Chem 201 Midterm
Fall, 2018

Beauchamp   Name _____Key_____

Problems	Points	Credit
1. Functional Group Nomenclature (1 large structure)	30	
2. Resonance, Formal Charge, Arrows	18	
3. Cyclohexane Conformations, Newman Projections	30	
4. Newman Projections, Conformational Energies	25	
5. Stereochemical Analysis	30	
6. 3D Structure, Resonance, Hybridization, Angles, Shapes (1)	36	
7. 2D Lewis Structures (1, large)	25	
8. Functional Groups, Names or Types of Isomers or Special Types of Carbons and Substituents, Degrees of Unsaturation	28	
9. Forces of Interaction and Physical Properties	19	
10. Properties of Atoms, (ionization potential, Z_{eff}, radii, electronegativity), Logic Arguments of Organic Chemistry (inductive, resonance, steric)	26	
Total	267	

This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement where appropriate. Partial credit is given for any partially correct responses. Do your best to show me what you know in the time available.
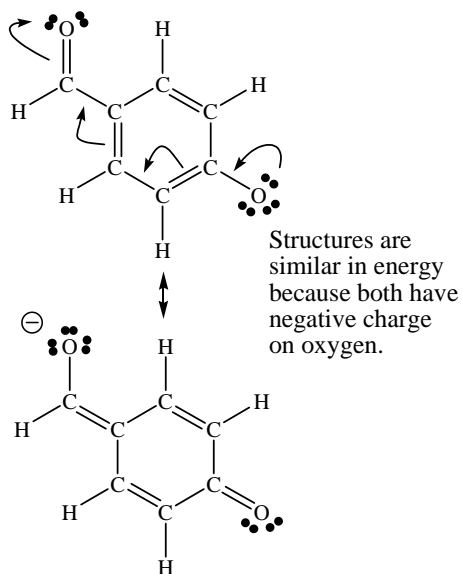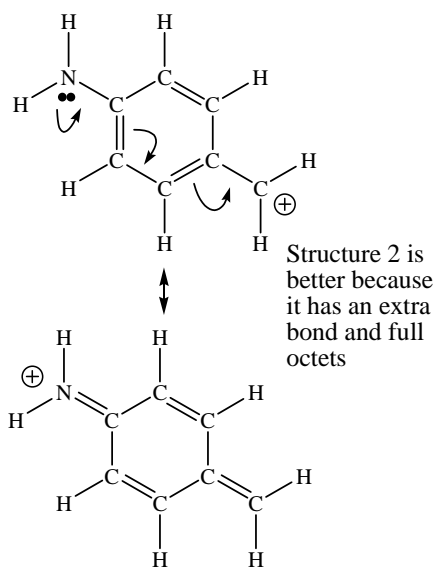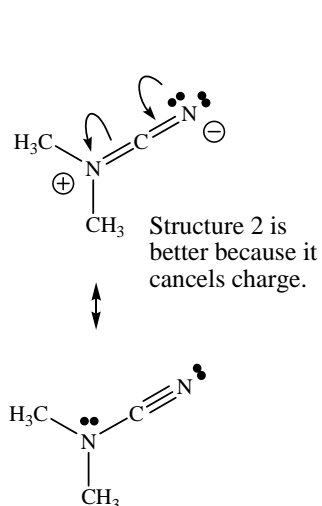
The wise does at once what the fool does at last.   Baltasar Gracian

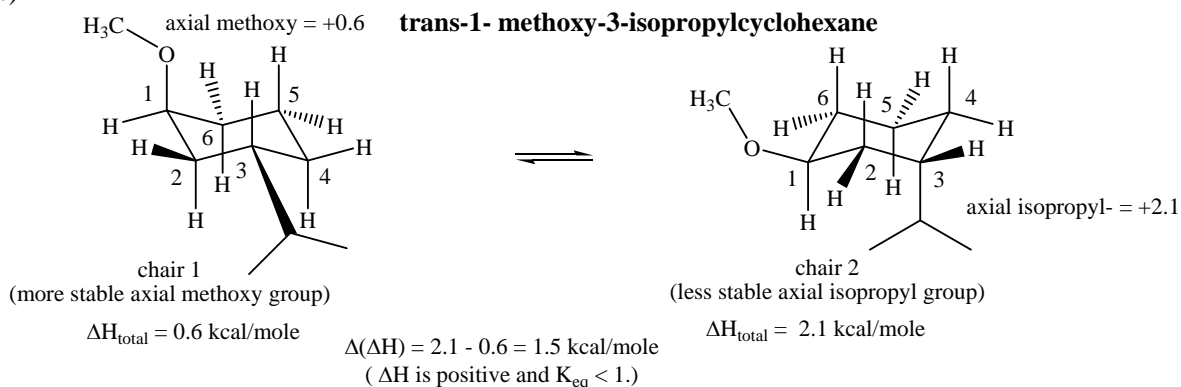1. Provide an acceptable name for the following molecule. Only specify R and S where shown as 3D. (30 pts)
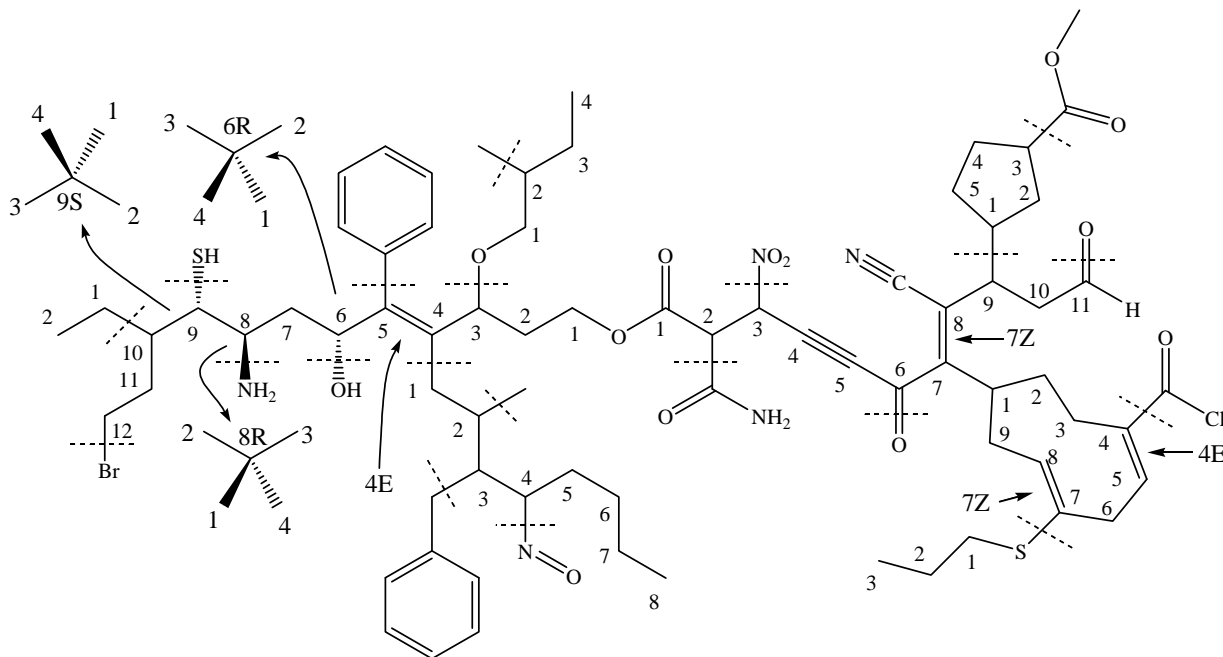
(4E,6R,8R,9S) 3-(2-methylbutoxy)-4-(2-methyl-3-benzyl-4-nitrosooctyl)-5-phenyl-6-hydroxy-8-amino-9-mercapto-

10-ethyl-12-bromododec-4-enyl 2-amido-3-nitro-6,11-dioxo-7-(4-chlorocarbonyl-7-propylthiocyclonona-4E,7Z-dienyl)-

8-cyano-9-(3-methoxycarbonylcyclopentyl)undec-7Z-en-4-ynoate

2. Indicate all formal charges present in the following structures. Assume all electrons are shown as lines or dots. If other reasonable resonance structures are possible, draw the **best** other resonance structure using the proper arrow conventions. Indicate which resonance structure is better or if they are equivalent with a brief reason why. (18 pts)
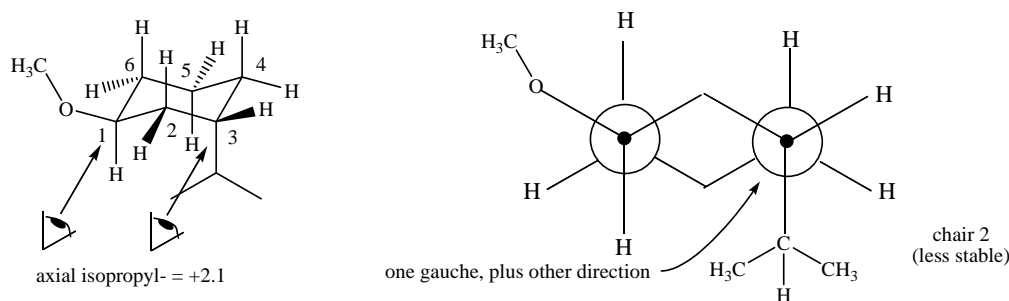

Structure 2 is better because it cancels charge.

Structure 2 is better because it has an extra bond and full octets

Structures are similar in energy because both have negative charge on oxygen.

3. Draw all possible chair conformations of trans-1- methoxy-3-isopropylcyclohexane. The axial energy of a methoxy group is 0.6 kcal/mole and the axial energy of isopropyl is 2.1 kcal/mole. The gauche energy of methoxy/isopropyl is 0.9 kcal/mole. Make the left most ring carbon C_1 and number towards the front. Show **all** axial and equatorial groups in the first chair. Which conformation is more stable? Provide a reason for your answer. Draw a Newman projection of the <u>least</u> stable conformation using the $C_1 \rightarrow C_6$ and $C_3 \rightarrow C_4$ bonds to sight along. Point out any gauche interactions of the substituents shown in your Newman projection. Sketch an energy diagram that shows how the energy changes (lower to higher) with the conformational changes and estimate the ratio of the two conformations at equilibrium. Show your work.
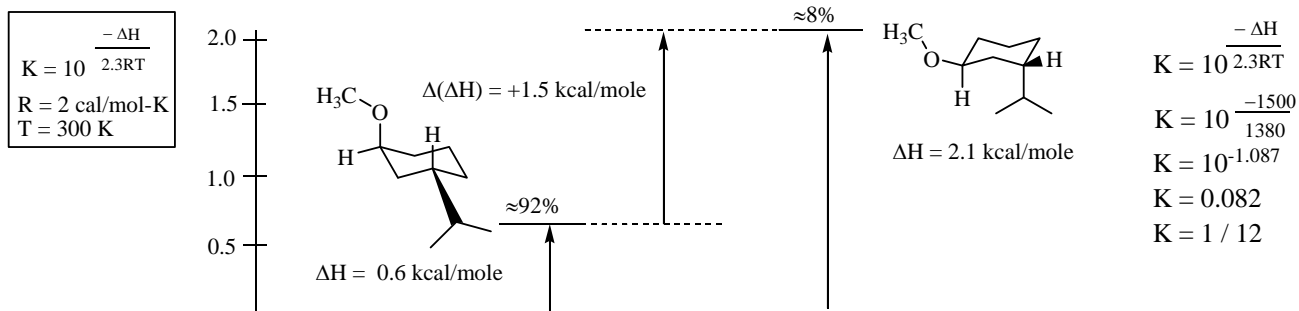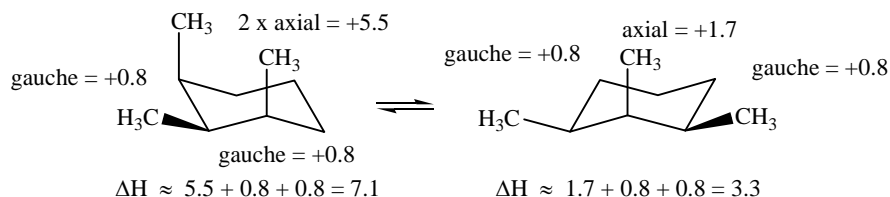
a. (15 pts)

axial methoxy = +0.6   **trans-1- methoxy-3-isopropylcyclohexane**

axial isopropyl- = +2.1

chair 1
(more stable axial methoxy group)
$\Delta H_{total} = 0.6$ kcal/mole

$\Delta(\Delta H) = 2.1 - 0.6 = 1.5$ kcal/mole
(ΔH is positive and $K_{eq} < 1$.)

chair 2
(less stable axial isopropyl group)
$\Delta H_{total} = 2.1$ kcal/mole

b. Newman projection $(C_1 \rightarrow C_6$ and $C_3 \rightarrow C_4$) – <u>least</u> stable, point out any gauche interactions with the substituent(s). (5 pts)

axial isopropyl- = +2.1

one gauche, plus other direction

chair 2
(less stable)

c. Energy diagram and relative percents $(K_{eq} = ?)$ (5 pts)

$K = 10^{\frac{-\Delta H}{2.3RT}}$
$R = 2$ cal/mol-K
$T = 300$ K

$\Delta(\Delta H) = +1.5$ kcal/mole

≈8%

≈92%

$\Delta H = 0.6$ kcal/mole

$\Delta H = 2.1$ kcal/mole

$K = 10^{\frac{-\Delta H}{2.3RT}}$

$K = 10^{\frac{-1500}{1380}}$

$K = 10^{-1.087}$

$K = 0.082$

$K = 1 / 12$

d. Calculate an approximate ΔH difference between the two conformations. Use that value to estimate a K_{eq}. (Assume $R = 2$ cal/mol-K and $T = 300$ K.) Use energy values provided in the box. Show your work. (5 pts)

CH_3 2 x axial = +5.5
gauche = +0.8
CH_3
H_3C
gauche = +0.8
$\Delta H \approx 5.5 + 0.8 + 0.8 = 7.1$

gauche = +0.8   axial = +1.7
CH_3
H_3C gauche = +0.8
CH_3
$\Delta H \approx 1.7 + 0.8 + 0.8 = 3.3$

The energy table is not shown here.

$\Delta(\Delta H) = 3.3 - 7.1 = -3.8$ kcal/mole

$K = 10^{\frac{-(-3800)}{1380}} = 10^{2.75} = 570 / 1$

4. Use a Newman projection of the C3→C4 bond of 2,2,3-trimethyl-4-phenylhexane to **show the most stable conformation first**. Rotate through all of the eclipsed and staggered conformations. Using the energy values provided in the tables below, calculate the relative energies of the different conformations. Plot the changes in energy in the graph diagram provided. Calculate a ratio of least stable to most stable based on ΔH values. Hint: Draw a 2D structure first and "bold" the bond viewed in your Newman projection, then decide your line of sight. (25 pts)
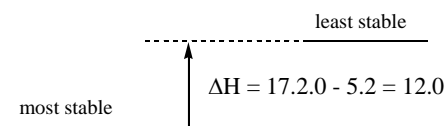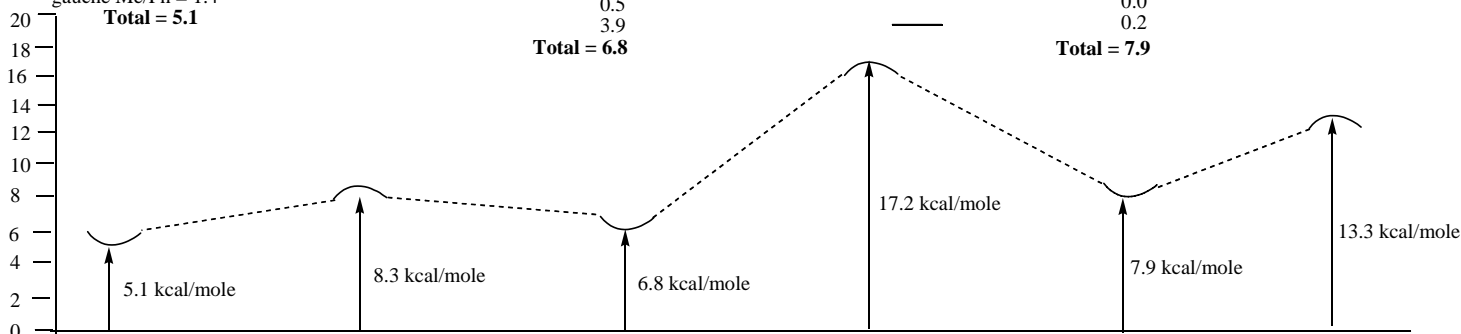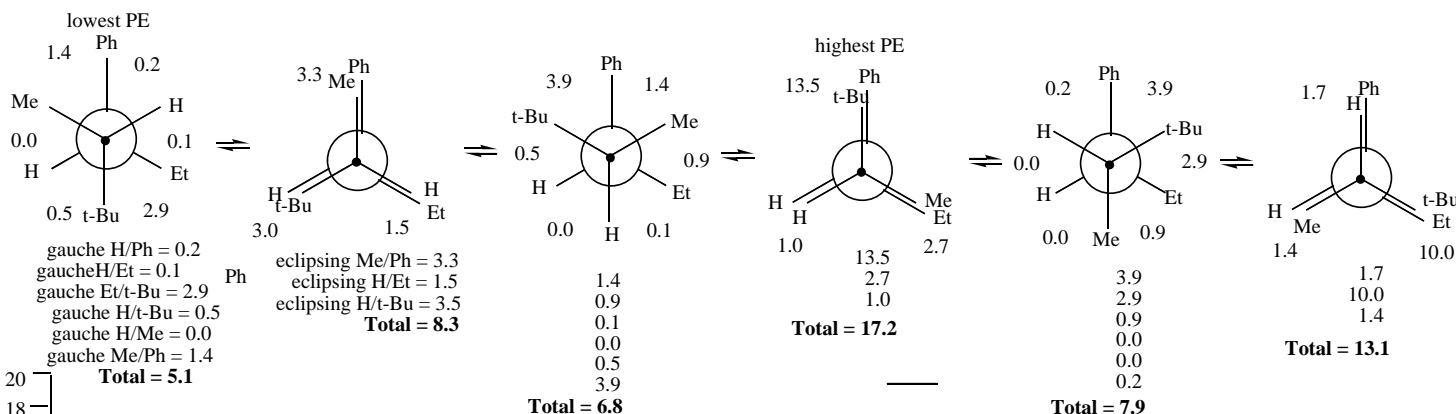
= Ph

t-Bu =

= Et

Me =

$C_3 \rightarrow C_4$

2,2,3-trimethyl-4-phenylhexane
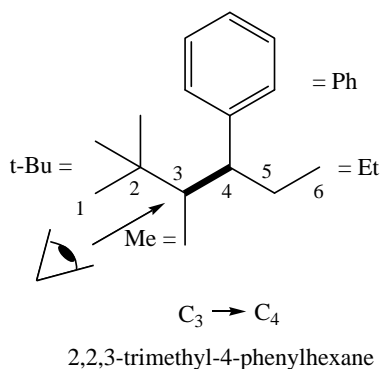
Approximate Eclipsing Energy Values (kcal/mole)
Some were estimated by me.

	H	Me	Et	i-Pr	t-Bu	Ph	Br
H	1.0	1.4	1.5	1.6	3.5	1.7	1.6
Me	1.4	2.5	2.7	3.0	8.5	3.3	2.8
Et	1.5	2.7	3.3	4.5	10.0	3.8	3.1
i-Pr	1.6	3.0	4.5	7.8	13.0	8.1	3.6
t-Bu	3.5	8.5	10.0	13.0	23.0	13.5	9.1
Ph	1.7	3.3	3.8	8.1	13.5	8.3	4.2
Br	1.6	2.8	3.1	3.6	9.1	4.2	3.0

Approximate Gauche Energy Values (kcal/mole)
Some were estimated by me.

	H	Me	Et	i-Pr	t-Bu	Ph	Br
H	0	0	0.1	0.2	0.5	0.2	0.1
Me	0	0.8	0.9	1.1	2.7	1.4	1.0
Et	0.1	0.9	1.1	1.5	2.9	1.7	1.2
i-Pr	0.2	1.1	1.5	2.4	3.5	2.1	1.6
t-Bu	0.5	2.7	2.9	3.5	7.2	3.9	3.3
Ph	0.2	1.4	1.7	2.1	3.9	2.7	1.9
Br	0.1	1.0	1.2	1.6	3.3	1.9	1.1

$\Delta G \approx \Delta H$

$K_{eq} = 10^{\frac{-\Delta H}{2.3RT}}$

Newman projections:

lowest PE

gauche H/Ph = 0.2
gauche H/Et = 0.1
gauche Et/t-Bu = 2.9
gauche H/t-Bu = 0.5
gauche H/Me = 0.0
gauche Me/Ph = 1.4
Total = 5.1

eclipsing Me/Ph = 3.3
eclipsing H/Et = 1.5
eclipsing H/t-Bu = 3.5
Total = 8.3

1.4
0.9
0.1
0.0
0.5
3.9
Total = 6.8

highest PE

13.5
2.7
1.0
Total = 17.2

3.9
2.9
0.9
0.0
0.0
0.2
Total = 7.9

1.7
10.0
1.4
Total = 13.1

17.2 kcal/mole

13.3 kcal/mole

7.9 kcal/mole

6.8 kcal/mole

8.3 kcal/mole

5.1 kcal/mole

least stable

most stable

ΔH = 17.2.0 - 5.2 = 12.0

$\Delta(\Delta H) = 17.2 - 5.1 = 12.1$ kcal/mole

$K_{eq} = 10^{\frac{-12,100}{1380}}$

$K_{eq} = 10^{-8.77} = 1.7 \times 10^{-9} = 1 / 590,000,000 = $ (least) / (most)

5. Use the following set of Fischer projections to answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration. (30 pts)

(3 pts)   A

B

C

D

E

spin 180°
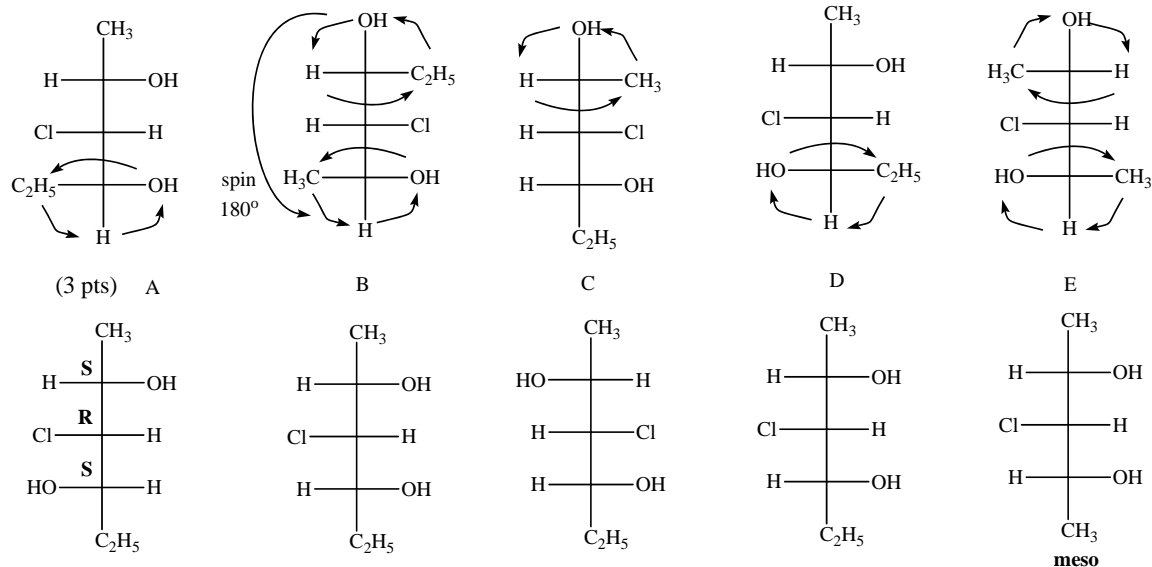
a. Which are optically active?   A   B   C   D   E

b. Which are meso?   A   B   C   D   E   (17 pts)

c. Which is not an isomer with the others?   A   B   C   D   E

d. Which pairs are enantiomers?   AB   AC   AD   AE   BC   BD   BE   CD   CE   DE

e. Which pairs are identical?   AB   AC   AD   AE   BC   BD   BE   CD   CE   DE

f. Which pairs are diastereomers?   AB   AC   AD   AE   BC   BD   BE   CD   CE   DE

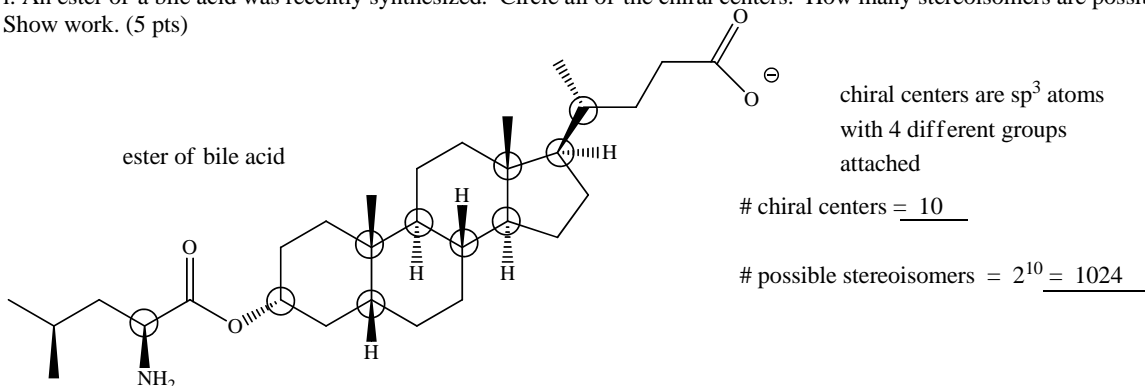g. Which pairs, when mixed in equal amounts will not rotate plane polarized light?   AB   AC   AD   AE   BC   BD   BE   CD   CE   DE

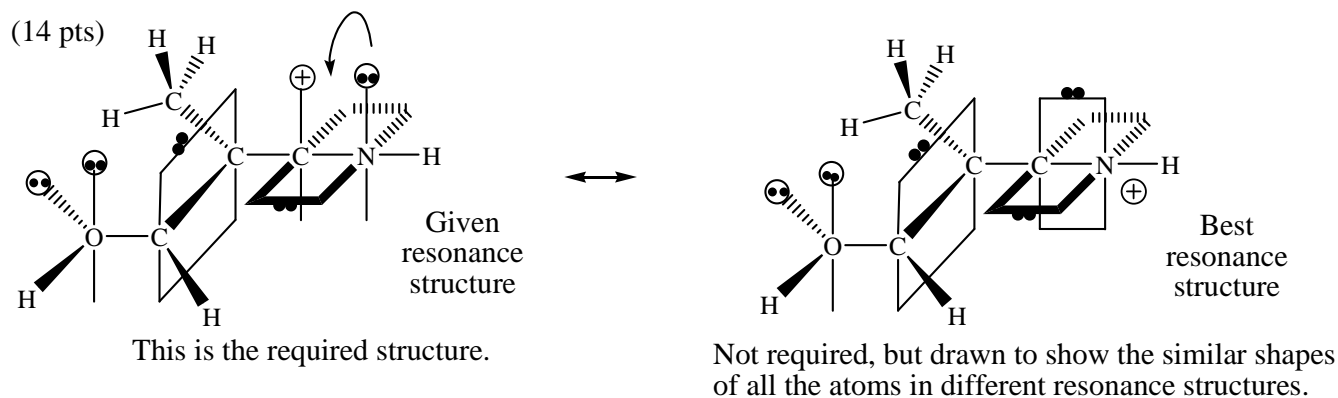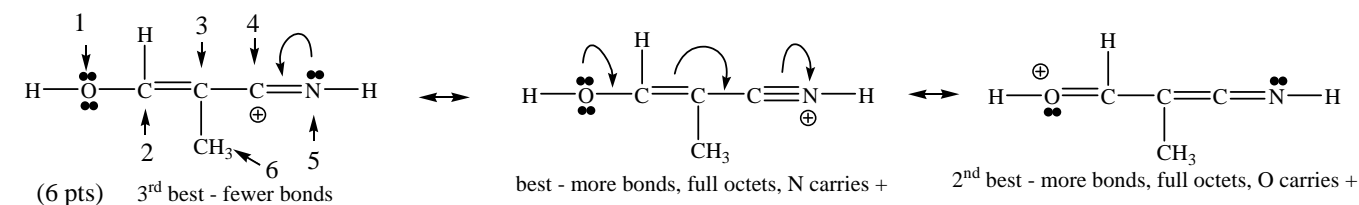h. Draw any stereoisomers of 3-chloroohexan-2,4-ol as Fischer projections, which are not shown above. If there are none, indicate this. (5 pts)

not shown   not shown   C   A   B= D   not shown   not shown   not shown
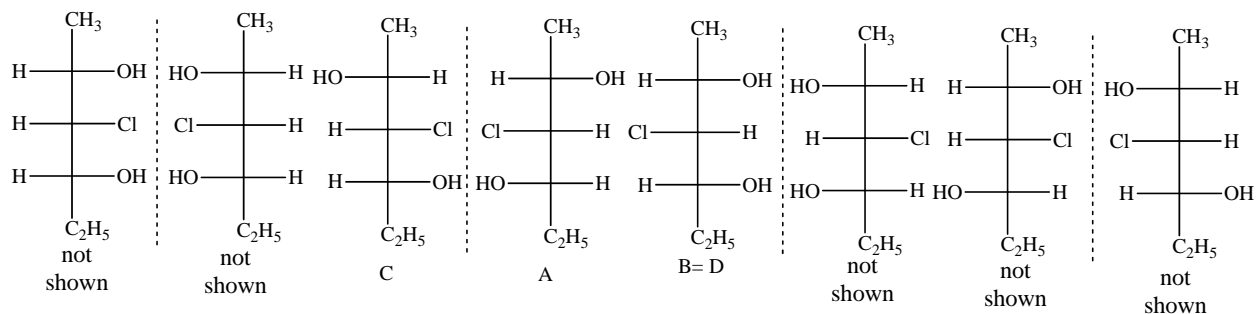
i. An ester of a bile acid was recently synthesized. Circle all of the chiral centers. How many stereoisomers are possible? Show work. (5 pts)
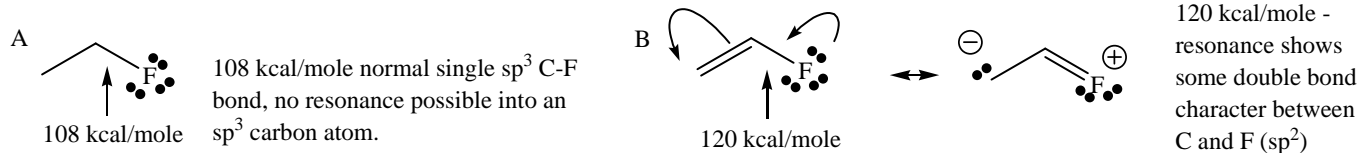
ester of bile acid

chiral centers are sp³ atoms with 4 different groups attached

chiral centers = 10

possible stereoisomers = 2^{10} = 1024

6. Draw two additional "**better**" 2D resonance structures of the given structure. Assume all nonhydrogen atoms have full octets unless + is written next to carbon. Add in any necessary lone pairs and use proper curved arrows to show electron movement. Which structure(s) is(are) best and why? Draw a 3D structure **for the given resonance structure**. Show bonds in front of the page as wedges, bonds in back of the page as dashed lines and bonds in the page as simple lines. Show orbitals for pi bonds and lone pairs along with their electrons. Identify the hybridization, bond angles and descriptive shape for all numbered atoms in the **given** structure. (30 pts)
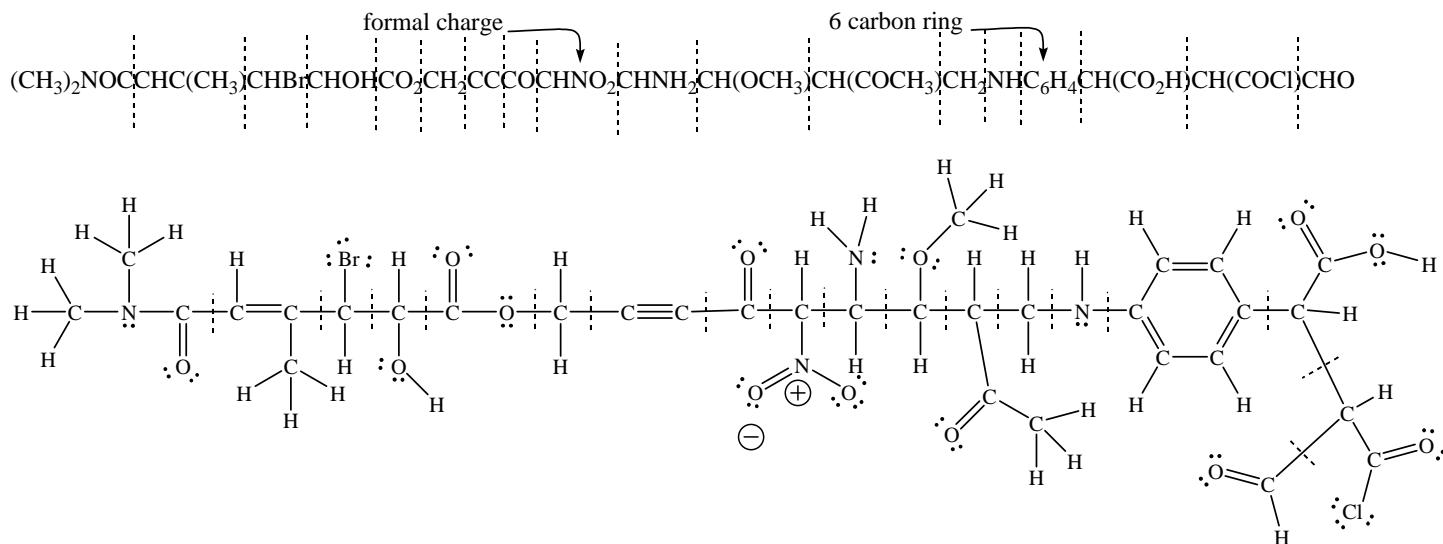
(6 pts)   3rd best - fewer bonds

best - more bonds, full octets, N carries +

2nd best - more bonds, full octets, O carries +

(14 pts)

Given resonance structure

Best resonance structure

This is the required structure.

Not required, but drawn to show the similar shapes of all the atoms in different resonance structures.

Use the given (first) Lewis structure to answer this part. (12 pts)

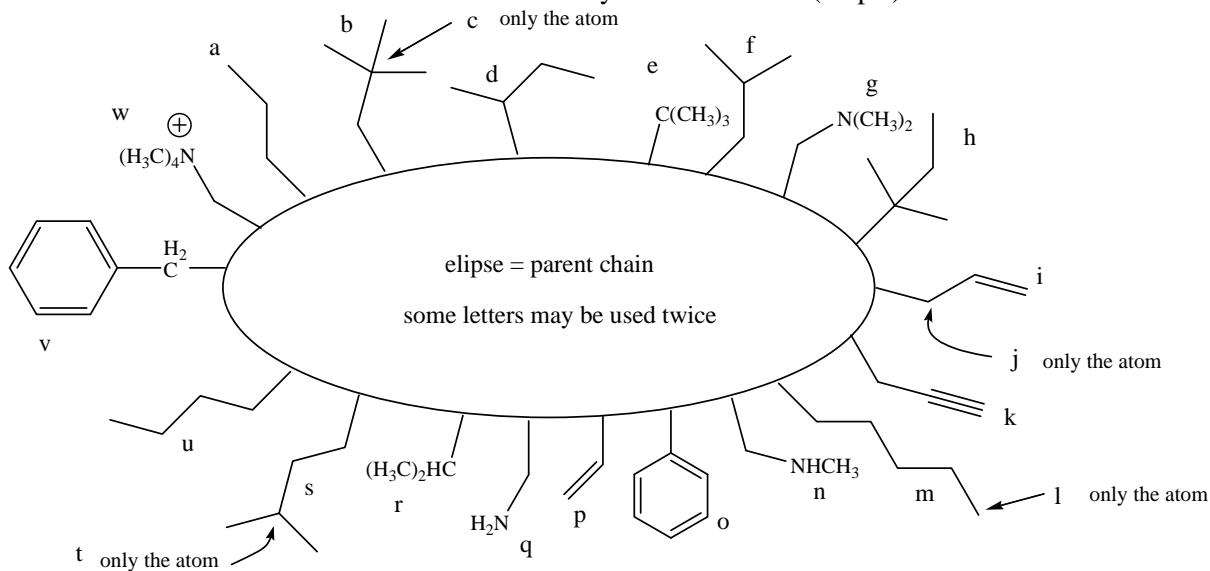| Atom	Shape	Hybridization	Bond Angles	# sigma bonds	# pi bonds	# lone pairs
1	trigonal planar	sp^2	120	2	0	2
2	trigonal planar	sp^2	120	3	1	0
3	trigonal planar	sp^2	120	3	1	0
4	linear	sp	180	2	1	0
5	linear	sp	180	2	1	1
6	tetrahedral	sp^3	109	4	0	0

Explain the different C-F bond energies. Use structures in your explanation. Include any necessary lone pairs, formal charge, curved arrows, etc. What is the hybridization of the fluorine atom in A and B? (4 pts)

A

108 kcal/mole

108 kcal/mole normal single sp^3 C-F bond, no resonance possible into an sp^3 carbon atom.

B

120 kcal/mole

120 kcal/mole - resonance shows some double bond character between C and F (sp^2)

7. Draw an acceptable Lewis structure (2D) for the following structure. Show <u>all</u> single, double and triple bonds with one, two or three lines. Include all lone pairs of electrons as two dots. Include formal charge, if present at the atom where present. (25 pts)

formal charge ⟶   6 carbon ring ⟶

$(CH_3)_2NOCCHC(CH_3)CHBrCHOHCO_2CH_2CCCOCHNO_2CHNH_2CH(OCH_3)CH(COCH_3)CH_2NHC_6H_4CH(CO_2H)CH(COCl)CHO$

8. Match each letter with its common name. Some letters may be used twice. (25 pts)

c   only the atom

$(H_3C)_4N$

$C(CH_3)_3$

$N(CH_3)_2$

elipse = parent chain

some letters may be used twice

j   only the atom

$(H_3C)_2HC$

H_2N

$NHCH_3$

l   only the atom

t   only the atom

1° carbon atom __l__	methylene __j__	isobutyl __f__	neopentyl __b__	allyl __i__
2° carbon atom __j__	methine __t__	sec-butyl __d__	1° amine __q__	vinyl __p__
3° carbon atom __t__	n-propyl __a__	t-butyl __e__	2° amine __n__	benzyl __v__
4° carbon atom __c__	isopropyl __r__	n-pentyl __m__	3° amine __g__	phenyl __o__
methyl __l__	n-butyl __u__	isopentyl __s__	4° ammonium ion __w__	propargyl __k__
		t-pentyl __h__		

Use the given molecular formula to calculate the degree of unsaturation. Show work. $C_{21}H_{24}BrClFN_3O_5$, (3 pts)

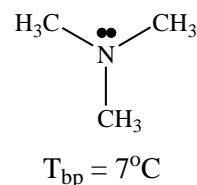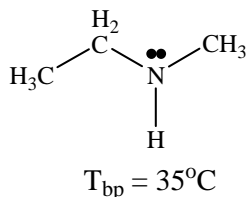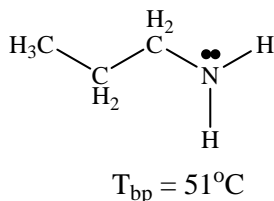$$C_{21}H_{24}BrClFN_3O_5 \quad \begin{array}{l} 2(21) + 2 + 3 = 47 \text{ single bonding positions} \\ -24 + 1 + 1 + 1 = 27 \text{ single bonding groups} \\ \hline \text{missing groups} = 20 \div 2 = 10 \text{ degrees of unsaturation} \end{array}$$

9. a. The active site of an important liver enzyme has just been discovered. Several key regions are shown in the enzyme active site, just below. As an employee of Bronco Pharmaceutical, you are trying to design an inhibitor molecule that will strongly bind to the key regions of the active site so that the normal substrate cannot get in and react. Four possible inhibitors are shown below. Pick the molecule you think will block the enzyme cavity the best and draw it in the active site. Dashes represent "behind" the page, heavy lines indicate in "front" of the page and simple lines are "in" the page. R represents a nonpolar group. Give a very brief explanation for why your choice will work best. (7 pts)
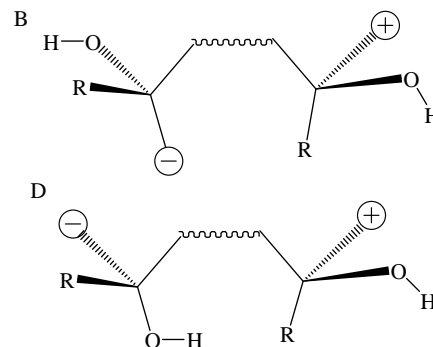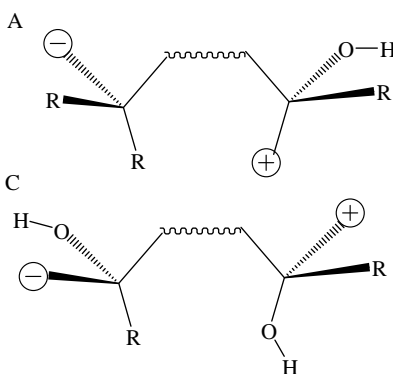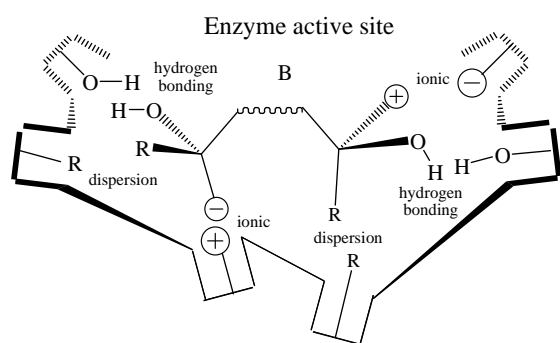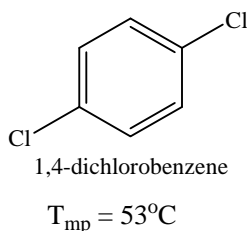

Enzyme active site

B works best. All 6 interactions match up well uisng B, so it should have a high affinity for the enzyme active site and bind strongly. All of the others have some mismatches.

b. Propyl amine, ethylmethylamine and trimethyl amine have boiling points of 7°C, 35°C and 51°C. Match each temperature with the correct compound and provide an explanation for you answer. (7 pts)

$T_{bp} = 51^oC$ $T_{bp} = 35^oC$ $T_{bp} = 7^oC$

The first structure has 2 polar hydrogen atoms (bonded to the nitrogen) that can hydrogen bond, so has stronger attractions with its neighbors (higher boiling point), the second structure has 1 polar hydrogen atom, so has weaker attractions than the first but stronger than the third which has zero polar hydrogen atoms, and the lowest boiling point.

c. 1,3-dichlorobenene and 1,4-dichlorobenzene have melting points of -22 and 53°C, in no particular order. Match each temperature with the correct compound and provide an explanation for you answer. (5 pts)


1,4-dichlorobenzene

$T_{mp} = 53^oC$

The linear symmetry (more symmetrical shape) of the 1,4-dichloro isomer allows closer packing in the lattice structure. Since the molecules are closer they have stronger interactions that have to be overcome before the lattice breaks down at the melting point. That requires more energy, which we see as a higher melting point.
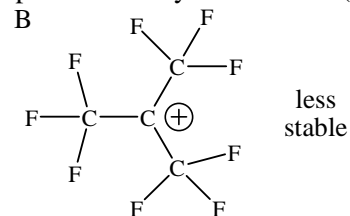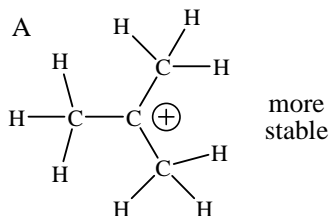
1,3-dichlorobenzene

$T_{mp} = -22^oC$
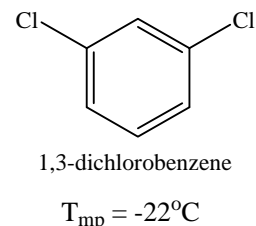
10. Logic arguments of organic and biochemistry

a. The first molecule in each row is a reference point. Explain if the indicated substitution will be stabilizing, destabilizing or have no effect relative to the reference structure. Provide an explanation for your answer. (10 pts)

i.

A   more
stable

B   less
stable
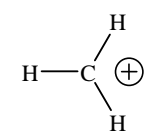
ref. structure

All of the structures are very electron deficient carbocations that would like to have more electron density. "R" groups are inductively electron donating relative to hydrogen atoms, so structure A should help stabilize the carbocation by shifting its sigma electron towards the electron deficient carbon. The problem with the "R" groups in B is that the fluorines are all pulling electrons AWAY from the electron deficient carbocation and that would be very destabilizing. Structure A more stable than the reference compound and structure B is less stable than the reference carbocation.

ii.

C   less
stable

D   more
stable
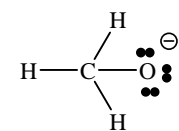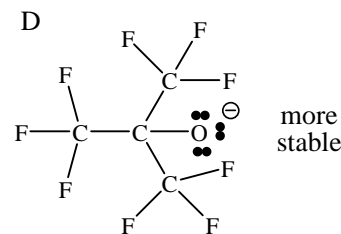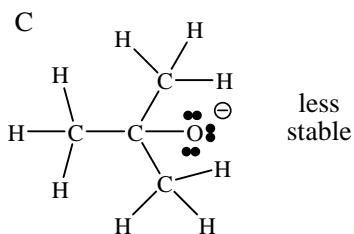
ref. structure

All of the structures have too much electron density. In structure C the R groups are pushing even more electron density towards the negative charge which is destabilizing. In structure D the fluorines are all trying to pull more electron density towrads themselves, away from the negative charge, which statilizes the excess charge on the oxygen.

b. Which atom has the higher first ionization potential and why? (F or S)   (16 pts, 4 pts each)

F is farther to the right (higher Z_{eff}) and higher in a column (closer to the nucleus). Both of those predict a stronger attraction for electrons, so ionization potentials are F > S. IP_1 (F) = 402 kcal/mole and IP_1 (S) = 239 kcal/mole

c. Which neutral atom has the larger atomic radius and why? (S or Cl)

Sulfur and chlorine are in the same row. S has a Z_{eff} of +6 and Cl has a Z_{eff} of +7, so Cl will hold on to its electrons tighter than S. This should contract the electron cloud making the radius of sulfur (r_S = 88 pm) larger than chlorine (r_{Cl} = 79 pm).

d. Which anion has the larger radius and why? (Br^{-1} or Se^{-2})

Both Br^{-1} and Se^{-2} are in the same row and have a full n=3 shell (full octets). Selenium has Z_{eff} of +6 and bromine has a Z_{eff} of +7, so Br will hold on to its electrons tighter than Se so bromine is smaller than selenide. Also there is an excess of 2 electrons instead of 1 electron The radius of selenide (r_{Se-2} = 184 pm) is larger than bromide (r_{Br-} = 182 pm)

e. Which cation has the larger radius and why? (Na^+ or Mg^{+2})

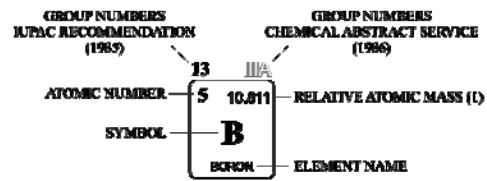Both Na^+ and Mg^{+2} have lost all of their n=3 valence electrons and have full n=1 and 2 shells (core electrons = $1s^2$, $2s^2,2p^6$). Na has Z_{eff} of +1 and Mg has a Z_{eff} of +2, so Mg will hold on to its electrons tighter than Na. The radius of Mg^{+3} (r_{Mg+2} = 86 pm) should be smaller than Na^+ (r_{Na+} = 116 pm).

You can't build a reputation on what you are going to do.   Henry Ford

PERIODIC TABLE OF THE ELEMENTS

GROUP

PERIOD

Legend:
- GROUP NUMBERS IUPAC RECOMMENDATION (1985)
- GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986)
- ATOMIC NUMBER — 5
- RELATIVE ATOMIC MASS (1) — 10.811
- SYMBOL — B
- ELEMENT NAME — BORON

Group (IUPAC)	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.008 H HYDROGEN																	2 4.0026 He HELIUM
2	3 6.94 Li LITHIUM	4 9.0122 Be BERYLLIUM											5 10.81 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 28.085 Si SILICON	15 30.974 P PHOSPHORUS	16 32.06 S SULPHUR	17 35.45 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 65.38 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.971 Se SELENIUM	35 79.904 Br BROMINE	36 83.798 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 95.95 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 (267) Rf RUTHERFORDIUM	105 (268) Db DUBNIUM	106 (271) Sg SEABORGIUM	107 (272) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (276) Mt METNERIUM	110 (281) Ds DARMSTADTIUM	111 (280) Rg ROENTGENIUM	112 (285) Cn COPERNICIUM	113 (286) Nh NIHONIUM	114 (287) Fl FLEROVIUM	115 (289) Mc MOSCOVIUM	116 (291) Lv LIVERMORIUM	117 (294) Ts TENNESSINE	118 (294) Og OGANESSON

LANTHANIDE

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	70 173.05 Yb YTTERBIUM	71 174.97 Lu LUTETIUM

ACTINIDE

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

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(1) Atomic weights of the elements 2013,
Pure Appl. Chem., 88, 265-291 (2016)