substrate substituent.
- **Alanine → asparagine**: the side-chain fragments change from $[*]C$ to $[*]CC(=O)N$. The pocket-facing asparagine carbonyl oxygen provides a hydrogen-bond acceptor.

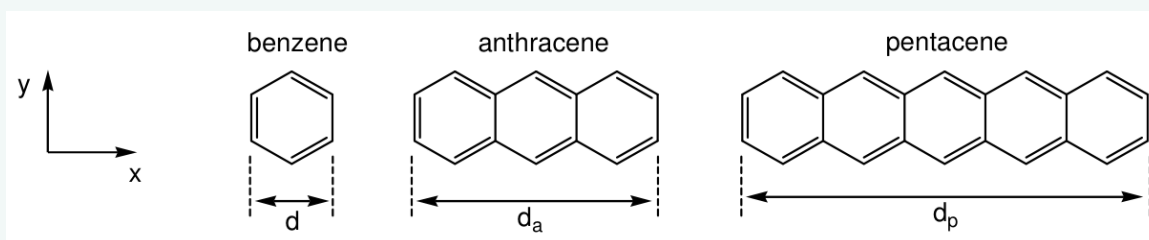
Dienophile 5 combines larger N-substituents with a terminal hydroxyl group positioned to **donate a hydrogen bond to the asparagine carbonyl oxygen**.

The distinction from dienophile 6 is significant: **N-acryloylmorpholine**, $C=CC(=O)N1CCOCC1$, has an ether oxygen but no hydroxyl hydrogen. It cannot donate the same hydrogen bond to the pocket-facing carbonyl oxygen.

The answers were checked against the official answers published by the organisers.

Problem 8: Linear polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are atmospheric pollutants, components of organic light emitting diodes and components of the interstellar medium. This problem deals with so-called linear PAHs, i.e., those being just one benzene ring wide whereas the length is varied. Specific examples are benzene, anthracene and pentacene whose structures are shown below. Their physical and chemical properties depend on the extent to which the π electron cloud is delocalized over the molecule.



8.1 The distance across the benzene ring is $d = 240$ pm. Use this information to estimate the distances along the horizontal (x) axis for anthracene and pentacene, d_a and d_p , respectively.

Assume for simplicity that the π electrons of benzene can be modelled as being confined to a square. Within this model, the conjugated π electrons of PAHs may be considered as free particles in a two dimensional rectangular box in the x - y plane.

For electrons in a two-dimensional box along the x - and y -axes, the quantized energy states of the electrons are given by

$$E = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right) \frac{h^2}{8m_e}$$

In this equation, n_x and n_y are the quantum numbers for the energy state and are integers between 1 and ∞ , h is Planck's constant, m_e is the mass of the electron and L_x and L_y are the dimensions of the box.

For this problem, treat the π electrons of the PAHs as particles in a two dimensional box. In this case, the quantum numbers n_x and n_y are independent.

8.2 Assume that the benzene unit has x and y dimensions that are each of length d . Derive a general formula for the quantized energies of linear PAHs as a function of quantum numbers n_x and n_y , the length d , the number of fused rings w , and the fundamental constants h and m_e .

The energy level diagram below for pentacene shows qualitatively the energies and quantum numbers n_x, n_y , for all levels occupied by π electrons and the lowest unoccupied energy level, with the electrons of opposite spins represented as the arrows pointing up or down. The levels are labelled with quantum numbers $(n_x; n_y)$.

Pentacene:

—	(3; 2)
↑↓	(9; 1)
↑↓	(2; 2)
↑↓	(1; 2)
↑↓	(8; 1)
↑↓	(7; 1)
↑↓	(6; 1)
↑↓	(5; 1)
↑↓	(4; 1)
↑↓	(3; 1)
↑↓	(2; 1)
↑↓	(1; 1)

8.3 The energy level diagram for anthracene is shown below. Note that some energy levels may have the same energy. Draw the correct number of up and down arrows to represent the π electrons in this diagram. Also, the blanks in parentheses within this diagram are the quantum numbers n_x, n_y , which you need to determine. Fill these blanks with the pertinent values of n_x, n_y for each filled and the lowest unfilled energy level(s).

Anthracene:

— (;)
 — (;) — (;)
 — (;)
 — (;)
 — (;)
 — (;)
 — (;)
 — (;)
 — (;)

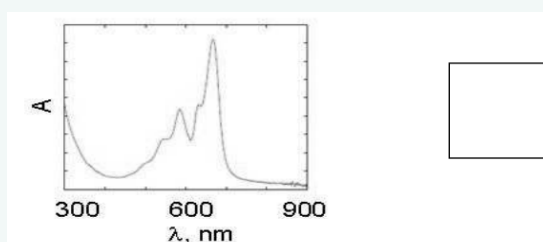
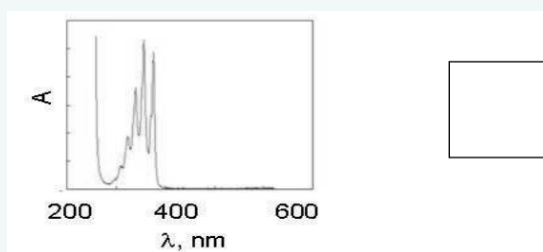
8.4 Use this model to create an energy level diagram for benzene and fill the pertinent energy levels with electrons. Include energy levels up to an including the lowest unoccupied energy level. Label each energy level in your diagrams with the corresponding n_x, n_y . Do not assume that the particle-in-a-square-box model used here gives the same energy levels as other models.

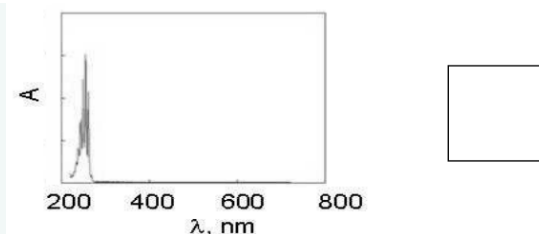
Often the reactivity of PAHs correlates inversely with the energy gap ΔE between the highest energy level occupied by π electrons and the lowest unoccupied energy level.

8.5 Calculate the energy gap ΔE (in joules) between the highest occupied and lowest unoccupied energy levels for benzene, anthracene and pentacene. Use your result from parts 8.3 and 8.4 for anthracene or benzene, respectively, or use (2, 2) for the highest occupied energy level and (3, 2) for the lowest unoccupied energy level for these two molecules (these may not be the true values).

8.6 Rank benzene (B), anthracene (A), and pentacene (P) in order of increasing reactivity by placing the corresponding letters from left to right in the box below.

8.7 The electronic absorption spectra (molar absorptivity vs. wavelength) for anthracene (A), benzene (B), and pentacene (P) are shown below. Based on a qualitative understanding of the particle in the box model, indicate which molecule corresponds to which spectrum by writing the appropriate letter in the box to its right.

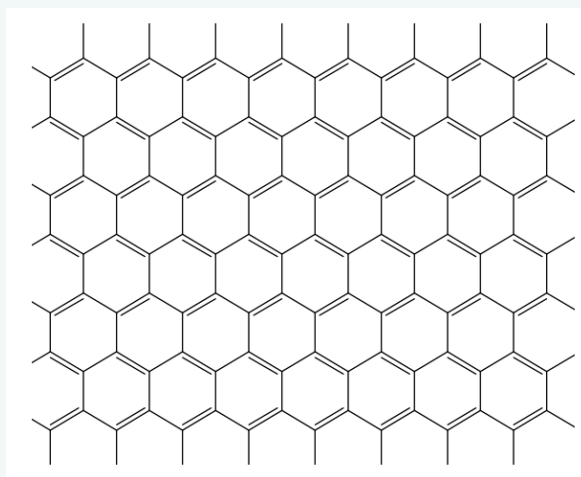




Graphene is a sheet of carbon atoms arranged in a two-dimensional honeycomb pattern. It can be considered as an extreme case of a polyaromatic hydrocarbon with essentially infinite length in the two dimensions. The Nobel Prize for Physics was awarded in 2010 to Andrei Geim and Konstantin Novoselov for groundbreaking experiments on graphene.

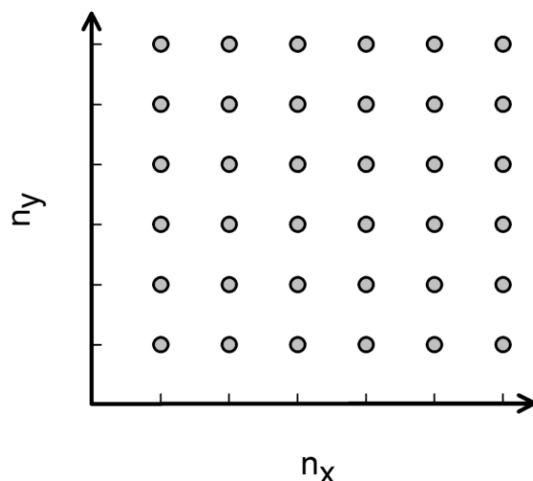
Consider a sheet of graphene with planar dimensions of $L_x = 25 \text{ nm}$ by $L_y = 25 \text{ nm}$. A section of this sheet is shown below. The area of one hexagonal 6-carbon unit is $\sim 52\,400 \text{ pm}^2$.

8.8 Calculate the number of π electrons in a $(25 \text{ nm} \times 25 \text{ nm})$ sheet of graphene. For this problem you can ignore edge electrons (i.e. those outside the full hexagons in the picture).



We can think about the π electrons in graphene as being free electrons in a 2-dimensional box. In systems containing large numbers of electrons, there is no single highest occupied energy level. Instead, there are many states of nearly the same energy above which the remaining are empty. These highest occupied states determine the so-called Fermi level. The Fermi level in graphene consists of multiple combinations of n_x and n_y quantum numbers.

8.9 Determine the energy of the Fermi level for the $25 \text{ nm} \times 25 \text{ nm}$ square of graphene relative to the lowest filled level. The lowest filled level has a non-zero energy; however, it is negligible, and can be assumed to be zero. To solve this problem it might be helpful to represent the (n_x, n_y) quantum states as points on a 2-D grid (as shown below) and consider how the energy levels are filled with pairs of electrons. For the number of electrons use your result from part 8.8 or use a value of 1000 (this may not be the true value).



8.10 The conductivity of graphene-like materials correlates inversely with the energy gap between the lowest unoccupied and highest occupied energy levels. Use your analysis and understanding of π electrons in PAHs and graphene to predict whether the conductivity of a $25 \text{ nm} \times 25 \text{ nm}$ square of graphene, at a given temperature, is less than, equal to or greater than the conductivity of a $1 \text{ m} \times 1 \text{ m}$ square of graphene (which is the largest obtained to date). Circle the correct answer:

less

equal

greater

Official English text of the problem.

Answers

Molecular identifiers used throughout: **benzene (B)**, c1ccccc1; **anthracene (A)**, c1ccc2cc3ccccc3cc2c1; **pentacene (P)**, c1ccc2cc3cc4cc5ccccc5cc4cc3cc2c1.

Define $E_0 = h^2 / (8m_e d^2)$.

• **8.1:** $d_a = 720 \text{ pm}$, $d_p = 1200 \text{ pm}$.

• **8.2:** $E_{n_x, n_y} = \frac{h^2}{8m_e d^2} \left(\frac{n_x^2}{w^2} + n_y^2 \right)$.

• **8.3:** In increasing energy, the doubly occupied states are

$(1, 1)$, $(2, 1)$, $(3, 1)$, $(4, 1)$, $(5, 1)$, $(1, 2)$, $(2, 2)$.

The lowest unoccupied states are the degenerate pair $(6, 1)$, $(3, 2)$. The additional uppermost line in the printed diagram is $(4, 2)$, also empty.

• **8.4:** $(1, 1)$ at $2E_0$ contains $\uparrow\downarrow$; the degenerate states $(1, 2)$ and $(2, 1)$ at $5E_0$ each contain $\uparrow\downarrow$; $(2, 2)$ at $8E_0$ is empty.

• **8.5:** $\Delta E_B = 3.14 \times 10^{-18} \text{ J}$, $\Delta E_A = 5.81 \times 10^{-19} \text{ J}$, $\Delta E_P = 1.26 \times 10^{-19} \text{ J}$.

• **8.6:** Increasing reactivity: $B < A < P$.

• **8.7:** Spectra from top to bottom: A, P, B .

- **8.8:** $N_\pi \approx 2.4 \times 10^4$ electrons.
- **8.9:** $E_F - E_{1,1} \approx 1.46 \times 10^{-18}$ J.
- **8.10:** Circle **less**.

Solution

8.1

Adjacent rings share a vertical edge, so each additional ring adds another horizontal distance d . Therefore,

$$d_a = 3d = 3(240 \text{ pm}) = 720 \text{ pm},$$

$$d_p = 5d = 5(240 \text{ pm}) = 1200 \text{ pm}.$$

8.2

For a linear PAH containing w rings, the stipulated box dimensions are

$$L_x = wd, \quad L_y = d.$$

Substituting into the given energy expression gives

$$E_{n_x, n_y} = \frac{h^2}{8m_e} \left(\frac{n_x^2}{w^2 d^2} + \frac{n_y^2}{d^2} \right) = \frac{h^2}{8m_e d^2} \left(\frac{n_x^2}{w^2} + n_y^2 \right).$$

Thus, with $E_0 = h^2/(8m_e d^2)$,

$$\frac{E_{n_x, n_y}}{E_0} = \frac{n_x^2}{w^2} + n_y^2.$$

8.3

Each carbon atom contributes one π electron. The first ring contains six carbon atoms, and each additional fused ring adds four, so

$$N_\pi = 6 + 4(w - 1) = 4w + 2.$$

Anthracene, $C_{14}H_{10}$, has $w = 3$ and therefore 14 π electrons. Each spatial state holds two electrons of opposite spin, so the seven lowest spatial states are doubly occupied.

For anthracene,

$$\frac{E}{E_0} = \frac{n_x^2}{9} + n_y^2.$$

Fill the printed diagram as follows, reading this table from top to bottom:

E/E_0	State (n_x, n_y)	Electron arrows
52/9	(4, 2)	Empty
5	(6, 1) and (3, 2), side by side	Both empty
40/9	(2, 2)	$\uparrow\downarrow$
37/9	(1, 2)	$\uparrow\downarrow$
34/9	(5, 1)	$\uparrow\downarrow$
25/9	(4, 1)	$\uparrow\downarrow$
2	(3, 1)	$\uparrow\downarrow$
13/9	(2, 1)	$\uparrow\downarrow$

E/E_0	State (n_x, n_y)	Electron arrows
10/9	(1, 1)	$\uparrow\downarrow$

The two lowest empty states have equal energy because

$$\frac{E_{6,1}}{E_0} = \frac{36}{9} + 1 = 5, \quad \frac{E_{3,2}}{E_0} = \frac{9}{9} + 4 = 5.$$

Hence the highest occupied state is (2, 2), and the lowest unoccupied states are (6, 1) and (3, 2). Their left-right order in the diagram is interchangeable.

8.4

Benzene, C_6H_6 , has six π electrons. Since $w = 1$,

$$\frac{E}{E_0} = n_x^2 + n_y^2.$$

The required diagram has three energy heights:

E/E_0	State(s)	Electron arrows
8	(2, 2)	Empty
5	(1, 2) and (2, 1), side by side	$\uparrow\downarrow$ in each
2	(1, 1)	$\uparrow\downarrow$

Draw one occupied line at $2E_0$, two occupied lines at the same height $5E_0$, and one empty line at $8E_0$. The six electrons completely fill the first three spatial states.

8.5

Using the standard constants

$$h = 6.626 \times 10^{-34} \text{ J s}, \quad m_e = 9.109 \times 10^{-31} \text{ kg},$$

and $d = 240 \times 10^{-12} \text{ m}$,

$$E_0 = \frac{h^2}{8m_e d^2} \approx 1.046 \times 10^{-18} \text{ J}.$$

For benzene, the highest occupied energy is $5E_0$, and the lowest unoccupied energy is $8E_0$. Thus,

$$\Delta E_B = (8 - 5)E_0 = 3E_0 = \boxed{3.14 \times 10^{-18} \text{ J}}.$$

For anthracene, the highest occupied energy is $(40/9)E_0$, and the lowest unoccupied energy is $5E_0$.

Therefore,

$$\Delta E_A = \left(5 - \frac{40}{9}\right)E_0 = \frac{5}{9}E_0 = \boxed{5.81 \times 10^{-19} \text{ J}}.$$

Pentacene, $C_{22}H_{14}$, has $w = 5$. Its supplied diagram identifies the highest occupied state as (9, 1) and the lowest unoccupied state as (3, 2):

$$E_{H,P} = \left(\frac{81}{25} + 1\right)E_0 = \frac{106}{25}E_0,$$

$$E_{L,P} = \left(\frac{9}{25} + 4\right)E_0 = \frac{109}{25}E_0.$$

Hence,

$$\Delta E_P = \left(\frac{109 - 106}{25}\right)E_0 = \frac{3}{25}E_0 = \boxed{1.26 \times 10^{-19} \text{ J}}.$$

8.6

The calculated gaps satisfy

$$\Delta E_B > \Delta E_A > \Delta E_P.$$

Using the stated inverse correlation between reactivity and the energy gap, the order of increasing reactivity is

$$\text{benzene} < \text{anthracene} < \text{pentacene}.$$

Write **B A P** from left to right.

8.7

Increasing the extent of the conjugated system generally reduces the relevant excitation energies. Since the energy of an absorbed photon is

$$E_{\text{photon}} = \frac{hc}{\lambda},$$

smaller excitation energies correspond to longer wavelengths.

The spectra therefore have the following assignments:

Spectrum	Assignment	Reason
Top	A — anthracene	Absorption extends to intermediate wavelengths, approximately 300–400 nm.
Middle	P — pentacene	Absorption extends farthest into the visible region, approximately 600–700 nm.
Bottom	B — benzene	Absorption occurs at the shortest wavelengths, in the ultraviolet.

Thus the letters from top to bottom are **A, P, B**.

8.8

Graphene is an extended planar honeycomb network of carbon atoms. The problem does not specify a finite molecular boundary, so there is no unique finite molecular SMILES for the sheet.

Each interior carbon atom belongs to three hexagons. Consequently, each hexagon accounts for

$$6 \left(\frac{1}{3} \right) = 2$$

carbon atoms, and hence two π electrons.

The sheet area is

$$A = (25\,000 \text{ pm})^2 = 6.25 \times 10^8 \text{ pm}^2.$$

The approximate number of hexagons is

$$N_{\text{hex}} = \frac{6.25 \times 10^8 \text{ pm}^2}{52\,400 \text{ pm}^2} = 1.19275 \times 10^4.$$

Therefore,

$$N_{\pi} = 2N_{\text{hex}} = 2.38550 \times 10^4 \approx 2.4 \times 10^4 \text{ electrons}.$$

8.9

For a square of side L ,

$$E_{n_x, n_y} = \frac{h^2}{8m_e L^2} (n_x^2 + n_y^2).$$

Thus equal-energy states lie on circles in the (n_x, n_y) plane. Because both quantum numbers are positive, the occupied states lie in the positive quadrant.

Define the radius of the occupied region by

$$R_F^2 = n_x^2 + n_y^2$$

at the Fermi energy. For many occupied states, their number is approximately the area of a quarter-circle:

$$N_{\text{spatial}} \approx \frac{\pi R_F^2}{4}.$$

Each spatial state accommodates two electrons, so

$$N_\pi \approx 2 \frac{\pi R_F^2}{4} = \frac{\pi R_F^2}{2},$$

and therefore

$$R_F^2 \approx \frac{2N_\pi}{\pi}.$$

Substitution into the energy expression gives

$$E_F \approx \frac{h^2}{8m_e L^2} \frac{2N_\pi}{\pi} = \boxed{\frac{h^2 N_\pi}{4\pi m_e L^2}}.$$

Using the electron count before rounding,

$$E_F \approx \frac{(6.626 \times 10^{-34} \text{ J s})^2 (2.38550 \times 10^4)}{4\pi (9.109 \times 10^{-31} \text{ kg}) (25 \times 10^{-9} \text{ m})^2} \approx 1.464 \times 10^{-18} \text{ J}.$$

The lowest state is $(1, 1)$, with energy

$$E_{1,1} = \frac{h^2}{4m_e L^2} \approx 1.93 \times 10^{-22} \text{ J}.$$

This is negligible compared with E_F , as stipulated. Thus,

$$\boxed{E_F - E_{1,1} \approx 1.46 \times 10^{-18} \text{ J}}.$$

8.10

The state-counting result in 8.9 can be written as

$$N(E) \approx \frac{4\pi m_e A}{h^2} E.$$

The density of available states is therefore proportional to the sheet area. A larger sheet has much more closely spaced levels near the Fermi energy and a smaller characteristic gap between occupied and unoccupied levels.

Although the Fermi energy remains approximately constant at fixed electron density, the level spacing decreases as the sheet grows. Under the inverse relationship between gap and conductivity specified in the question, the smaller sheet has lower conductivity:

$$\boxed{\sigma_{25 \text{ nm} \times 25 \text{ nm}} < \sigma_{1 \text{ m} \times 1 \text{ m}}}.$$

Circle **less**.

The solution was checked against the official solution.