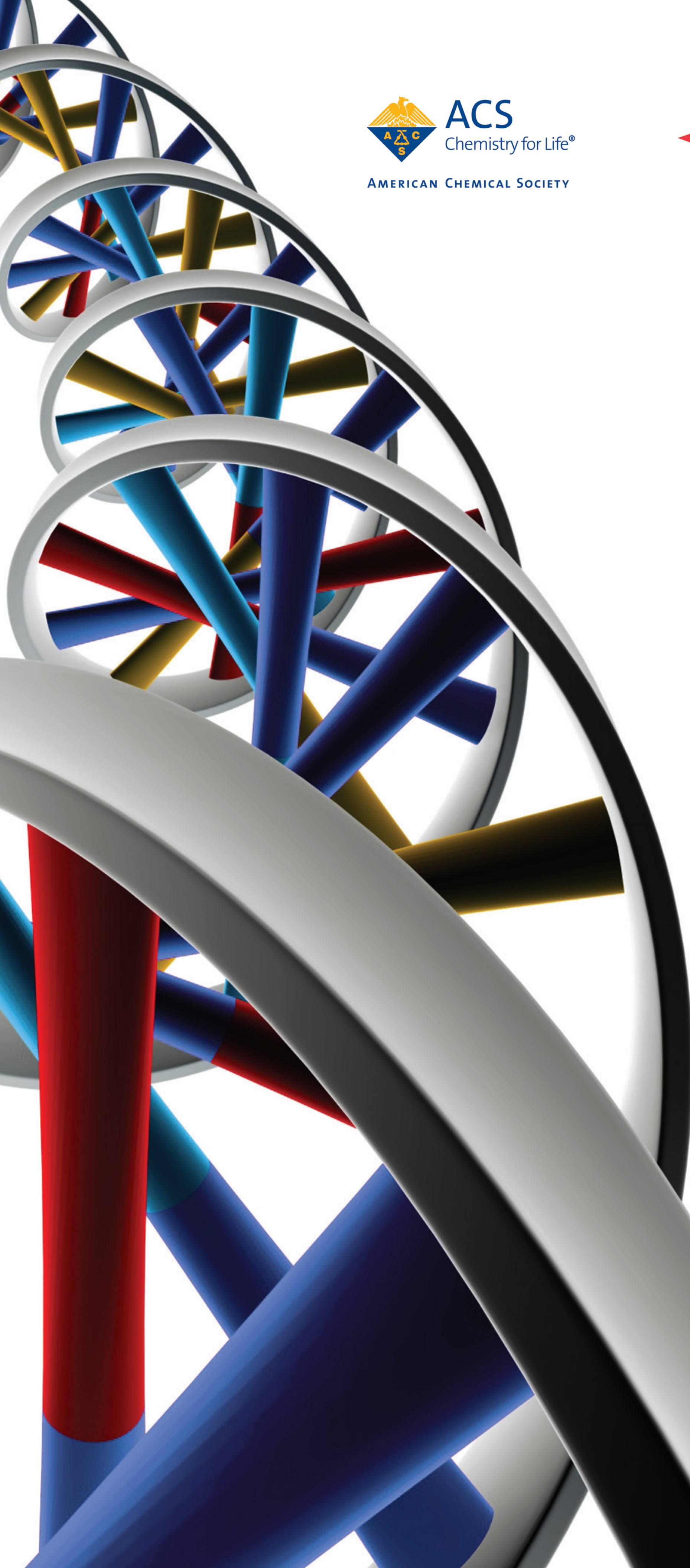

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IChO 44
2012 International Chemistry Olympiad

Theoretical Problems

44th International Chemistry Olympiad

July 26, 2012

United States of America

Name: Code:

Instructions

- Write your name and code on each page.
- This examination has **8** problems and Periodic Table on 49 pages.
- You have 5 hours to work on the exam problems. **Begin** only when the **START** command is given.
- Use only the pen and the calculator provided.
- All results must be written in the appropriate boxes. Anything written elsewhere will not be graded. Use the back side of the exam sheets if you need scratch paper.
- Write relevant calculations in the appropriate boxes when necessary. Full marks will be given for correct answers only when your work is shown.
- When you have finished the examination, put your papers into the envelope provided. Do not seal the envelope.
- You must **stop** working when the **STOP** command is given.
- Do not leave your seat until permitted by the supervisors.
- The official English version of this examination is available on request only for clarification.

Physical Constants, Formulas and Equations

Avogadro's constant, N_A = 6.0221 × 10^{23} mol^{-1}

Boltzmann constant, k_B = 1.3807 × 10^{-23} $J{\cdot}K^{-1}$

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

Speed of light, c = 2.9979 × 10^{8} $m{\cdot}s^{-1}$

Planck's constant, h = 6.6261 × 10^{-34} J·s

Mass of electron, m_e = 9.10938215 × 10^{-31} kg

Standard pressure, P = 1 bar = 10^5 Pa

Atmospheric pressure, P_{atm} = 1.01325 × 10^5 Pa = 760 mmHg = 760 Torr

Zero of the Celsius scale, 273.15 K

1 nanometer (*nm*) = 10^{-9} m

1 picometer (*pm*) = 10^{-12} m

Equation of a circle, $x^2 + y^2 = r^2$

Area of a circle, □r^2

Perimeter of a circle, 2□r

Volume of a sphere, 4□r^3/3

Area of a sphere, 4□r^2

Bragg's Law of Diffraction: $\sin\theta = n\lambda/2d$

Name: Code:

Key: Atomic number → 1; Atomic weight → 1.00794; Atomic symbol → H; Covalent radius, Å → 0.28

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 1.00794 **H** 0.28																	2 4.00260 **He** 1.40
2	3 6.941 **Li**	4 9.01218 **Be**											5 10.811 **B** 0.89	6 12.011 **C** 0.77	7 14.0067 **N** 0.70	8 15.9994 **O** 0.66	9 18.9984 **F** 0.64	10 20.1797 **Ne** 1.50
3	11 22.9898 **Na**	12 24.3050 **Mg**											13 26.9815 **Al**	14 28.0855 **Si** 1.17	15 30.9738 **P** 1.10	16 32.066 **S** 1.04	17 35.4527 **Cl** 0.99	18 39.948 **Ar** 1.80
4	19 39.0983 **K**	20 40.078 **Ca**	21 44.9559 **Sc**	22 47.867 **Ti** 1.46	23 50.9415 **V** 1.33	24 51.9961 **Cr** 1.25	25 54.9381 **Mn** 1.37	26 55.845 **Fe** 1.24	27 58.9332 **Co** 1.25	28 58.6934 **Ni** 1.24	29 63.546 **Cu** 1.28	30 65.39 **Zn** 1.33	31 69.723 **Ga** 1.35	32 72.61 **Ge** 1.22	33 74.9216 **As** 1.20	34 78.96 **Se** 1.18	35 79.904 **Br** 1.14	36 83.80 **Kr** 1.90
5	37 85.4678 **Rb**	38 87.62 **Sr**	39 88.9059 **Y**	40 91.224 **Zr** 1.60	41 92.9064 **Nb** 1.43	42 95.94 **Mo** 1.37	43 (97.905) **Tc** 1.36	44 101.07 **Ru** 1.34	45 102.906 **Rh** 1.34	46 106.42 **Pd** 1.37	47 107.868 **Ag** 1.44	48 112.41 **Cd** 1.49	49 114.818 **In** 1.67	50 118.710 **Sn** 1.40	51 121.760 **Sb** 1.45	52 127.60 **Te** 1.37	53 126.904 **I** 1.33	54 131.29 **Xe** 2.10
6	55 132.905 **Cs**	56 137.327 **Ba**	57-71 **La-Lu**	72 178.49 **Hf** 1.59	73 180.948 **Ta** 1.43	74 183.84 **W** 1.37	75 186.207 **Re** 1.37	76 190.23 **Os** 1.35	77 192.217 **Ir** 1.36	78 195.08 **Pt** 1.38	79 196.967 **Au** 1.44	80 200.59 **Hg** 1.50	81 204.383 **Tl** 1.70	82 207.2 **Pb** 1.76	83 208.980 **Bi** 1.55	84 (208.98) **Po** 1.67	85 (209.99) **At**	86 (222.02) **Rn** 2.20
7	87 (223.02) **Fr**	88 (226.03) **Ra** 2.25	89-103 **Ac-Lr**	104 (261.11) **Rf**	105 (262.11) **Db**	106 (263.12) **Sg**	107 (262.12) **Bh**	108 (265) **Hs**	109 (266) **Mt**	110 (271) **Ds**	111 (272) **Rg**	112 (285) **Cn**	113 (284) **Uut**	114 (289) **Fl**	115 (288) **Uup**	116 (292) **Lv**	117 (294) **Uus**	118 (294) **UUo**

57 138.906 **La** 1.87	58 140.115 **Ce** 1.83	59 140.908 **Pr** 1.82	60 144.24 **Nd** 1.81	61 (144.91) **Pm** 1.83	62 150.36 **Sm** 1.80	63 151.965 **Eu** 2.04	64 157.25 **Gd** 1.79	65 158.925 **Tb** 1.76	66 162.50 **Dy** 1.75	67 164.930 **Ho** 1.74	68 167.26 **Er** 1.73	69 168.934 **Tm** 1.72	70 173.04 **Yb** 1.94	71 174.04 **Lu** 1.72
89 (227.03) **Ac** 1.88	90 232.038 **Th** 1.80	91 231.036 **Pa** 1.56	92 238.029 **U** 1.38	93 (237.05) **Np** 1.55	94 (244.06) **Pu** 1.59	95 (243.06) **Am** 1.73	96 (247.07) **Cm** 1.74	97 (247.07) **Bk** 1.72	98 (251.08) **Cf** 1.99	99 (252.08) **Es** 2.03	100 (257.10) **Fm**	101 (258.10) **Md**	102 (259.1) **No**	103 (260.1) **Lr**

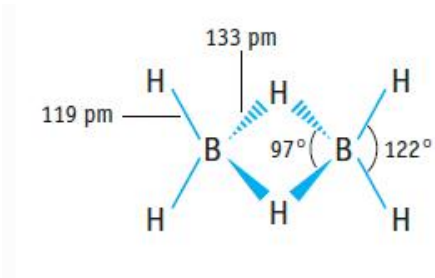
Name: Code:

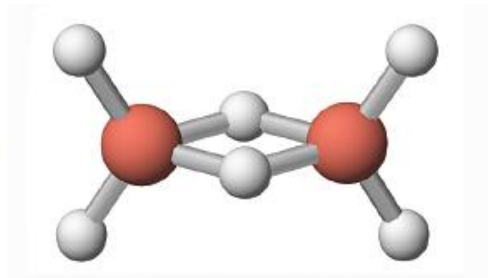
PROBLEM 1 7.5% of the total

a–i	a–ii	a-iii	b	C	Problem 1	
4	**2**	**2**	**2**	**10**	**20**	**7.5%**

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.





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

Substance	State (25 ˚C, 1 bar)	Mass Percent Boron	Molar mass (g/mol)
A	Liquid	83.1	65.1
B	Solid	88.5	122.2

A = _____ B_5H_{11}________ B = ______ $B_{10}H_{14}$______

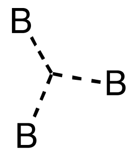
2 points each = 4 points

Name: Code:

ii. 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

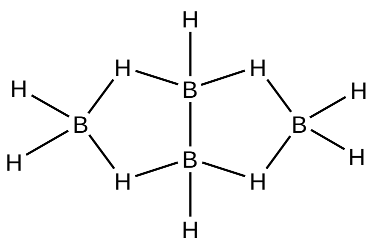
t = the number of 3-center BBB bonds in the molecule



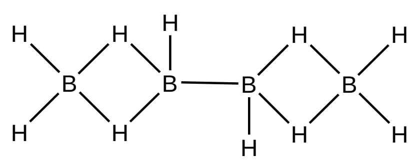
y = the number of two-center B–B bonds in the molecule

x = the number of BH_2 groups in the molecule

The *styx* number for B_2H_6 is 2002. Propose a structure for tetraborane, B_4H_{10}, with a *styx* number of 4012.



actual structure



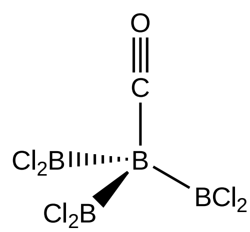
unknown but acceptable structure

2 points for either of these structures

Name: Code:

iii. A boron-based compound is composed of boron, carbon, chlorine, and oxygen (B_4CCl_6O). Spectral measurements indicate 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. Given that the molecular formula of the compound is B_4CCl_6O, suggest a structure for the molecule.

Structure:



2 points. Not required to show the stereochemistry

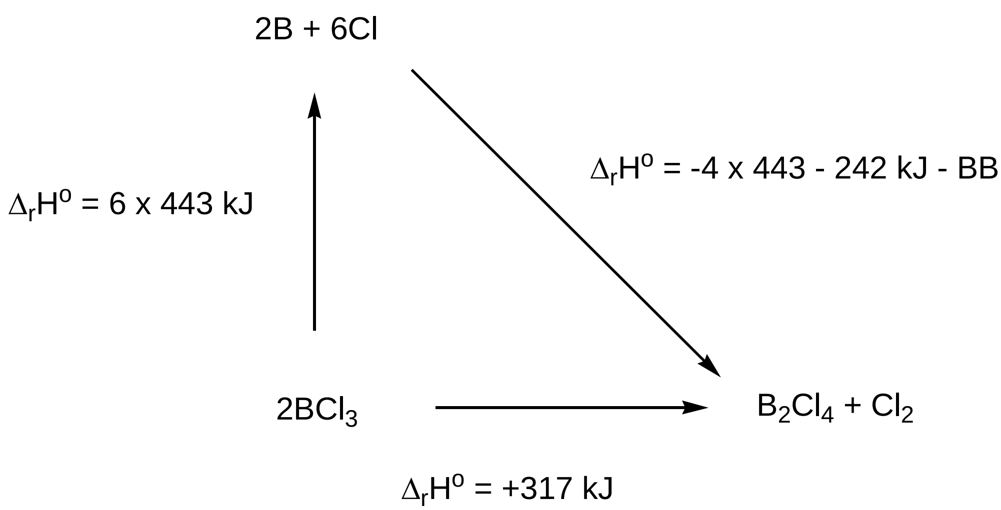
b. Thermochemistry of Boron Compounds

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

Bond	**Bond Dissociation Enthalpy (kJ/mol)**
B–Cl	443
Cl–Cl	242

Compound	$\Delta_f H°$ **(kJ/mol)**
BCl_3(g)	–403
B_2Cl_4(g)	–489

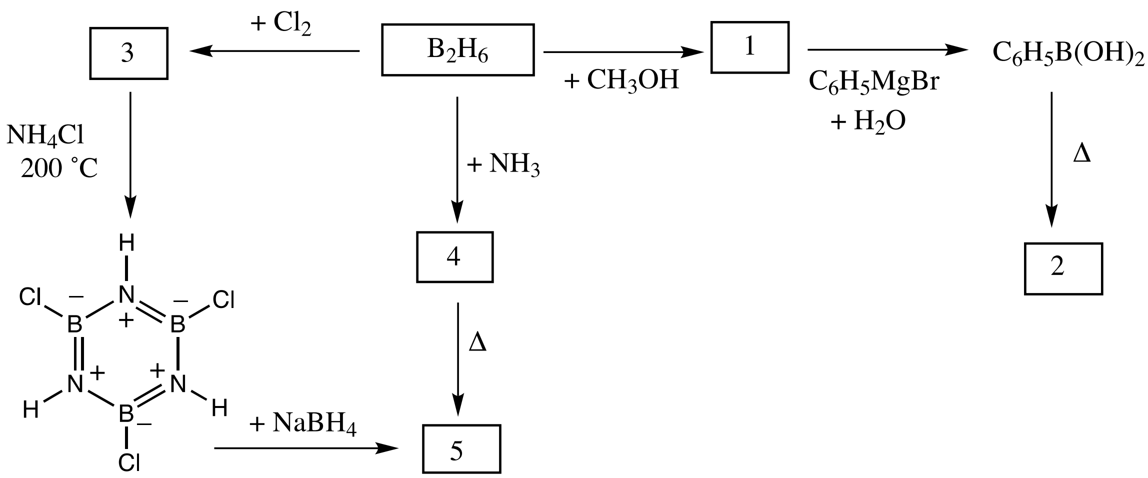
A Born-Haber cycle gives a B-B bond dissociation enthalpy of 327 kJ/mol



2 points

c. Chemistry of Diborane

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



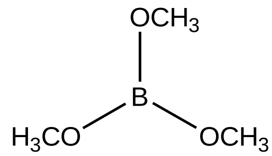
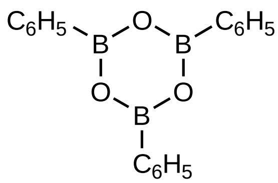
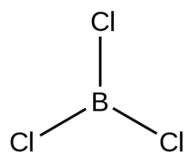
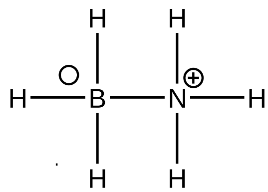
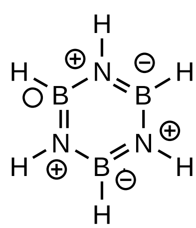
NOTES:

a. The boiling point of compound 5 is 55 ˚C.

b. Excess reagents used in all reactions.

c. 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 ˚C/molal

Name: Code:

Number	Molecular Structure of Compound
1	$B(OCH_3)_3$ 
2	 A dimer or tetramer $[C_6H_5BO]_x$ are also acceptable (x = 2, 4).
3	BCl_3 
4	BNH_6  Formal charges not necessary
5	$B_3N_3H_6$  Formal charges not necessary

10 points, 2 points each but only 1 point for formula only

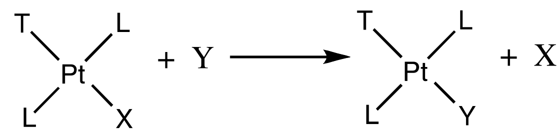
Name: Code:

PROBLEM 2 7.8% of the total

a–i	a–ii	b-i	b-ii	c	Problem 2	7.8%
4	4	6	1	5	20	

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

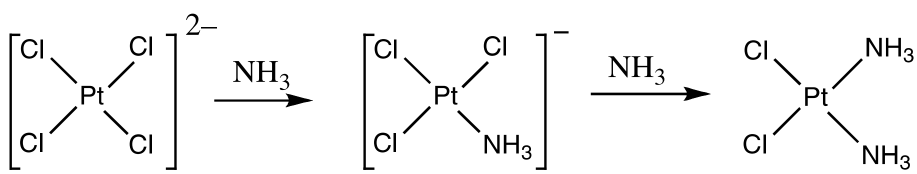
Platinum and other Group 10 metals form square planar complexes and the mechanisms of their reactions have been studied extensively. For example, it is known that substitution reactions of these complexes proceed with retention of stereochemistry.



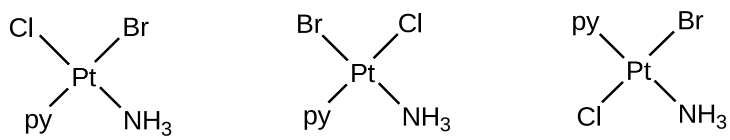
It is also known that the rate of substitution of ligand X by Y depends on the nature of the ligand *trans* to X, that is, on ligand T. This is known as the ***trans effect.*** When T is one of the molecules or ions in the following list, the rate of substitution at the trans position decreases from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

$$CN^- > H^- > NO_2^-, I^- > Br^-, Cl^- > \text{pyridine}, NH_3, OH^-, H_2O$$

The preparations of *cis*- and *trans*-$Pt(NH_3)_2Cl_2$ depend on the *trans* affect. The preparation of the *cis* isomer, a cancer chemotherapy agent commonly called cisplatin, involves the reaction of K_2PtCl_4 with ammonia.



i. Draw all possible stereoisomers for square planar platinum(II) compounds with the formula $Pt(py)(NH_3)BrCl$ (where py = pyridine, C_5H_5N).

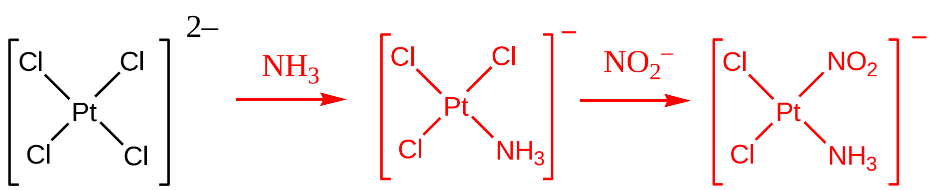


4 points. Penalty of -1 for excessive number of structures

3D perspective structures not required. Need clear indication of relative location of ligands.

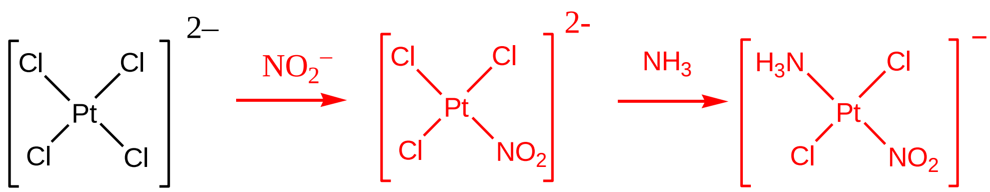
ii. Write reaction schemes including intermediate(s), if any, to show the preparation in aqueous solution for each of the stereoisomers of $[Pt(NH_3)(NO_2)Cl_2]^-$ using, as reagents, $PtCl_4^{2-}$, NH_3, and NO_2^-. The reactions are controlled kinetically by the *trans* effect.

cis-isomer:



2 points

trans-isomer:



2 points

b. Kinetic Studies of Substitution Reactions of Square Planar Complexes

Substitutions of the ligand X by Y in square planar complexes

$$ML_3X + Y \rightarrow ML_3Y + X$$

can occur in either or both of two ways:

• *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.

$$ML_3X \xrightarrow[**]{+\,Y} [ML_3XY] \xrightarrow{-\,X} ML_3Y$$

** = rate determining step, Rate constant = k_Y

• *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.

$$ML_3X \xrightarrow[**]{+\,S} [ML_3XS] \xrightarrow{-\,X} [ML_3S] \xrightarrow[-\,S]{+\,Y} ML_3Y$$

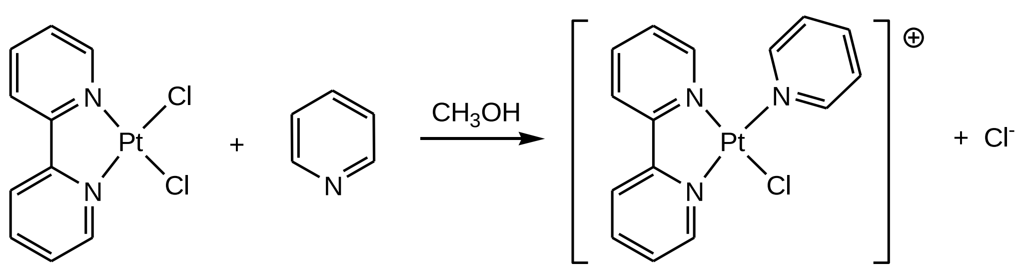
** = rate determining step, Rate constant = k_S

The overall rate law for such substitutions is

$$\text{Rate} = k_s[ML_3X] + k_Y[Y][ML_3X]$$

When [Y] >> $[ML_3X]$, then Rate = $k_{obs}[ML_3X]$.

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 (C_5H_5N). (The ML_3X scheme above applies to ML_2X_2.)



Data for reaction at 25 ˚C in methanol where [pyridine] >> the concentration of the platinum complex are given in the table below.

Name: Code:

Concentration of pyridine (mol/L)	k_{obs} (s^{-1})
0.122	7.20×10^{-4}
0.061	3.45×10^{-4}
0.030	1.75×10^{-4}

i. 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.

$k_Y = 5.8 \times 10^{-3}\ s^{-1}M^{-1}$
$k_S = 0\ s^{-1}$ (allow small range of values, $\pm 0.2 \times 10^{-3}$)

6 points
- 1 point for each unit
- 1 point for each number
- 2 points for method

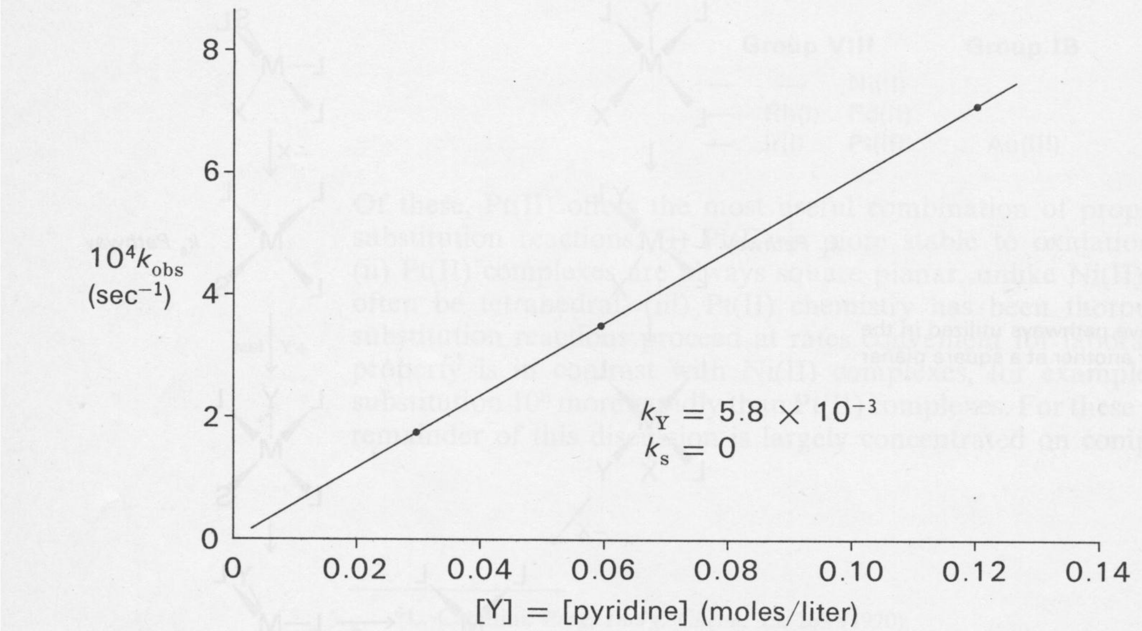


Figure 13–2. Verification of the rate law $k_{obs} = k_s + k_Y$[pyridine] for the reaction of Pt(bipy)Cl_2 with pyridine to give Pt(bipy)(py)Cl^+. Data taken from L. Cattalini, A. Orio, and A. Doni, *Inorg. Chem.*, **5**, 1517 (1966).

$k_Y = 5.8 \times 10^{-3}\ s^{-1}M^{-1}$
$k_S = 0\ s^{-1}$ (allow small range of values, + or – 0.2×10^{-3})

6 points

1 point for each unit
1 point for each number
2 points for method

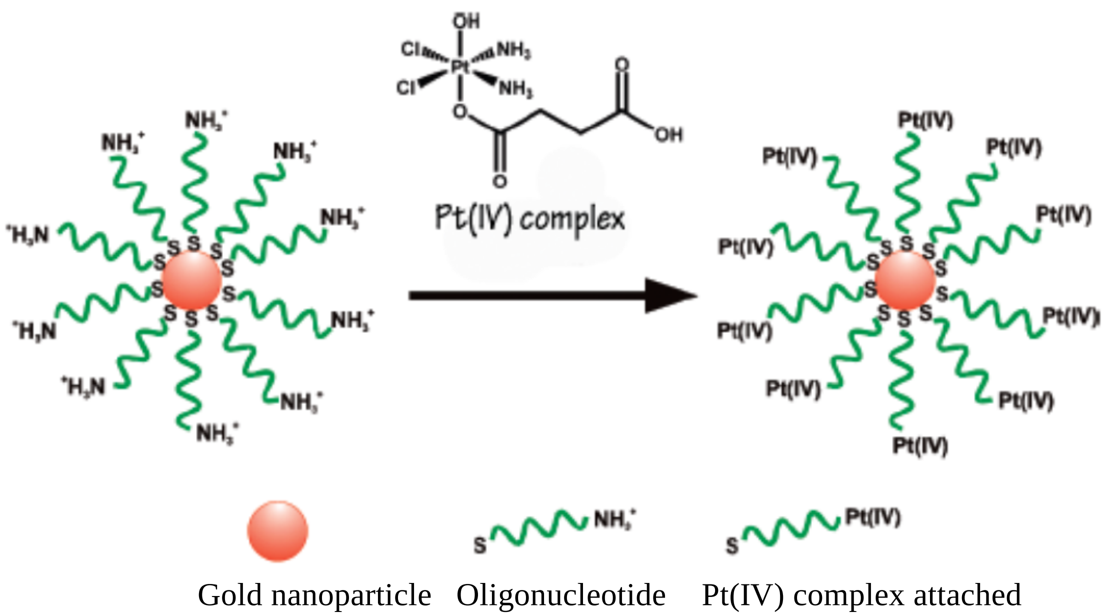
ii. When [pyridine] = 0.10 mol/L, which of the following is true? (Tick the box next to the correct answer.)

	Most pyridine product is formed by the solvent-assisted (k_S) substitution pathway.
X	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.

1 point for (b)

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.



Experiments showed that a gold nanoparticle with a diameter of 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 mL and that the solution was 1.0 x 10^{-6} M in Pt. **Calculate the mass of gold and of platinum used in this experiment**. (The density of gold = 19.3 g/cm^3 and the volume of a sphere = $(4/3)\pi r^3 = 4.18879\ r^3$.)

Mass of platinum

a) Amount of Pt used = (1.0 x 10^{-6} mol/1000 mL)(1.0 mL) = 1.0 x 10^{-9} mol Pt

This is equivalent to **2.0 x 10^{-7} g Pt**

1 point

Mass of gold

b) (90 groups/nanoparticle)(0.98 Pt bound complexes)

= 88 Pt complexes/nanoparticle or 88 Pt atoms per nanoparticle

c) 1.0 x 10^{-9} mol Pt is equivalent to 6.0 x 10^{14} Pt atoms

d) (6.0 x 10^{14} Pt atoms)(1 nanoparticle/88 Pt atoms) = 6.8 x 10^{12} nanoparticles

e) Size of gold nanoparticles:

Radius = 6.5 x 10^{-7} cm and volume of gold nanoparticle = 1.2 x 10^{-18} cm^3

Mass of gold nanoparticle = 2.3 x 10^{-17} g

Amount of gold in a nanoparticle = 1.2 x 10^{-19} mol

Atoms of gold in a nanoparticle = 7.1 x 10^4 atoms

f) Mass of gold:

Total number of gold atoms = (6.8 x 10^{12} particles)(7.1 x 10^4 atoms/particle)

= 4.8 x 10^{17} atoms of gold

Equivalent to **1.5 x 10^{-4} g gold**

4 points

Name: Code:

PROBLEM 3 7.5 % of the Total

a	b	c-i	c-ii	Problem 3	
4	12	6	12	34	7.5%

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.

$$MoS_4^{2-} + H_2O(l) \rightleftharpoons MoOS_3^{2-} + H_2S(aq) \qquad K_1 = 1.3\times10^{-5}$$
$$MoOS_3^{2-} + H_2O(l) \rightleftharpoons MoO_2S_2^{2-} + H_2S(aq) \qquad K_2 = 1.0\times10^{-5}$$
$$MoO_2S_2^{2-} + H_2O(l) \rightleftharpoons MoO_3S^{2-} + H_2S(aq) \qquad K_3 = 1.6\times10^{-5}$$
$$MoO_3S^{2-} + H_2O(l) \rightleftharpoons MoO_4^{2-} + H_2S(aq) \qquad K_4 = 6.5\times10^{-6}$$

a. If at equilibrium a solution contains 1×10^{-7} M MoO_4^{2-} and 1×10^{-6} M $H_2S(aq)$, what would be the concentration of MoS_4^{2-}?

Multiplying the mass action laws for the four given reactions produces:

$$\frac{MoO_4^{2-}(H_2S)^4}{MoS_4^{2-}} = \frac{1\times10^{-7}(1\times10^{-6})^4}{MoS_4^{2-}} = 1.4\times10^{-20}$$

$[MoS_4^{2-}]$ = 7×10^{-12} Units: M

3 points for correct MoS_4^{2-} answer; 1 point correct units

Solutions containing $MoO_2S_2^{2-}$, $MoOS_3^{2-}$ 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 L mol^{-1} cm^{-1}	ε at 395 nm L mo^{-1} cm^{-1}
MoS_4^{2-}	11870	120
$MoOS_3^{2-}$	0	9030
$MoO_2S_2^{2-}$	0	3230

b. A solution *not* at equilibrium contains a mixture of MoS_4^{2-}, $MoOS_3^{2-}$ and $MoO_2S_2^{2-}$ and no other Mo-containing species. The total concentration of all species containing Mo is 6.0×10^{-6} M. In a 10.0 cm absorption cell, the absorbance of the solution at 468 nm is 0.365 and at 395 nm is 0.213. Calculate the concentrations of all three Mo-containing anions in this mixture.

MoS_4^{2-} concentration is determined by absorbance at 468 nm:

$0.365 = (11870)(10.0)(MoS_4^{2-})$. $(MoS_4^{2-}) = 3.08\times10^{-6}$ M 4 points

From conservation of Mo,

$(MoOS_3^{2-}) + (MoO_2S_2^{2-}) = Mo_{Total} - (MoS_4^{2-}) = 6.0\times10^{-6} - 3.08\times10^{-6} = 2.9\times10^{-6}$

By rearrangement,

$(MoO_2S_2^{2-}) = 2.9\times10^{-6} - (MoOS_3^{2-})$

From optical absorbance at 395 nm,

$0.213 = (120)(10.0)(3.08\times10^{-6}) + (9030)(10.0)(MoOS_3^{2-}) + (3230)(10.0)(MoO_2S_2^{2-})$

$0.213 = (120)(10.0)(3.08\times10^{-6}) + (9030)(10.0)(MoOS_3^{2-}) + (3230)(10.0)(2.9\times10^{-6} - (MoOS_3^{2-}))$

$(MoOS_3^{2-}) = 2.0\times10^{-6}$ M 4 points

$(MoO_2S_2^{2-}) = 2.9\times10^{-6} - (MoOS_3^{2-}) = 0.9\times10^{-6}$ M

$(MoO_2S_2^{2-}) = 0.9\times10^{-6}$ M 4 points

$MoO_2S_2^{2-}$ ______

$MoOS_3^{2-}$ _______

MoS_4^{2-} ________

c. A solution initially containing 2.0×10^{-7} M MoS_4^{2-} hydrolyzes in a closed system. The H_2S product accumulates until equilibrium is reached. Calculate the final equilibrium concentrations of H_2S(aq), and all five Mo-containing anions (that is, MoO_4^{2-}, MoO_3S^{2-}, $MoO_2S_2^{2-}$, $MoOS_3^{2-}$ and MoS_4^{2-}). Ignore the possibility that H_2S might ionize to HS^- under certain pH conditions. *(One-third credit is given is given for writing the six independent equations that constrain the problem, and two-thirds credit is given for the correct concentrations.)*

i. Write the six independent equations that determine the system.

Mass balance for Mo:

$2.0\times10^{-7} = (MoS_4^{2-}) + (MoOS_3^{2-}) + (MoO_2S_2^{2-}) + (MoO_3S^{2-}) + (MoO_4^{2-})$ 2 points

Mass balance for S:

$8.0\times10^{-7} = 4(MoS_4^{2-}) + 3(MoOS_3^{2-}) + 2(MoO_2S_2^{2-}) + (MoO_3S^{2-}) + (H_2S)$ 2 points

Equilibrium constants:

$1.3\times10^{-5} = (MoOS_3^{2-})(H_2S)/(MoS_4^{2-})$
$1.0\times10^{-5} = (MoO_2S_2^{2-})(H_2S)/(MoOS_3^{2-})$
$1.6\times10^{-5} = (MoO_3S^{2-})(H_2S)/(MoO_2S_2^{2-})$
$6.5\times10^{-6} = (MoO_4^{2-})(H_2S)/(MoO_3S^{2-})$

0.5 point each = 2 points

Six equations in any format will be accepted provided they somehow introduce the four equilibrium constants and the two correct mass balance constraints.

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

It is likely that multiple approaches will be found for solving these equations. Here is one approach:

The maximum possible H_2S concentration is $8.0x10^{-7}$ M, the amount formed if complete hydrolysis occurs. At this H_2S concentration, MoO_3S^{2-} is only about 12% of (MoO_4^{2-}) and the remaining thio anions are much less abundant. Therefore, because the problem justifies a solution that is precise only to two significant figures, the mass balance equations can be truncated:

$2.0\times10^{-7} = (MoO_3S^{2-}) + (MoO_4^{2-})$ (Mo mass balance)
$8.0\times10^{-7} = (MoO_3S^{2-}) + (H_2S)$ (S mass balance)

Subtracting the first from the second and rearranging gives:

$(MoO_4^{2-}) = (H_2S) - 6.0\times10^{-7}$

Likewise, the S mass balance can be rearranged,

$(MoO_3S^{2-}) = 8.0\times10^{-7} - (H_2S)$

Employing the equilibrium constant for the reaction involving MoO_4^{2-} and MoO_3S^{2-}

$$6.5\times10^{-6} = \frac{(MoO_4^{2-})(H_2S)}{(MoO_3S^{2-})} = \frac{[(H_2S)-(6.0\times10^{-7})](H_sS)}{[(8.0\times10^{-7})-(H_2S)]}$$

Rearrangement and solution by the quadratic formula gives (H_2S). Back substitution gives the remaining concentrations.

H_2S __7.8×10^{-7} M__ MoO_4^{2-} ___1.8×10^{-7} M ___ MoO_3S^{2-}___2.1×10^{-8} M___

$MoO_2S_2^{2-}$ ___1.0×10^{-9} M $MoOS_3^{2-}$ ___8.1×10^{-11} M___MoS_4^{2-} ___4.9×10^{-12} M___

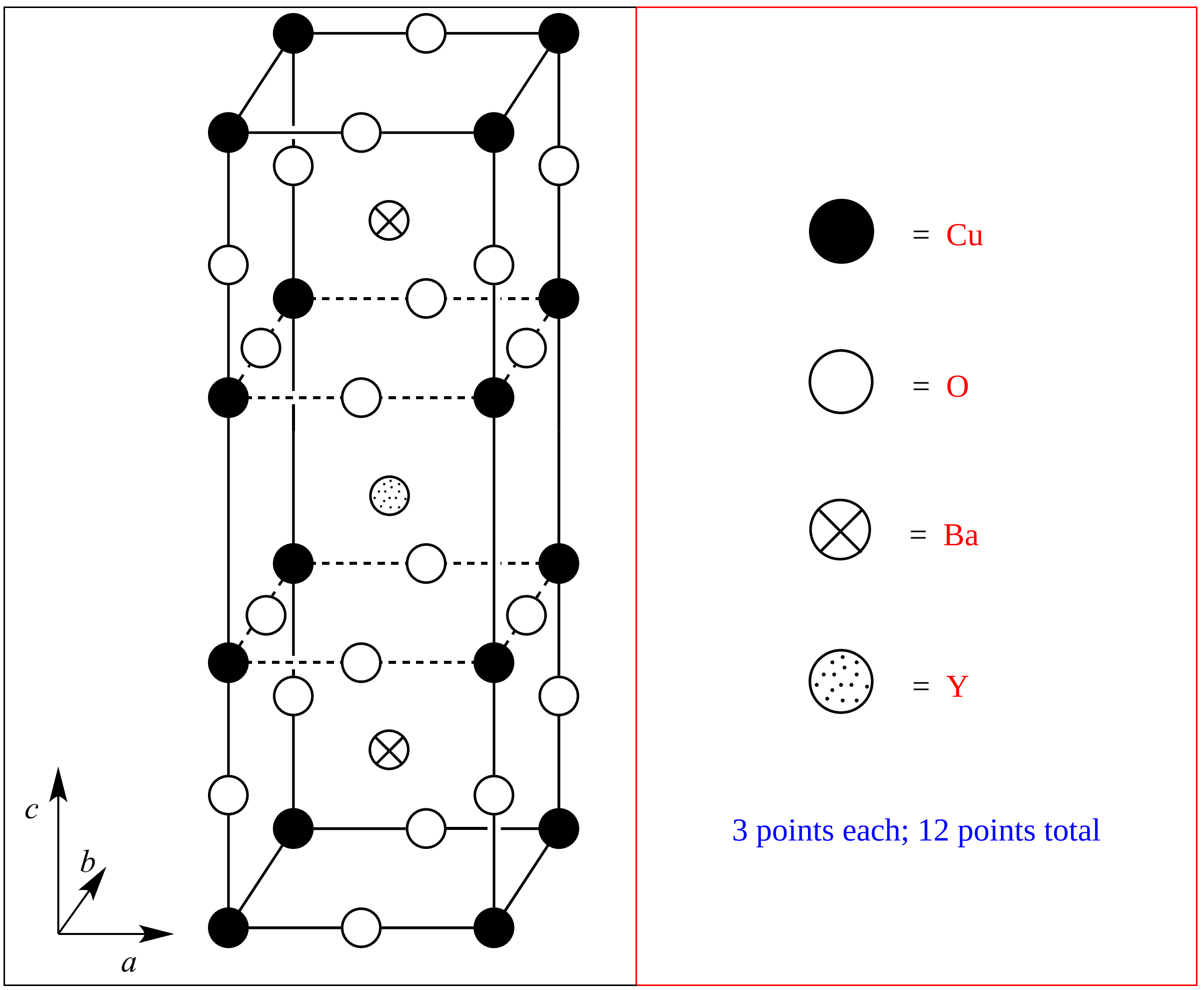
2 points each answer; 12 points total

PROBLEM 4 7.8% of the Total

a	b	c	d-i	d-ii	d-iii	d-iv	e-i	e-ii	Problem 4	
12	14	10	4	2	2	4	4	8	60	7.8%

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 $YBa_2Cu_3O_7$, but its actual composition is variable according to the formula $YBa_2Cu_3O_{7-\delta}$ ($0 < \delta < 0.5$).

a. 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 $a \approx b \approx (c/3)$.

b. A sample of YBCO with $\delta = 0.25$ was subjected to X-ray diffraction using Cu Kα radiation (λ = 154.2 pm). The lowest-angle diffraction peak was observed at 2θ = 7.450º. Assuming that $a = b = (c/3)$, calculate the values of a and c.

$$\sin\theta = n\lambda/2d$$
$$d = (1)(154.2 \text{ pm})/2\sin(3.725^\circ)$$
$$d = 1187 \text{ pm}$$
Lowest-angle => d = longest axis = c
$$c = 1187 \text{ pm}$$
$$a = c/3 = 396 \text{ pm}$$

8 points for calculating d; 6/8 points if student uses θ in radians and reports a positive value (0/8 points if negative distance); 6/8 points if uses 2θ instead of θ.
6 points for correctly assigning a and c.

14 points total

a = 396 pm

c = 1187 pm

c. Estimate the density of this sample of YBCO (with $\delta = 0.25$) in g cm^{-3}. If you do not have the values for a and c from part (b), then use a = 500. pm, c = 1500. pm.

$$V_{\text{unit cell}} = a \times b \times c = 3a^3 = 3(396 \text{ pm})^3 = 1.863 \times 10^{-22} \text{ cm}^3$$
$$m_{\text{unit cell}} = (1/N_A)(88.91 + 2\times137.33 + 3\times63.55 + 6.75\times16.00)$$
$$m_{\text{unit cell}} = (662.22 \text{ g/mol})/(6.0221 \times 10^{23} \text{ mol}^{-1}) = 1.100 \times 10^{-21} \text{ g}$$
$$\text{Density} = (1.100 \times 10^{-21} \text{ g})/(1.863 \times 10^{-22} \text{ cm}^3) = 5.90 \text{ g cm}^{-3}$$

4 points for V
4 points for $m_{\text{unit cell}}$
2 points for ρ

Density = 5.90 g cm^{-3}

10 points total

d. When YBCO is dissolved in 1.0 M aqueous HCl, 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 directly to a solution that 1.0 M in both KI and HCl under Ar, the solution turns yellow-brown but no gas evolution is observed.

i. Write a balanced net ionic equation for the reaction when solid $YBa_2Cu_3O_{7-\delta}$ dissolves in aqueous HCl with evolution of O_2.

$$YBa_2Cu_3O_{7-\delta}\,(s) + 13\,H^+\,(aq) \rightarrow$$
$$Y^{3+}\,(aq) + 2\,Ba^{2+}\,(aq) + 3\,Cu^{2+}\,(aq) + (0.25[1-2\delta])O_2\,(g) + 6.5\,H_2O\,(l)$$

2 points species, 2 points coefficients

ii. Write a balanced net ionic equation for the reaction when the solution from (**i**) reacts with excess KI in acidic solution after the dissolved oxygen is expelled.

$$2\,Cu^{2+}\,(aq) + 5\,I^-\,(aq) \rightarrow 2\,CuI\,(s) + I_3^-\,(aq)$$
–or–
$$2\,Cu^{2+}\,(aq) + 4\,I^-\,(aq) \rightarrow 2\,CuI\,(s) + I_2\,(aq)$$

1 point species, 1 point coefficients. Iodo complexes of Cu(I) (e.g., CuI_2^-) will be given full marks as products

iii. Write a balanced net ionic equation for the reaction when the solution from (**ii**) is titrated with thiosulfate ($S_2O_3^{2-}$).

$$I_3^-\,(aq) + 2\,S_2O_3^{2-}\,(aq) \rightarrow 3\,I^-\,(aq) + S_4O_6^{2-}\,(aq)$$
–or–
$$I_2\,(aq) + 2\,S_2O_3^{2-}\,(aq) \rightarrow 2\,I^-\,(aq) + S_4O_6^{2-}\,(aq)$$

1 point species, 1 point coefficients

iv. Write a balanced net ionic equation for the reaction when solid $YBa_2Cu_3O_{7-\delta}$ dissolves in aqueous HCl containing excess KI in an Ar atmosphere.

$$YBa_2Cu_3O_{7-\delta}\,(s) + (14-2\delta)\,H^+\,(aq) + (9-3\delta)\,I^-\,(aq) \rightarrow$$
$$Y^{3+}\,(aq) + 2\,Ba^{2+}\,(aq) + 3\,CuI\,(s) + (7-\delta)\,H_2O\,(l) + (2-\delta)\,I_3^-\,(aq)$$

–or–

$$YBa_2Cu_3O_{7-\delta}\,(s) + (14-2\delta)\,H^+\,(aq) + (7-2\delta)\,I^-\,(aq) \rightarrow$$
$$Y^{3+}\,(aq) + 2\,Ba^{2+}\,(aq) + 3\,CuI\,(s) + (7-\delta)\,H_2O\,(l) + (2-\delta)\,I_2\,(aq)$$

2 points species, 2 points coefficients

e. Two identical samples of YBCO with an unknown value of δ were prepared. The first sample was dissolved in 5 mL of 1.0 M aqueous HCl, evolving O_2. After boiling to expel gases, cooling, and addition of 10 mL of 0.7 M KI solution under Ar, titration with thiosulfate to the starch endpoint required 1.542×10^{-4} mol thiosulfate. The second sample of YBCO was added directly to 7 mL of a solution that was 1.0 M in KI and 0.7 M in HCl under Ar; titration of this solution required 1.696×10^{-4} mol thiosulfate to reach the endpoint.

i. Calculate the number of moles of Cu in each of these samples of YBCO.

$n_{Cu} = n_{thiosulfate}$ in the first titration

$n_{Cu} = 1.542 \times 10^{-4}$ mol

4 points, errors in chemistry displayed in (d) will be carried forward without penalty

$n_{Cu} = 1.542 \times 10^{-4}$ mol

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

Total Cu = 1.542×10^{-4} mol

Cu(III) = $(1.696 \times 10^{-4}$ mol$) - (1.542 \times 10^{-4}$ mol$) = 1.54 \times 10^{-5}$ mol

So 90% of Cu is Cu(II), 10% is Cu(III)

For charge balance, $2(7-\delta) = 3 + 2\times2 + 3\times(0.90\times2 + 0.10\times3) = 13.30$

$\delta = 0.35$

4 points for partition of Cu(III)/Cu(II)

4 points for calculating δ

Alternatively, using the balanced equations in (d):

In the 1st titration, each mol YBCO = 1.5 mol I_3^- = 3 mol $S_2O_3^{2-}$

In the 2d titration, each mol YBCO = $(2-\delta)$ mol I_3^- = $(4-2\delta)$ mol $S_2O_3^{2-}$

So (1.542 × 10^{-4} mol)/(1.696 × 10^{-4} mol) = 3/(4–2δ) = 1.5/(2–δ)

2–δ = 1.650

δ = 0.35

4 points for translating (d) to a relation between titrations and δ

4 points for calculating δ

δ = 0.35

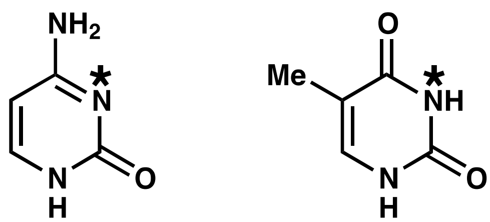
PROBLEM 5 7.0 % of the Total

a-i	a-ii	b	c	d	e	f	Problem 5	
2	4	4	2	12	6	4	34	**7.0%**

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.

a. 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.

i. <u>Select</u> (circle) which base, **C** or **T**, has the more nucleophilic N-3 atom.



C T

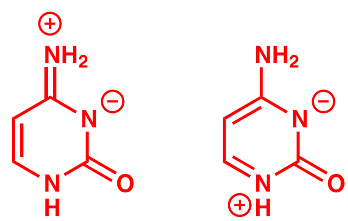
(i)

C (circled) **T**

2 points

ii. <u>Draw</u> two complementary resonance structures of the molecule you select to justify your answer.

(ii)

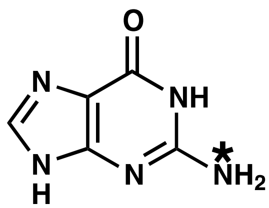


4 points (2 points each; 1 of these points for formal charges)

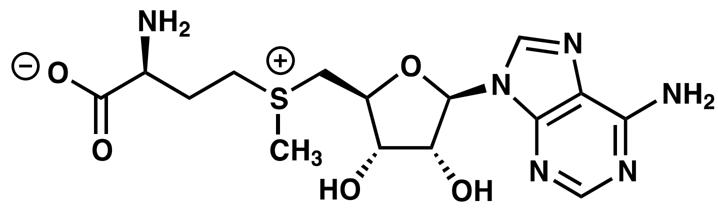
Full marks for this part if student chooses T in part (i) but draws two valid resonance structures

3 points for valid resonance structures of the base not selected in part (i)

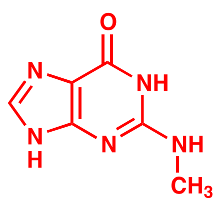
b. One common modification of DNA in nature is methylation of the indicated (*) position of guanine (**G**) by S-adenosyl methionine (SAM). **Draw** the structures of both of the products of the reaction between guanine and SAM.



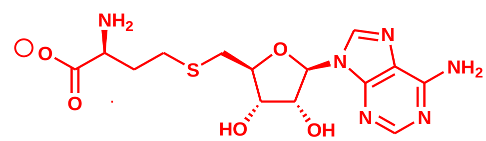
G



SAM

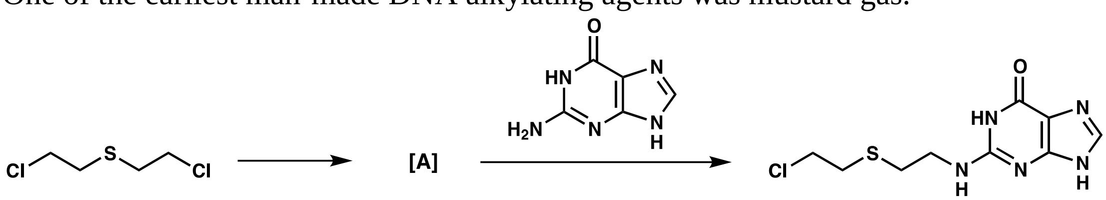


2 points; full marks if protonated; full marks for dimethylated

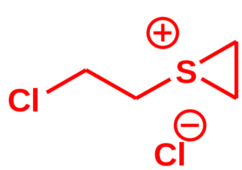


2 points; full marks if protonated

c. 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 equation above. **Draw** a structure for reactive intermediate **A**.

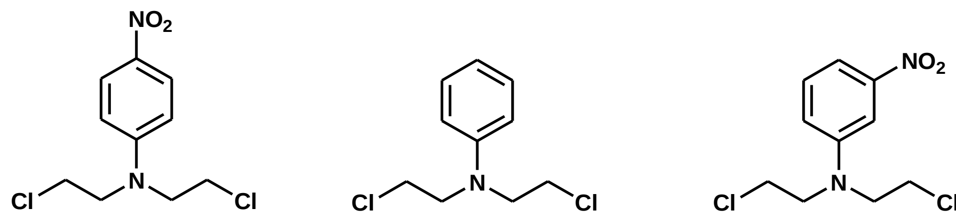


A

2 points

d. The nitrogen mustards react via an analogous pathway to the sulfur mustard of part c. 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. <u>**Select**</u> the most and least reactive from each of following groups of nitrogen mustards.

i.



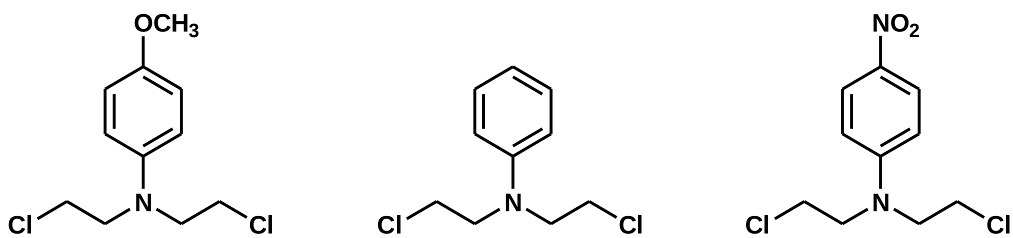
I II III

MOST REACTIVE: II

LEAST REACTIVE: I

4 points (2 points each)

ii.



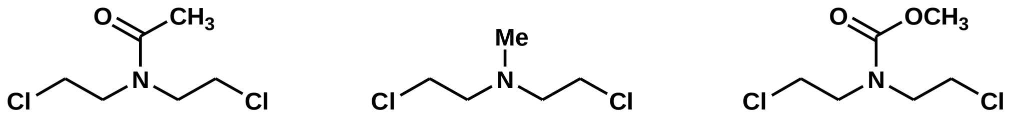
I II III

MOST REACTIVE: I

LEAST REACTIVE: III

4 points (2 points each)

iii.



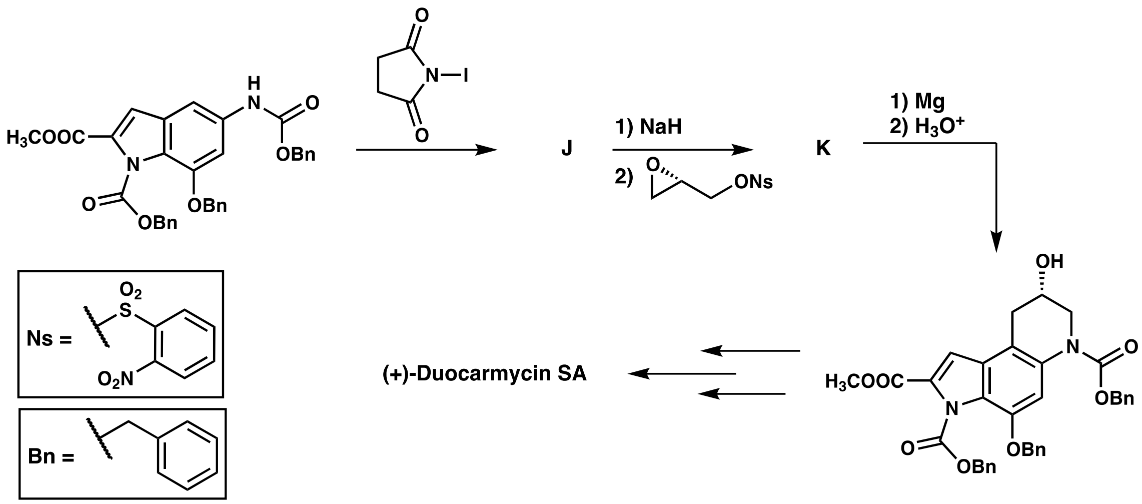
I II III

MOST REACTIVE: II

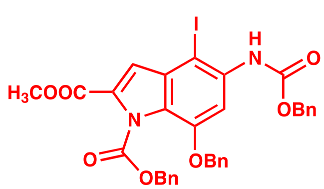
LEAST REACTIVE: I

4 points (2 points each)

e. 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. **Draw** the structures of isolable compounds **J** and **K**.

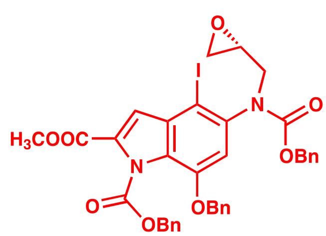


J



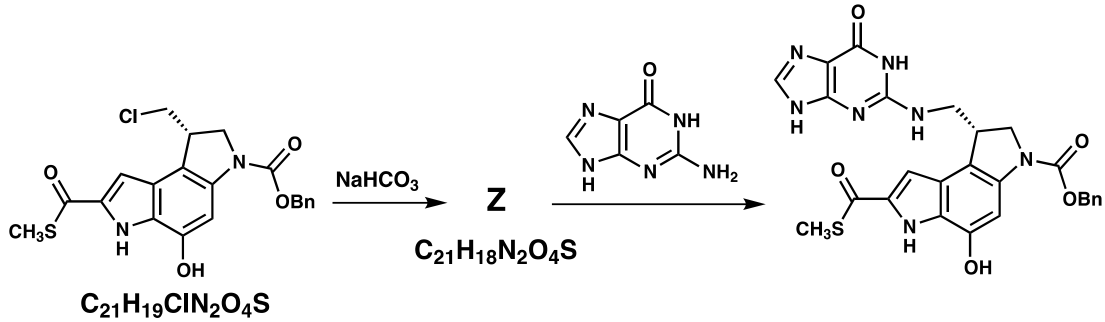
2 points; 1 point for other regioisomers

K

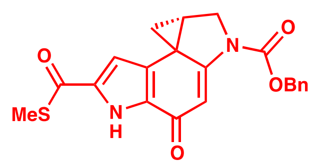


4 points (3 points for enantiomer, 3 points for epoxide opening and nosyl still present)

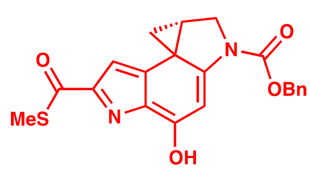
f. Related small molecules were synthesized to study the way in which the duocarmycins work. One such example is the thioester shown below. **Draw** the structure of reactive intermediate **Z**.

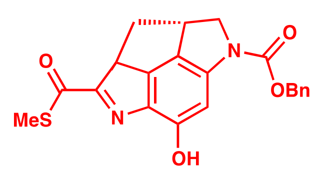


Correct Answer



Z





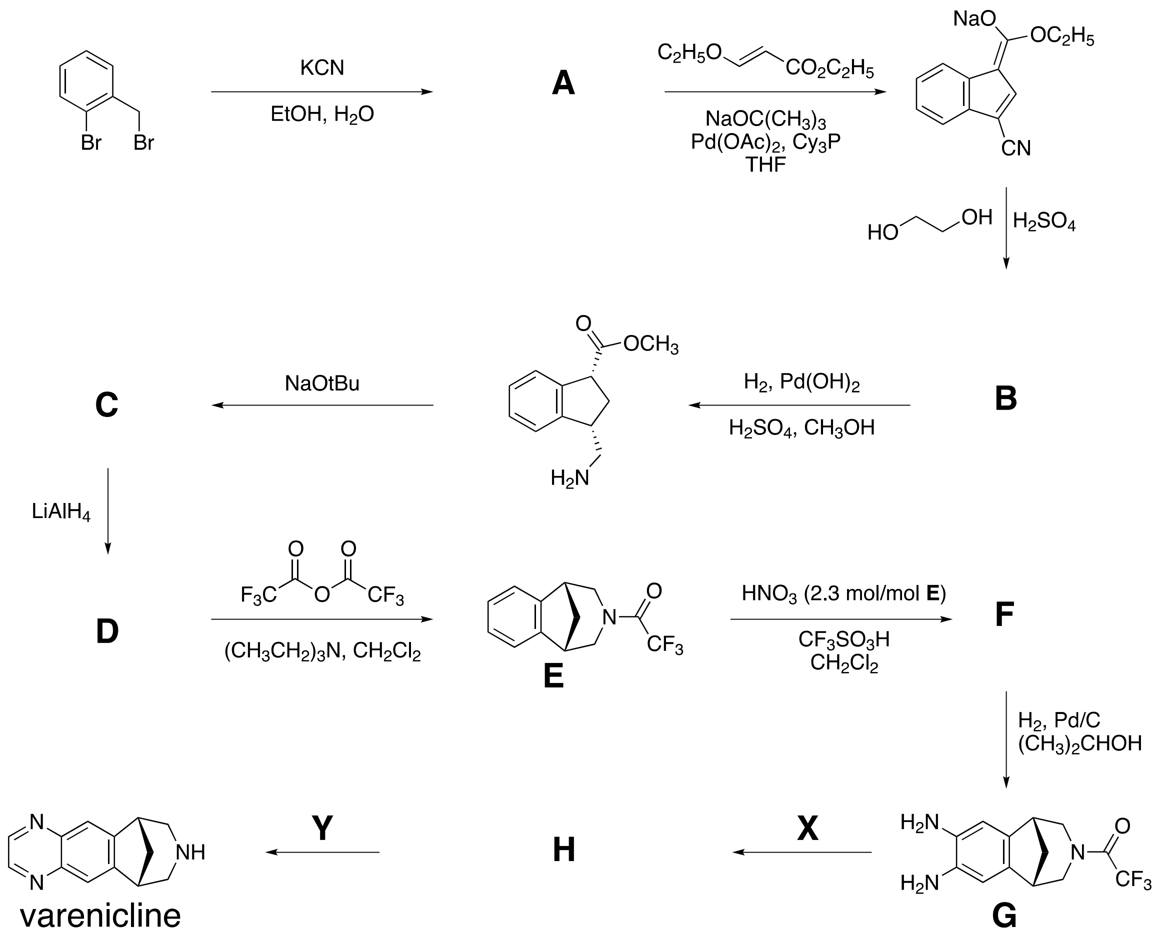
Full marks

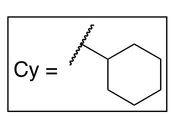
4 points
1 point for elimination product

PROBLEM 6 6.6 % of the Total

a	b	c	d	Problem 6	
2	4	6	8	20	**6.6%**

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.

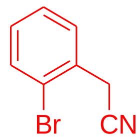




Name: Code:

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

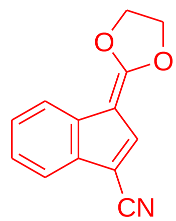
A



2 points

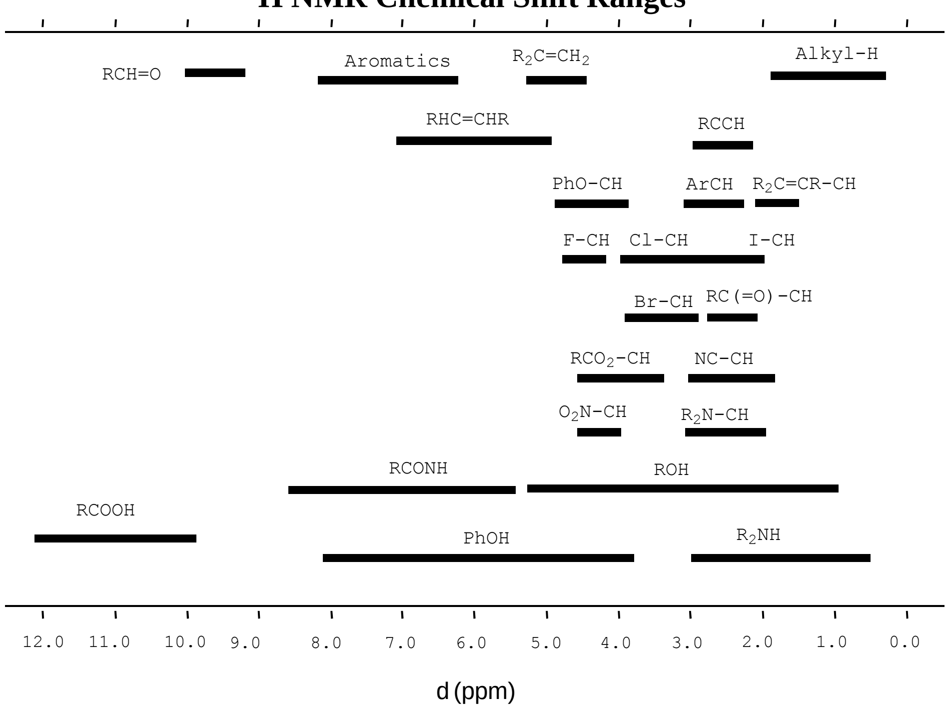
b. Suggest a structure for compound **B** consistent with the following ^{1}H-NMR data:
δ 7.75 (singlet, 1H), 7.74 (doublet, 1H, J = 7.9 Hz), 7.50 (doublet, 1H, J = 7.1 Hz), 7.22 (multiplet, 2 nonequivalent H), 4.97 (triplet, 2H, J = 7.8 Hz), 4.85 (triplet, 2H, J = 7.8 Hz)

B



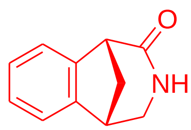
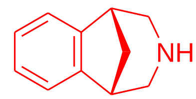
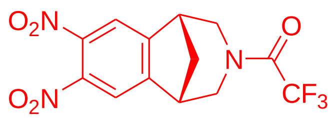
4 points (2 points for a feasible alternative if not NMR-consistent)

^{1}H NMR Chemical Shift Ranges*

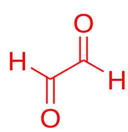
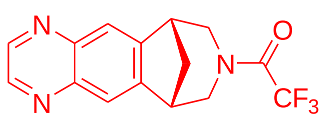


Name: Code:

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

C  2 points	**D**  2 points
F  2 points	

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

X  2 points	**Y** **Aqueous NaOH or any other amide hydrolyzing reagents** 2 points
H  2 points (Full credit given for whatever is the correct product of F and X)	

X and Y reversed receive full marks above, as long as G corresponds.

2 additional points for proper order of reagents.

Name: Code:

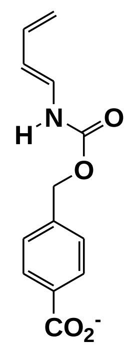
PROBLEM 7 7.5 % of the Total

a	b	c	d	e	f	Problem 6	7.5%
9	15	8	6	8	6	52	

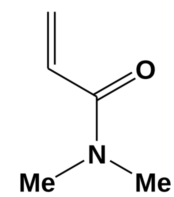
An artificial enzyme was designed to bind the two substrate molecules shown below (diene and dienophile) and catalyze a Diels-Alder reaction between them.

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

i. 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 (▬) and dashes (┅┅) 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.

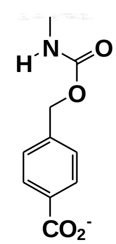


diene

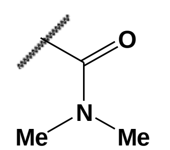


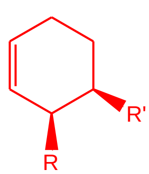
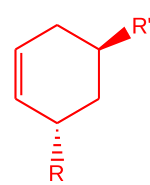
dienophile

R

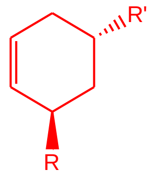
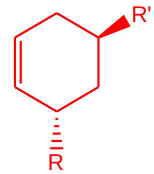


R'

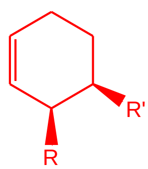
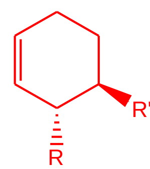


 1 point for any reasonable Diels-Alder product 2 points for regioisomeric relationship between compounds	

ii. 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 (▬) and dashes (┅┅) to show the stereochemistry of each product in your drawings. Use **R** and **R′** as in part (i).

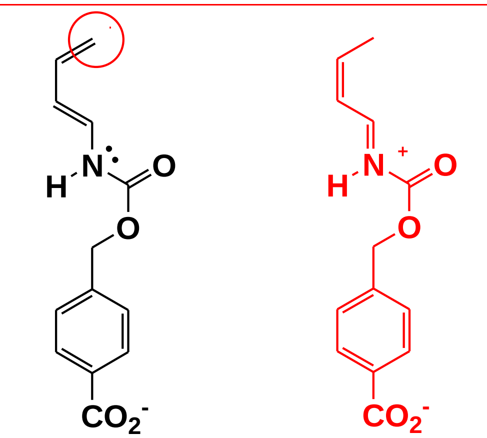
 1 point for any reasonable Diels-Alder product 2 point for enantiomeric relationship between compounds	

iii. 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 (▬) and dashes (┅┅) to show the stereochemistry of each product in your drawings. Use **R** and **R′** as in part (i).

 1 point for any reasonable Diels-Alder product 2 points for diastereomeric relationship between compounds	

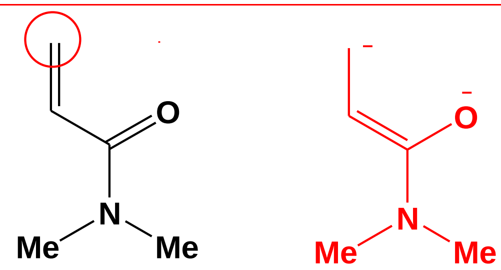
b. The rate and regioselectivity of a Diels-Alder reaction depend on the degree of electronic complementarity between the two reactants. The structures of the diene and the dienophile from part **a** are given below.

i. 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.



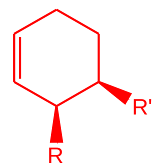
5 points (2 points for circled carbon; 2 points for resonance structure; 1 point for charges)

ii. 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.



5 points (2 points for circled carbon; 2 points for resonance structure; 1 point for charges)

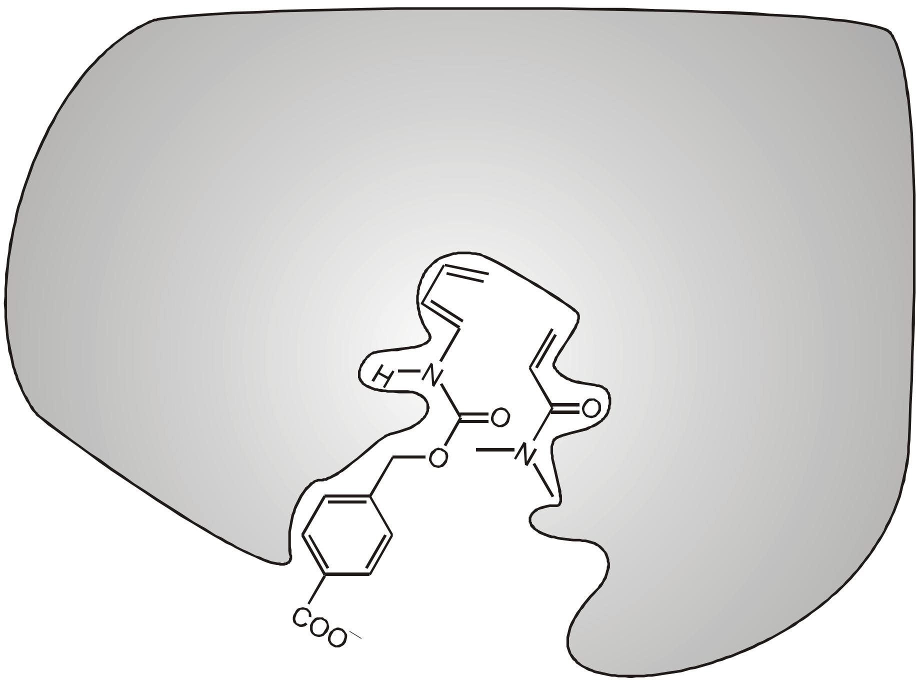
iii. Based on your assignments in parts (**i**) and (**ii**), predict the regiochemistry of the uncatalyzed Diels-Alder reaction of the diene and dienophile by drawing the major product. You need not show the stereochemistry of the product in your drawing.

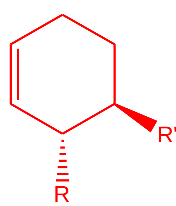


5 points. Stereochemistry not graded. Full marks as long as consistent with b(i) and b(ii)

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.

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**.





8 points; 4 points if wrong enantiomer; 2 points if wrong diastereomer; 0 points if wrong regioisomer

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").

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

True (circled) **False**

ii. Enzymes alter the equilibrium constant of the reaction to favor the product.

True **False** (circled)

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

True **False** (circled)

6 points; 2 points each

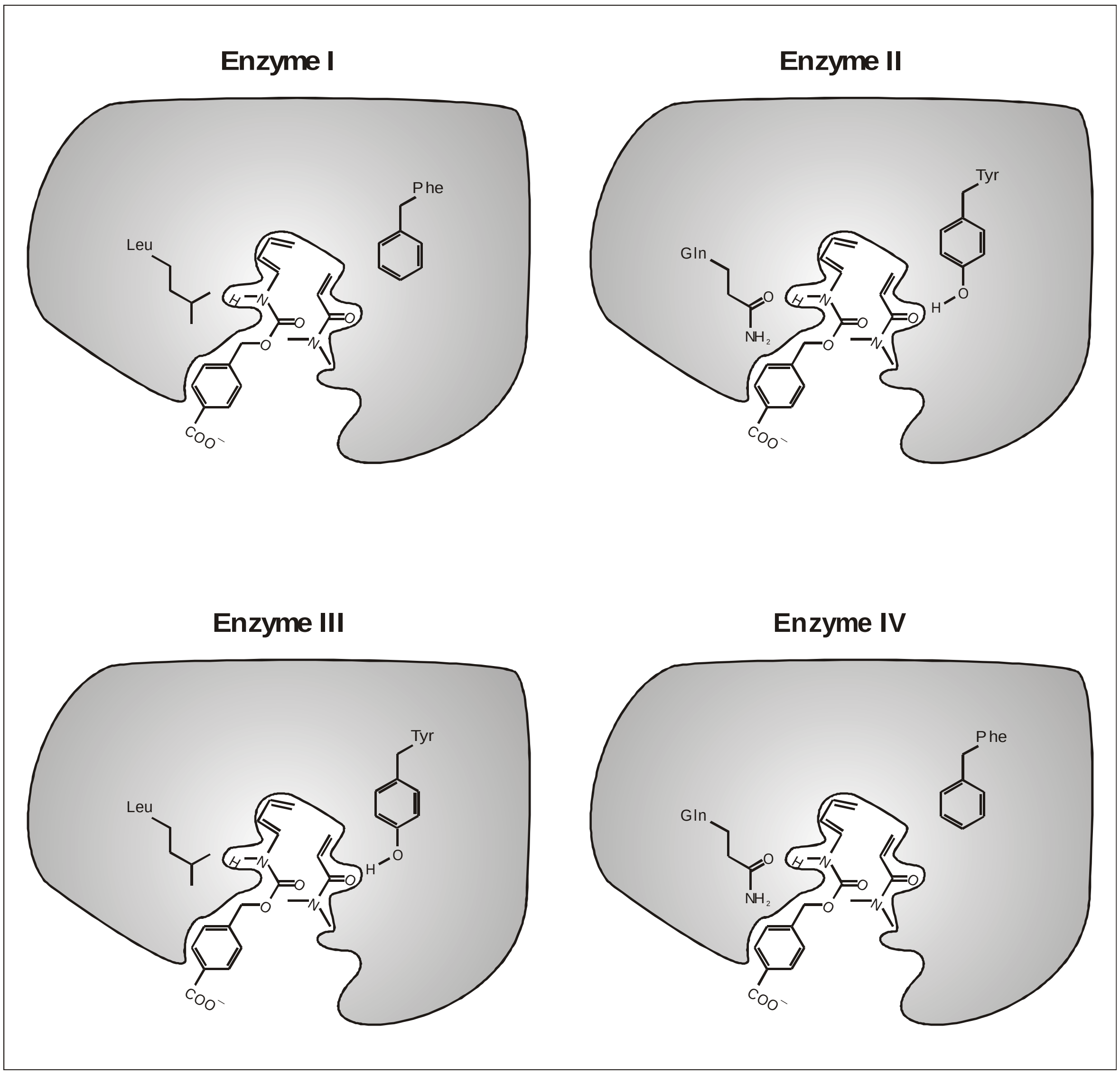
Name: Code:

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.

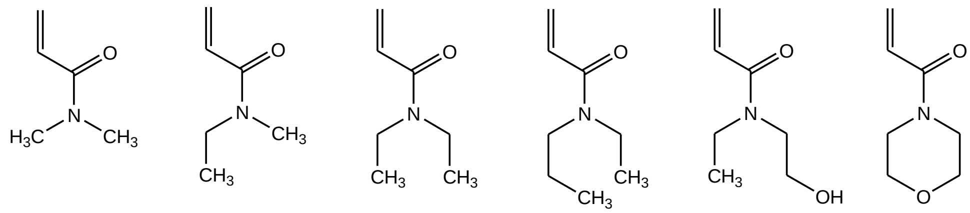
Of these four enzymes which one would cause the greatest increase in the rate of the Diels-Alder reaction compared to the uncatalyzed reaction?

Enzyme # II

8 points



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



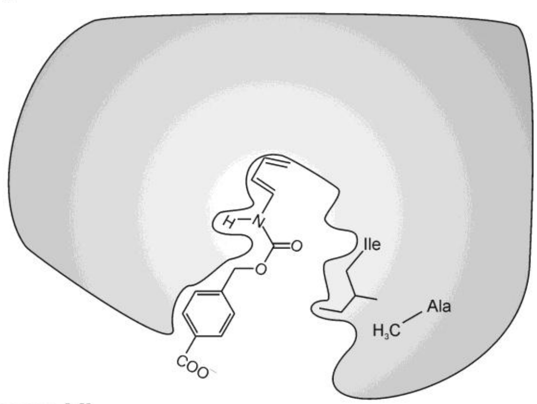
1 **2** **3** **4** **5** **6**

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**?

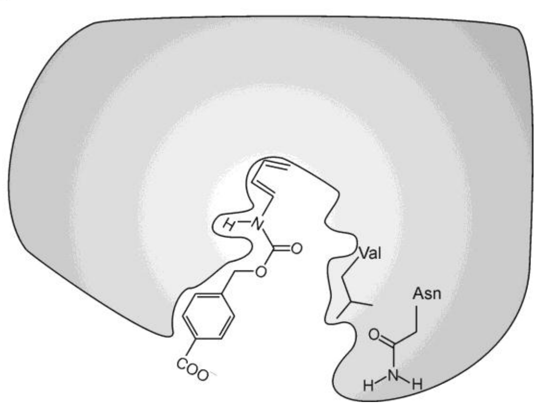
Dienophile # 5

6 points

Enzyme V



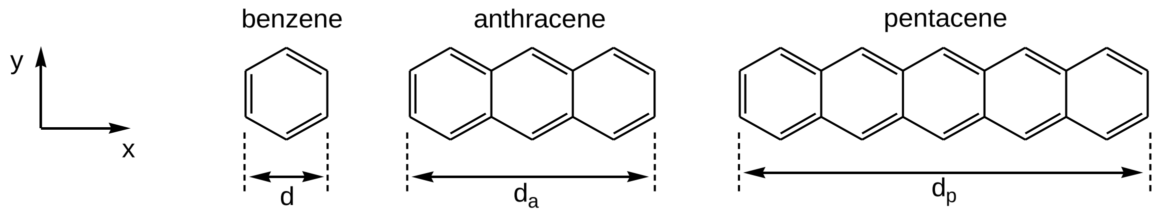
Enzyme VI



PROBLEM 8 8.3% of the Total

a	b-i	b-ii	b-iii	b-iv	b-v	c-i	c-ii	c-iii	Problem 8	
2	3	4	6	4	2	5	8	2	36	8.3%

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.



a. 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.

For anthracene, $d_a = 3(240\ pm) = 720\ pm$

For pentacene, $d_p = 5(240\ pm) = 1200\ pm$

1 point each
2 points total

b. Assume for simplicity that the π electrons of benzene can be modeled 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**.

i. For this problem, 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.

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

3 points

ii. 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 labeled 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)

Name: Code:

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:

__ (__; __)

__(_6_; _1_) __ (_3_; _2_)

↑↓ (_2_; _2_)

↑↓ (_1_; _2_)

↑↓ (_5_; _1_)

↑↓ (_4_; _1_)

↑↓ (_3_; _1_)

↑↓ (_2_; _1_)

↑↓ (_1_; _1_)

2 points for the correct placement of electrons and correct number of π electrons
2 points for the correct assignment of quantum numbers
4 points total
Note: Not penalty for labeling additional unoccupied energy levels

iii. Use this model to create an energy level diagram for benzene and fill the pertinent energy levels with electrons. Include energy levels up to and 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.

Benzene:

__ (_2_; _2_)

↑↓ (_2_; _1_) ↑↓ (_1_; _2_)

↑↓ (_1_; _1_)

2 points for the correct energy diagram
2 points for the correct placement of electrons and correct number of π electrons
2 points for the correct assignment of quantum numbers
6 points total

iv. 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. 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 ii) and iii) 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).

ΔE for benzene: $\Delta E = E(2;2) - E(1;2) = 3\frac{h^2}{8m_e d^2} = 3.14\times10^{-18}\,J$

Alternate solution:

$$\Delta E = E(3;2) - E(2;2) = 5\frac{h^2}{8m_e d^2} = 5.23\times10^{-18}\,J$$

ΔE for anthracene: $\Delta E = E(6;1) - E(2;2) = \frac{5}{9}\frac{h^2}{8m_e d^2} = 5.81\times10^{-19}\,J$

Alternate solution:

$$\Delta E = E(3;2) - E(2;2) = \frac{5}{9}\left(\frac{h^2}{8m_e d^2}\right) = 5.81\times10^{-19}\,J$$

ΔE for pentacene: $\Delta E = E(3;2) - E(9;1) = \frac{3}{25}\frac{h^2}{8m_e d^2} = 1.26\times10^{-19}\,J$

1 point for each, 3 points total

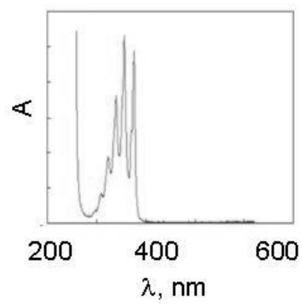
Rank benzene (**B**), anthracene (**A**), and pentacene (**P**) in order of increasing reactivity by placing the corresponding letters from left to right in the box below.

B **A** **P**

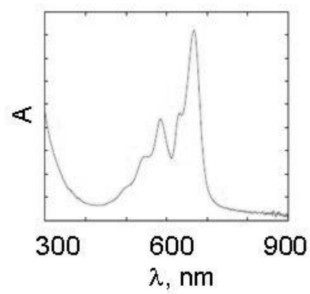
Least reactive -----------------------------------> Most reactive

1 point for correct ranking

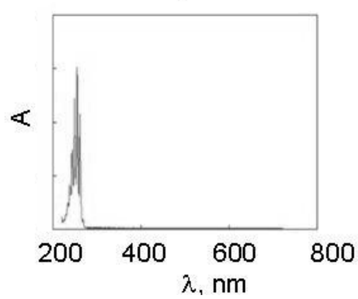
v. The electronic absorption spectra (molar absorptivity vs. wavelength) for benzene (**B**), anthracene (**A**), and pentacene (**P**) are shown below. Based on a qualitative understanding of the particle in the box model, indicate which molecule corresponds to which spectrum by writing the appropriate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



A



P



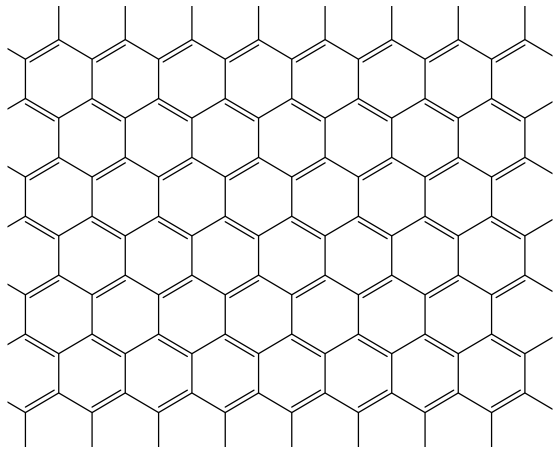
B

2 points: 0 correct = 0 points, 1 correct = 1 point , all correct = 2 points

Name: Code:

c. 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 nm by L_y=25 nm. A section of this sheet is shown below.



i. The area of one hexagonal 6-carbon unit is ~52400 pm^2. Calculate the number of π electrons in a (25 nm × 25 nm) sheet of graphene. For this problem you can ignore edge electrons (i.e., those outside the full hexagons in the picture).

The number of hexagonal units in the graphene sheet:

$$N_{units} = \frac{Area_{graphene}}{Area_{unit}} = \frac{(25000\ pm)^2}{52400\ pm^2} = 12000\ units$$

2points

Since each carbon atom in a graphene sheet is shared by three hexagonal units, each unit of the area 52400 pm^2 contains 6/3=2 carbon atoms contributing 2 π-electrons total.

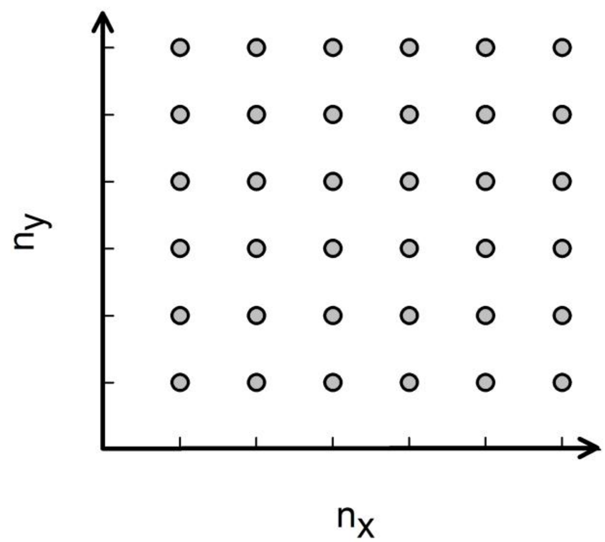
2points

Therefore, 12000 units contribute 12000 pairs of π-electrons.
Answer: 24,000 electrons.

1 point; total is 5 points

ii. 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. Determine the energy of the Fermi level for the 25 nm × 25 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 **i** or use a value of 1000 (this may not be the true value).



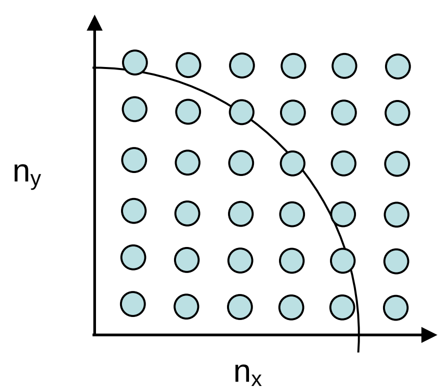
Two electrons fill each state, so the Fermi level has 12000 filled levels. This corresponds to the number of (n_x,n_y) pairs that are occupied.

Since $L_x=L_y$ and the lowest energy level's energy is approximated as zero,

$$\Delta E = E_{highest\_occupied} = \left(n_x^{\ 2} + n_y^{\ 2}\right)\frac{h^2}{8m_eL^2}$$

1 point

This is rearranged to the equation of a circle.



$$R^2 = \left(n_x^{\ 2} + n_y^{\ 2}\right) = \frac{E8m_eL^2}{h^2} = constant$$

2 points

The area of the populated grid is $Area_{grid} = \frac{\pi R^2}{4}$.

The area of each quantum number pair is 1.

1 point

Therefore, the number of points is given as

$$N_{points} = \frac{Area_{grid}}{Area_{pair}} = \frac{\pi R^2}{4} = N_{states} = 12000.$$

1 point

Rearranging and solving for energy yields the Fermi energy.

$$N_{states} = \frac{\pi R^2}{4} = \frac{\pi 8 m_e L^2 E}{4h^2} = 12000$$

$$E = \frac{4h^2(12000)}{\pi 8 m_e L^2} = 1.48 \times 10^{-18}\ \text{J}$$

3 points

Total: 8 points

Alternate solution:

$$N_{states} = \frac{\pi R^2}{4} = \frac{\pi 8 m_e L^2 E}{4h^2} = 1000$$

$$E = \frac{4h^2(1000)}{\pi 8 m_e L^2} = 1.23 \times 10^{-19}\ \text{J}$$

iii. 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 nm × 25 nm square of graphene, at a given temperature, is less than, equal to or greater than the conductivity of a 1 m × 1 m square of graphene (which is the largest obtained to date). Circle the correct answer:

less (circled) equal greater

The energy gaps decrease with the graphene sample size increase and the conductivity increases as the energy gap decreases.

2 points