2019 Fall Semester Midterm Examination

For General Chemistry II

Date: Oct 23 (Wed), ***Time Limit: 19:00 ~ 21:00***

Write down your information neatly in the space provided below; print your Student ID in the upper right corner of every page.

Professor Name	Class	Student I.D. Number	Name

Problem	points	Problem	points	TOTAL pts
1	/10	**6**	/9	**/100**
2	/12	**7**	/8	
3	/10	**8**	/10	
4	/10	**9**	/6	
5	/10	**10**	/15	

** This paper consists of 11 sheets with 10 problems (page 13 - 14: Equation, constants & periodic table, page 15: form for claiming credit). Please check all page numbers before taking the exam. Write down your work and answers in the Answer Sheet. Please numerical value of your answer with **<u>the appropriate unit</u>** when applicable. You will get 30% deduction for a missing unit.

NOTICE: SCHEDULES on RETURN and CLAIM of the MARKED EXAM PAPER.
(채점 답안지 분배 및 이의신청 일정)

1. Period, Location, and Procedure

1) Return and Claim Period: **Oct *28 (Mon, 7:00 ~ 8:00 p.m.)***
2) ***Location: Room for quiz sessions***
3) Procedure:

Rule 1: Students cannot bring their own writing tools into the room. (Use a pen only provided by TA)

Rule 2: Whether you have made a claim or not, you must submit the paper back to TA. (Do not go out of the room with it)

If you have any claims on it, you can submit the claim paper with your opinion. After writing your opinions on the claim form, please staple it to your mid-term paper. Submit them to TA. (The claim is permitted only during the designated period. Keep that in mind! A solution file with answers for the examination will be uploaded on the web.)

2. Final Confirmation

1) Period: **October 31 (Thu) – November 1(Fri)**
2) Procedure: During this period, you can check your final score of the examination *on the website* again.

***** For further information, please visit General Chemistry website at <u>www.gencheminkaist.pe.kr</u>.***

1. (total 10 pts)

Consider the following reaction mechanism:

$$\begin{aligned} 2\mathrm{NO} &\rightarrow \mathrm{N_2O_2} & \mathrm{Rate} &= \mathrm{k_1[NO]^2} \\ \mathrm{N_2O_2} &\rightarrow 2\mathrm{NO} & \mathrm{Rate} &= \mathrm{k_{-1}[N_2O_2]} \\ \mathrm{N_2O_2 + O_2} &\rightarrow 2\mathrm{NO_2} & \mathrm{Rate} &= \mathrm{k_2[N_2O_2][O_2]} \end{aligned}$$

(a) [5 pts] Use a steady-state approximation for the reaction intermediate to derive the rate of formation of NO_2, or d[NO_2]/dt.

(Answer)

$$\frac{\mathrm{d}[\mathrm{N}_2O_2]}{dt} = \mathrm{k}_1[NO]^2 - k_{-1}[N_2O_2] - k_2[N_2O_2][O_2] = 0$$

$$[\mathrm{N}_2O_2] = \frac{k_1[NO]^2}{k_{-1} + k_2[O_2]} \ldots + 2\mathrm{pt}$$

$$\therefore \frac{1}{2}\frac{\mathrm{d}[\mathrm{NO}_2]}{dt} = \mathrm{k}_2[N_2O_2][O_2] = \frac{k_1k_2[NO]^2[O_2]}{k_{-1} + k_2[O_2]}$$

$$\frac{\mathrm{d}[\mathrm{NO}_2]}{dt} = \frac{2k_1k_2[NO]^2[O_2]}{k_{-1} + k_2[O_2]} \ldots + 3\mathrm{pt}$$

(b) [5 pts] Suppose the concentration of O_2 is very large. Using this information, simplify the equation you derived in (a). Among the elementary reactions in the mechanism, which reaction becomes a rate-determining step?

(Answer)

$$\lim_{[O_2]\to\infty} \frac{\mathrm{d}[\mathrm{NO}_2]}{dt} = \lim_{[O_2]\to\infty} \frac{2k_1k_2[NO]^2[O_2]}{k_{-1} + k_2[O_2]} = 2k_1[NO]^2 \ldots + 3pt$$

Therefore, the first elementary reaction becomes a rate-determining step. …+ 2pt

2. (total 12 pts)

Consider the following reaction mechanism:

$$A(g) + bB(g) \rightarrow C(g)$$

$$\text{Rate} = k[A]$$

Where b is a positive integer.

The following table shows the pressure of a container where the reaction between A and B proceeds.

Trial	Initial total mass of reactants (g)	Total pressure inside the container (atm)		
		t =0 second	t = 100 s	t = ∞
1	10.0	12.0	8.0	4.0
2	13.0	18.0	14.0	10.0
3	x	16.0	10.0	y

For Trial 1, all A and B molecules are consumed at t = ∞. Assume that temperature is constant throughout the reaction and there is no reverse reaction.

(a) [4 pts] For Trial 1, what is the partial pressure of A at t = 0?

(Answer)

By Dalton's law, the total pressure in the container is equal to the sum of partial pressure of each individual gas. Therefore, pressure is directly proportional to the total number of molecules inside the container.

At the end of trial 1, only C molecules remain and exhibit 4 atm of pressure alone. Pressure decreased from 12 atm to 4 atm; this indicates that 3 molecules react to become one molecule. Therefore, b = 2.

Because all A and B molecules are consumed, their initial proportion must be exactly 1:2. Therefore, the partial pressure of A at t = 0 is $12.00 \ \text{atm} \times \frac{1}{3} = 4.00 \ atm.$

+ 2pts for the correct number of b

Full pts for the correct answer

(b) [4 pts] For Trial 2, what is the total mass of B at t = 0?

(Answer)

At t = 100 s, we can see that total pressure decreased by the same amount in trial 1. This indicates that partial pressure of A is the same in trial 1 and 2, because the rate of this reaction is first-order in A. Therefore, initial partial pressure of B is 14.0 atm.

From trial 1, we can figure out that 4.0 atm of A and 8.0 atm of B equals to 10.0 g. From trial 2, we can figure out that 4.0 atm of A and 14.0 atm of B equals to 13.0 g. If m_A = weight of A per atm and m_B = weight of B per atm,

$$4.0 \times m_A + 8.0 \times m_B = 10.0 \ g$$

$$4.0 \times m_A + 14.0 \times m_B = 13.0 \ g$$

Solving these equations yields:

$$m_A = 1.5\ g \cdot atm^{-1}, m_B = 0.5\ g \cdot atm^{-1}$$

$$\therefore \text{Total mass of B} = 0.5\text{g} \cdot \text{atm}^{-1} \times 14.0\ \text{atm} = 7.0\ g$$

+ 2pt for correct initial partial pressure of B

Full pts for the correct answer

(c) [4 pts] Calculate x (g) and y (atm).

(Answer)

At t = 100 s for trial 3, total pressure decreases by 6 atm. This rate is 1.5 times faster than that of trial 1 and trial 2, so partial pressure of A must be 1.5 times bigger. Therefore, there is 6.0 atm of A and 10.0 atm of B at t = 0.

$$\therefore x = 6.0\ \text{atm} \times 1.5\ \text{g} \cdot \text{atm}^{-1} + 10.0\ atm \times 0.5g \cdot atm^{-1} = 14.0\ g$$

For trial 3, B is a limiting reagent: 5.0 atm of A and 10.0 atm of B is consumed to give 5.0 atm of C with 1.0 atm of A remaining. Therefore, y = 5.0 atm + 1.0 atm = 6.0 atm

+ 2pt for correct x

+ 2pt for correct y

3. (total 10 pts)

Answer the following questions.

(a) [4 pts, each 2 pts] What are the two conservation laws important for spectroscopy?

(Answer)

(1) Energy conservation. (2) Angular momentum conservation.

(b) [6 pts, each 2 pts] Connect the relevant parties in the following two groups. (For example, A-i, B-ii, C-iii)

A. Bond lengths, bond angles

B. Bond force constants and effective reduced mass

C. Functional groups and their relative locations in molecules

i. Vibrational and NMR spectroscopy

ii. Microwave, IR, Raman spectroscopy

iii. Vibrational spectroscopy

(Answer)

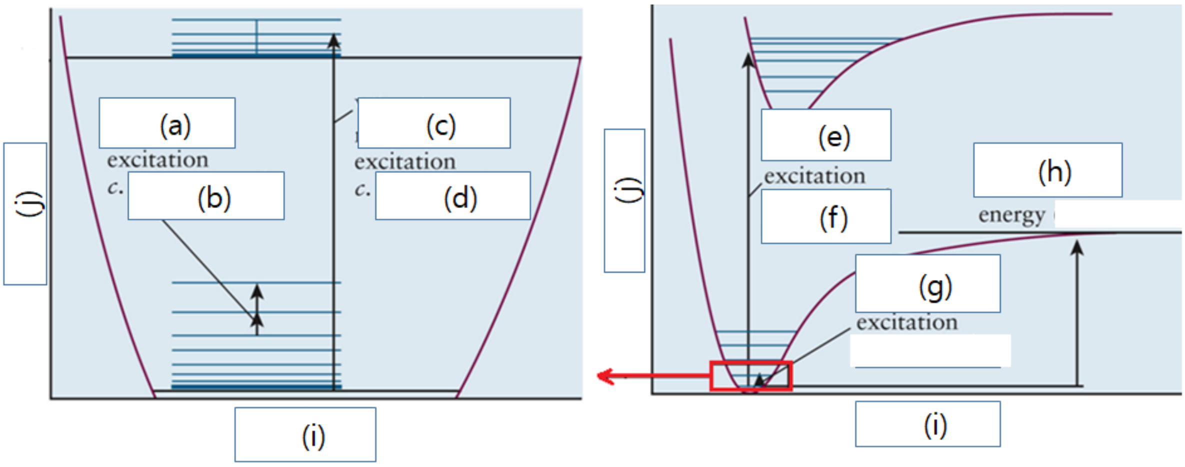
A-ii, B-iii, C-i

4. (total 10 pts, each 1 pt)

Fill the blanks in the following diagram using the given examples.

Examples: emission, fluorescence, bimolecular, unimolecular, nuclear, vibrational, rotational, rigid-rotor, harmonic oscillator, electronic, vibration-rotation, electronic-vibrational, rotation-electronic, dissociation, chemical, energy transfer, electron transfer, 0.1-1 nm, 1-10 nm, 10-100 nm, 0.01-0.1 cm^{-1}, 0.1 - 1 cm^{-1}, 20 - 200 cm^{-1}, 3000 cm^{-1}, 80000 cm^{-1}, 95 eV, 950 eV, 9500 eV, I, B, R_{AB}, Energy, hc, hv, $E=mc^2$.

Answer example) (a) chemical, (b) 0.01-0.1 cm^{-1}, etc.



(Answer)

(a) rotational, (b) 20 - 200 cm^{-1}, (c) vibration-rotation, (d) 3000 cm^{-1}, (e) electronic, (f) 80000 cm^{-1}, (g) vibrational, (h) dissociation, (i) R_{AB}, (j) Energy

5. (total 10 pts)

Answer the following questions.

(a) [3 pts] Which of the following molecules may show a rotational microwave absorption spectrum? Give a brief explanation.

$$H_2, \quad HCl, \quad CH_4, \quad CH_3Cl, \quad CH_2Cl_2$$

(Answer)

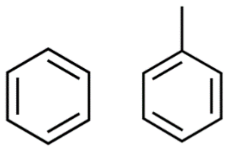
A molecule must have a permanent dipole moment.

HCl, CH_3Cl, CH_2Cl_2

+1 pt for each correct answer

- 1pt for each incorrect answer

(b) [3 pts] How many normal modes of vibration are there for the following molecules?



H-C≡C-C≡C-H

(Answer)

i) benzene: 3 x 12 – 6 = 30 vibrational modes

ii) toluene: ~~3 x 16 – 6 = 42~~ 3 x 15 – 6 = 39 vibrational modes

iii) This molecule is linear. It has 3 x 6 – 5 = 13 normal modes

+1 pt for each correct answer

(c) [4 pts, each 2pts] Consider the vibrational mode that corresponds to the uniform expansion of the benzene ring. (i) Is this mode infrared active? (ii) Is this mode Raman active? Give a brief explanation for each.

(Answer)

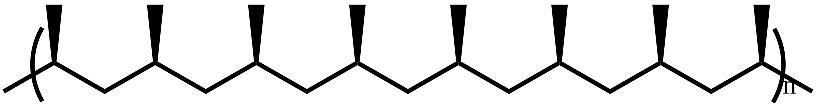
If the ring expands in a uniform fashion, overall dipole moment of the molecule does not change. Meanwhile, because all the bonds stretch symmetrically, bonds oscillate in phase and bond polarizability changes. Therefore, it is Raman active and infrared inactive.

+ 2pt for each correct explanation (IR and Raman)

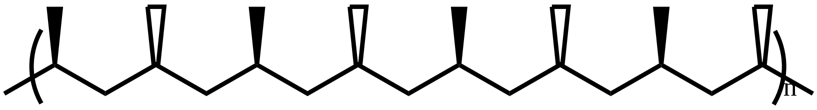
6. (total 9 pts, each 3 pts)

Polypropylene can exist in three different configurations. Draw the structures of polypropylene indicating the different stereochemistry. Provide the appropriate terms for each different configuration of the polymers.

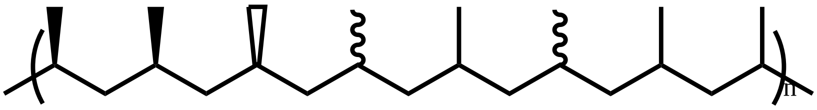
(Answer)



isotactic



syndiotactic



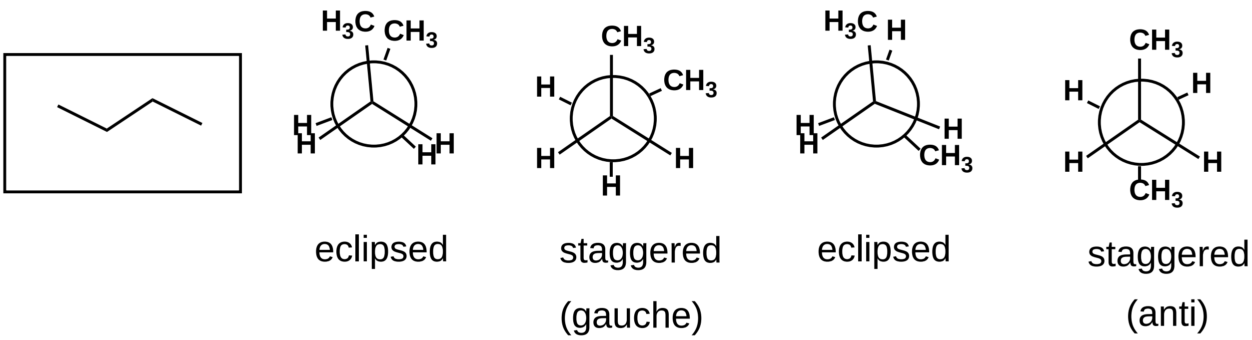
atactic

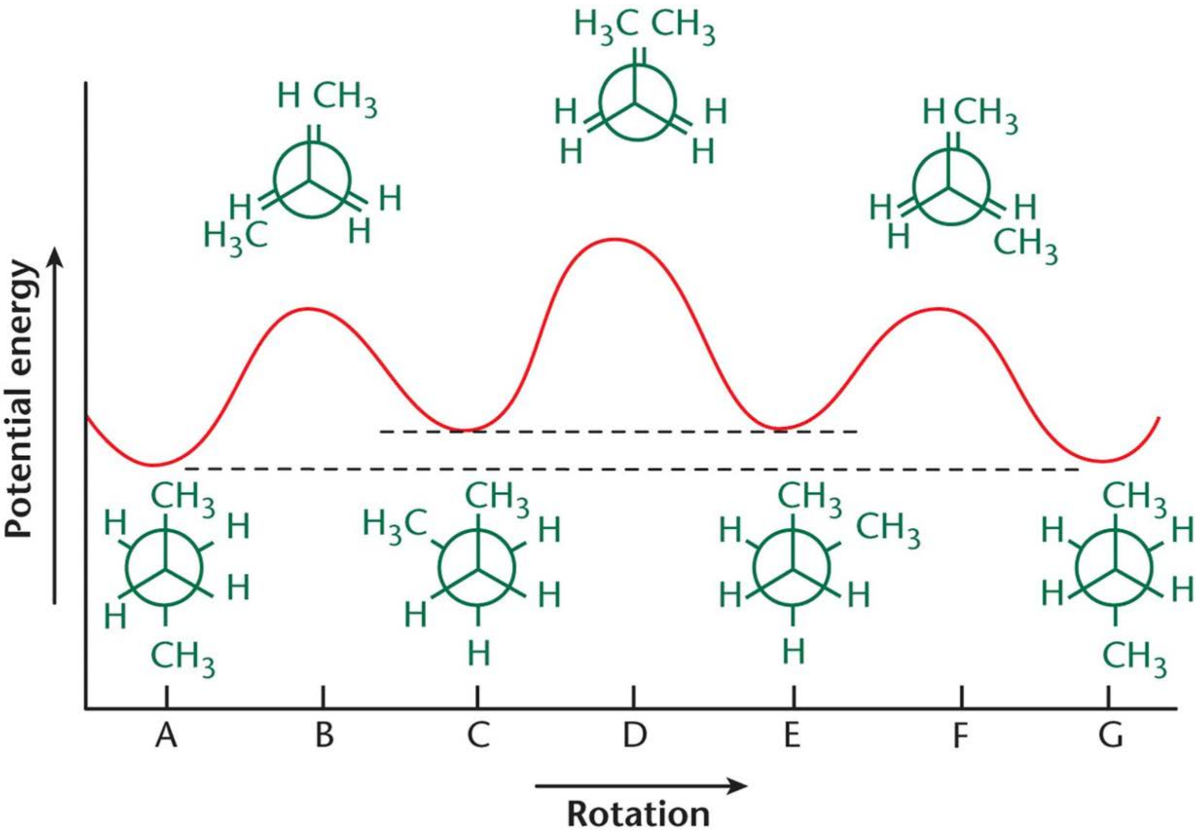
Regarding notation to present the tacticity (stereochemistry), any structural drawing which can be understandable should have credits.

7. (total 8 pts, each 2 pts)

Describe conformational isomers of n-butane. Present eclipsed, gauche, anti conformations of n-butane with their relative energy difference by presenting a graph (energy versus dihedral angle between two CH_3 groups of n-butane). You do not need to specify value of the energy differences but indicate that relative energies (which is higher and which is lower, etc) of the conformational isomers clearly.

(Answer)



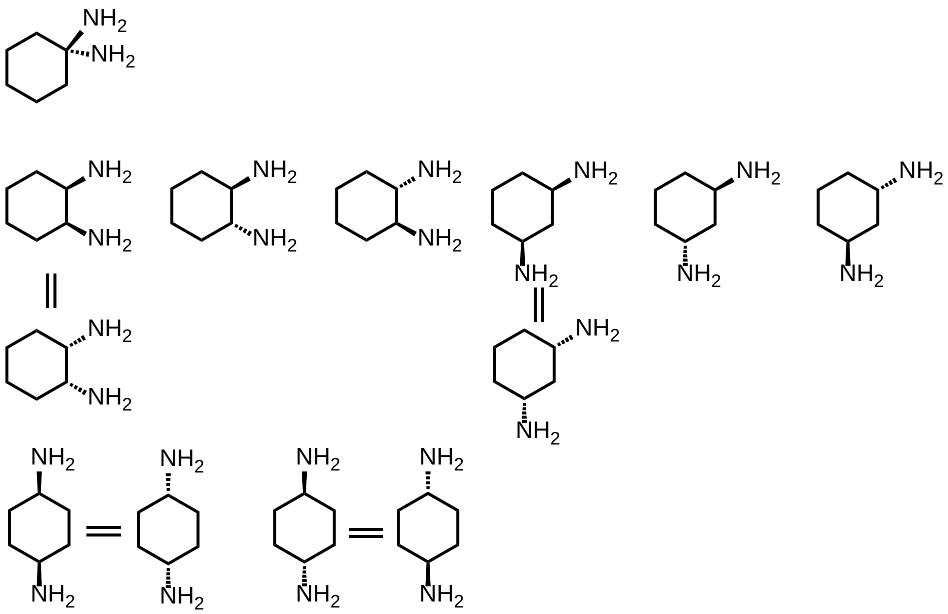


8. (total 10 pts)

The structure of cyclohexanediamine($C_6H_{14}N_2$) compound has two amine substituents on cyclohexane ring.

(a) [5 pts] Please write ***all possible structures*** for this compound(cyclohexanediamine), including ***stereoisomers.***

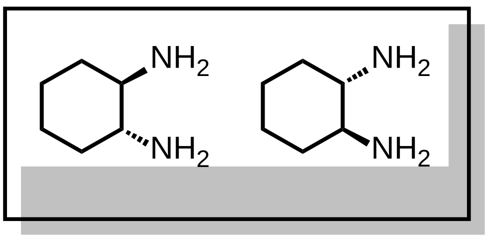
(Answer)

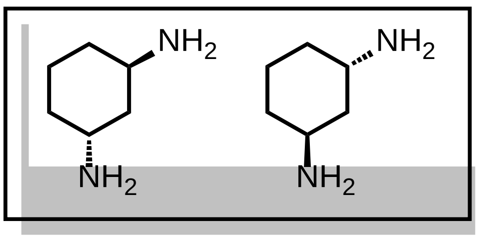


If draw all 9 isomers => 5 points,
If not, each isomer => 0.5 point.

(b) [2 pts] Among the structures in the answer (a), identify ***pairs of compounds*** that have same physical properties except optical rotation.

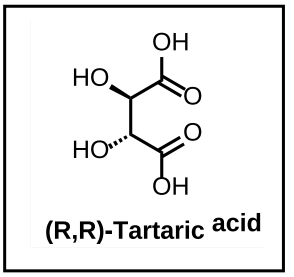
(Answer)



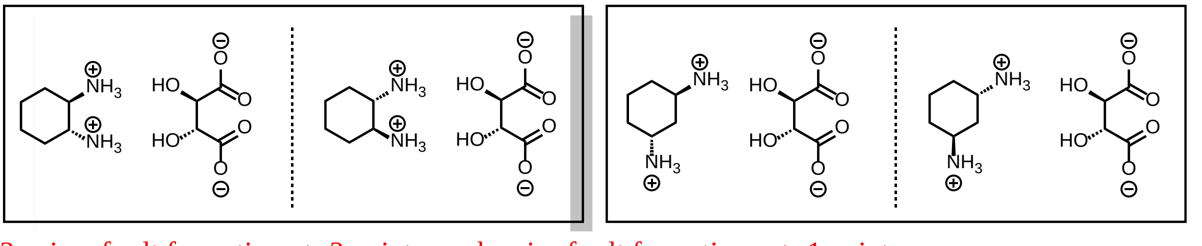


2 pairs, each pair => 1 point.

(c) [3 pts] The pairs in answer (b) could be distinguished and separated by reacting with (R,R)-tartaric acid shown below. Please draw all possible salt products with pairs in answer (b) and (R,R)-tartaric acid. Explain why the pair can be distinguished by this reaction.



(Answer)



2 pairs of salt formation => 2 points, each pair of salt formations => 1 point.
The salt products are diastereomers.=> 1 point.

9. (total 6 pts)

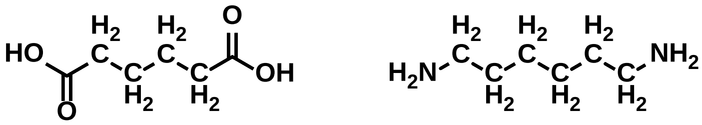
There are different types of polymerization reactions. Polymerization to form nylon 66 involves condensation reaction.

(a) [2 pts] What is a condensation reaction?

(Answer)

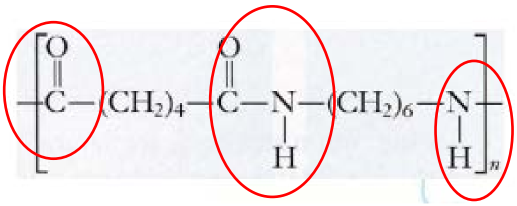
A reaction in which two molecules combine to form (1pt) a larger molecule, producing a small molecule (eg. H_2O) as a byproduct (1pt)

(b) [4 pts] Draw the monomer unit of nylon 66, which is generated by the repeated reaction of adipic acid and hexamethylenediamine.



Adipic acid **Hexamethylenediamine**

(Answer)



to get full, 4pts, :correct ends with bracket (2 pts)
amide bond formed (1pt)

rest of the structure should be correct (correct numbers of carbon, hydrogen…etc on the drawing)

10. (total 15 pts)

A ***natural product*** is a chemical compound or substance found in nature. In the field of organic chemistry, natural products are purified organic compounds isolated from natural sources that are produced by the pathways of primary or secondary metabolism. These natural products also can be prepared by chemical synthesis.

(a) [2 pts] Write the definition of a chiral center.

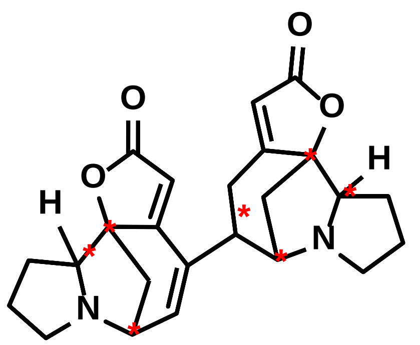
(Answer)

An atom that has all four (1pt) different groups (1pt) attached to it.

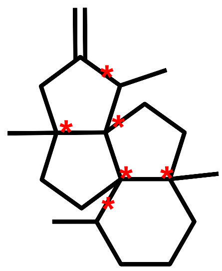
(b) [13 pts, each 1pt] Flueggenine C, a dimeric securinega alkaloid, is a natural product synthesized in Professor Sun Kyu Han's group. Another natural product, Waihoensene, which is a tetracyclic diterpene containing an angular triquinane, and was synthesized in Professor Hee-Yoon Lee's group. They were both synthesized for the first time.

Mark all the chiral centers (stereocenters) for Flueggenine C and Waihoenesene with asterisks (*).

(Answer)



Flueggenine C (Han, 2017)



Waihoensene (Lee, 2017)

Physical Constants

Avogadro's number	N_A = 6.02214179 x 10^{23} mol^{-1}
Bohr radius	a_0 = 0.52917720859 Å = 5.2917720859 x 10^{-11} m
Boltzmann's constant	K_B = 1.3806504 x 10^{-23} J K^{-1}
Electronic charge	e = 1.602176487 x 10^{-19} C
Faraday constant	F = 96485.3399 C mol^{-1}
Masses of fundamental particles:	
Electron	m_e = 9.10938215 x 10^{-31} kg
Proton	m_P = 1.672621637 x 10^{-27} kg
Neutron	m_n= 1.674927211 x 10^{-27} kg
Permittivity of vacuum	ε_o = 8.854187817 x 10^{-12} C^{-2} J^{-1} m^{-1}
Planck's constant	h = 6.62606896 x 10^{-34} J s
Ratio of proton mass to electron mass	m_P / m_e = 1836.15267247
Speed of light in a vacuum	c = 2.99792458 x 10^8 m s^{-1} (exactly)
Standard acceleration of terrestrial gravity	g = 9.80665 m s^{-2} (exactly)
Universal gas constant	R = 8.314472 J mol^{-1} K^{-1} = 0.0820574 L atm mol^{-1} K^{-1}

Values are taken from the 2006 CODATA recommended values,
as listed by the National Institute of Standards and Technology.

Conversion factors

Ångström	1 Å= 10^{-10} m
Atomic mass unit	1 u = 1.660538782 x 10^{-27} kg
	1 u = 1.492417830 x 10^{-10} J = 931.494028 MeV (energy equivalent form $E = mc^2$)
Calorie	1 cal = 4.184 J (exactly)
Electron volt	1 eV = 1.602177 x 10^{-19} J = 96.485335 kJ mol^{-1}
Foot	1 ft = 12 in = 0.3048 m (exactly)
Gallon (U. S.)	1 gallon = 4 quarts = 3.785412 L (exactly)
Liter	1 L = 10^{-3} m^{-3} = 10^3 cm^3 (exactly)
Liter-atmosphere	1 L atm = 101.325 J (exactly)
Metric ton	1 t = 1000 kg (exactly)
Pound	1 lb = 16 oz = 0.4539237 kg (exactly)
Rydberg	1 Ry = 2.17987197 x 10^{-18}J = 1312.7136 kJ mol^{-1} = 13.60569193 eV
Standard atmosphere	1 atm = 1.01325 x 10^5 Pa = 1.01325 x 10^5 kg m^{-1} s^{-2} (exactly)
Torr	1 torr = 133.3224 Pa

PERIODIC TABLE OF THE ELEMENTS

http://www.ktf-split.hr/periodni/en/

GROUP NUMBERS IUPAC RECOMMENDATION (1985) — 13

GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986) — IIIA

ATOMIC NUMBER — 5; RELATIVE ATOMIC MASS (1) — 10.811; SYMBOL — B; ELEMENT NAME — BORON

PERIOD	GROUP 1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 (VIIIB)	9 (VIIIB)	10 (VIIIB)	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 **H** HYDROGEN																	2 4.0026 **He** HELIUM
2	3 6.941 **Li** LITHIUM	4 9.0122 **Be** BERYLLIUM											5 10.811 **B** BORON	6 12.011 **C** CARBON	7 14.007 **N** NITROGEN	8 15.999 **O** OXYGEN	9 18.998 **F** FLUORINE	10 20.180 **Ne** NEON
3	11 22.990 **Na** SODIUM	12 24.305 **Mg** MAGNESIUM											13 26.982 **Al** ALUMINIUM	14 28.086 **Si** SILICON	15 30.974 **P** PHOSPHORUS	16 32.065 **S** SULPHUR	17 35.453 **Cl** CHLORINE	18 39.948 **Ar** ARGON
4	19 39.098 **K** POTASSIUM	20 40.078 **Ca** CALCIUM	21 44.956 **Sc** SCANDIUM	22 47.867 **Ti** TITANIUM	23 50.942 **V** VANADIUM	24 51.996 **Cr** CHROMIUM	25 54.938 **Mn** MANGANESE	26 55.845 **Fe** IRON	27 58.933 **Co** COBALT	28 58.693 **Ni** NICKEL	29 63.546 **Cu** COPPER	30 65.39 **Zn** ZINC	31 69.723 **Ga** GALLIUM	32 72.64 **Ge** GERMANIUM	33 74.922 **As** ARSENIC	34 78.96 **Se** SELENIUM	35 79.904 **Br** BROMINE	36 83.80 **Kr** KRYPTON
5	37 85.468 **Rb** RUBIDIUM	38 87.62 **Sr** STRONTIUM	39 88.906 **Y** YTTRIUM	40 91.224 **Zr** ZIRCONIUM	41 92.906 **Nb** NIOBIUM	42 95.94 **Mo** MOLYBDENUM	43 (98) **Tc** TECHNETIUM	44 101.07 **Ru** RUTHENIUM	45 102.91 **Rh** RHODIUM	46 106.42 **Pd** PALLADIUM	47 107.87 **Ag** SILVER	48 112.41 **Cd** CADMIUM	49 114.82 **In** INDIUM	50 118.71 **Sn** TIN	51 121.76 **Sb** ANTIMONY	52 127.60 **Te** TELLURIUM	53 126.90 **I** IODINE	54 131.29 **Xe** XENON
6	55 132.91 **Cs** CAESIUM	56 137.33 **Ba** BARIUM	57-71 **La-Lu** Lanthanide	72 178.49 **Hf** HAFNIUM	73 180.95 **Ta** TANTALUM	74 183.84 **W** TUNGSTEN	75 186.21 **Re** RHENIUM	76 190.23 **Os** OSMIUM	77 192.22 **Ir** IRIDIUM	78 195.08 **Pt** PLATINUM	79 196.97 **Au** GOLD	80 200.59 **Hg** MERCURY	81 204.38 **Tl** THALLIUM	82 207.2 **Pb** LEAD	83 208.98 **Bi** BISMUTH	84 (209) **Po** POLONIUM	85 (210) **At** ASTATINE	86 (222) **Rn** RADON
7	87 (223) **Fr** FRANCIUM	88 (226) **Ra** RADIUM	89-103 **Ac-Lr** Actinide	104 (261) **Rf** RUTHERFORDIUM	105 (262) **Db** DUBNIUM	106 (266) **Sg** SEABORGIUM	107 (264) **Bh** BOHRIUM	108 (277) **Hs** HASSIUM	109 (268) **Mt** MEITNERIUM	110 (281) **Uun** UNUNNILIUM	111 (272) **Uuu** UNUNUNIUM	112 (285) **Uub** UNUNBIUM		114 (289) **Uuq** UNUNQUADIUM				

LANTHANIDE

Period															
6	57 138.91 **La** LANTHANUM	58 140.12 **Ce** CERIUM	59 140.91 **Pr** PRASEODYMIUM	60 144.24 **Nd** NEODYMIUM	61 (145) **Pm** PROMETHIUM	62 150.36 **Sm** SAMARIUM	63 151.96 **Eu** EUROPIUM	64 157.25 **Gd** GADOLINIUM	65 158.93 **Tb** TERBIUM	66 162.50 **Dy** DYSPROSIUM	67 164.93 **Ho** HOLMIUM	68 167.26 **Er** ERBIUM	69 168.93 **Tm** THULIUM	70 173.04 **Yb** YTTERBIUM	71 174.97 **Lu** LUTETIUM

ACTINIDE

Period															
7	89 (227) **Ac** ACTINIUM	90 232.04 **Th** THORIUM	91 231.04 **Pa** PROTACTINIUM	92 238.03 **U** URANIUM	93 (237) **Np** NEPTUNIUM	94 (244) **Pu** PLUTONIUM	95 (243) **Am** AMERICIUM	96 (247) **Cm** CURIUM	97 (247) **Bk** BERKELIUM	98 (251) **Cf** CALIFORNIUM	99 (252) **Es** EINSTEINIUM	100 (257) **Fm** FERMIUM	101 (258) **Md** MENDELEVIUM	102 (259) **No** NOBELIUM	103 (262) **Lr** LAWRENCIUM

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.
However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

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<u>**Claim Form for General Chemistry Examination**</u> **Page (/)**

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