Chem 201 Sample Midterm
Beauchamp   Name _____ _____

| Problems	Points	Credit
1. Functional Group Nomenclature (1 large structure)	X	
2. Lewis Structures, Resonance, Formal Charge	X	
3. Cyclohexane Conformations, 2 substituents, Newman Projections, Relative Energies, K_{eq} Calculation	X	
4. Newman Projections, Conformational Energies, K_{eq} Calculation	X	
5. Stereochemical Analysis	X	
6. 2D Resonance Structures, 3D Structure, Hybridization, Angles, Shapes, Explain bond energies	X	
7. Dipole Moments and Inductive versus Resonance Effects	X	
8. Types of isomers from a given formula	X	
9. Physical Properties	X	
10. Draw a long 2D structure and identify functional groups	X	
11. Draw example molecule with functional groups and name them	X	
12. Ionization potential, relative sizes of atoms and ions	X	
13. Special naming terms to know and match	X	
Total	X	

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. Do your best to show me what you know in the time available.

There is no answer key for this sample midterm exam, just like there are no answers for you midterm exam. This is "game situation" practice. You are welcome to show me your work at an office hour for my comments or you can attend the study session where we will go over as many of the problems as time permits.

1. Provide an acceptable name for the following molecule. Only specify R and S where shown as 3D. (X pts)
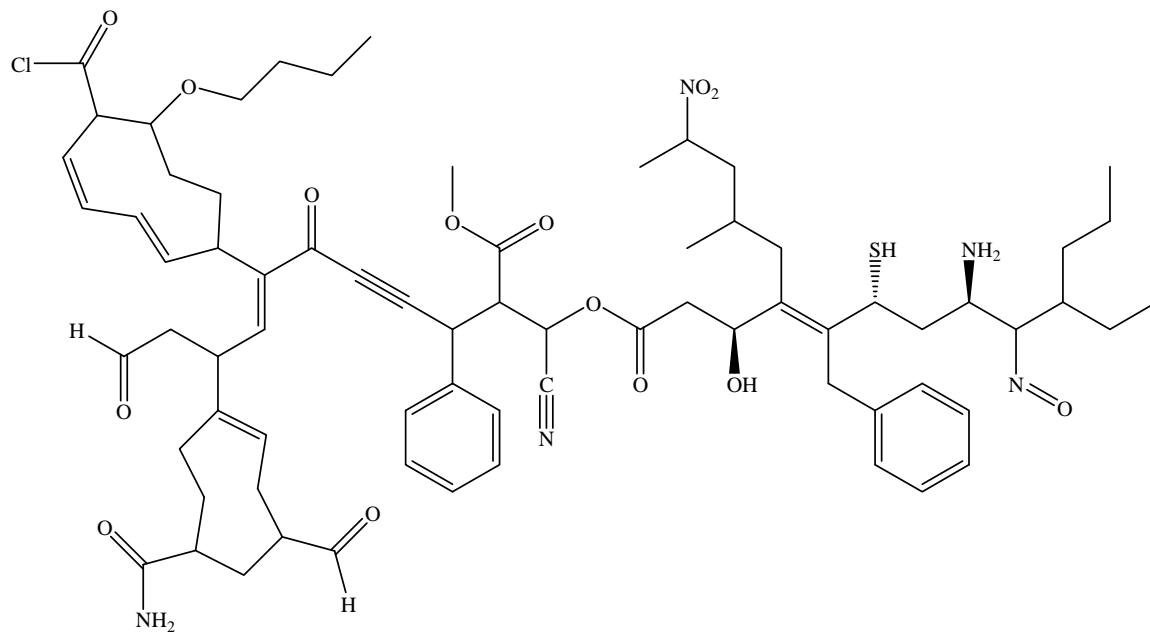
2. Indicate all formal charges present in the following structures. Assume all electrons are shown as lines or dots. If other reasonable resonance structures are possible, draw the best other resonance structure using the proper arrow conventions. Indicate which resonance structure is better or if they are equivalent. (X pts)
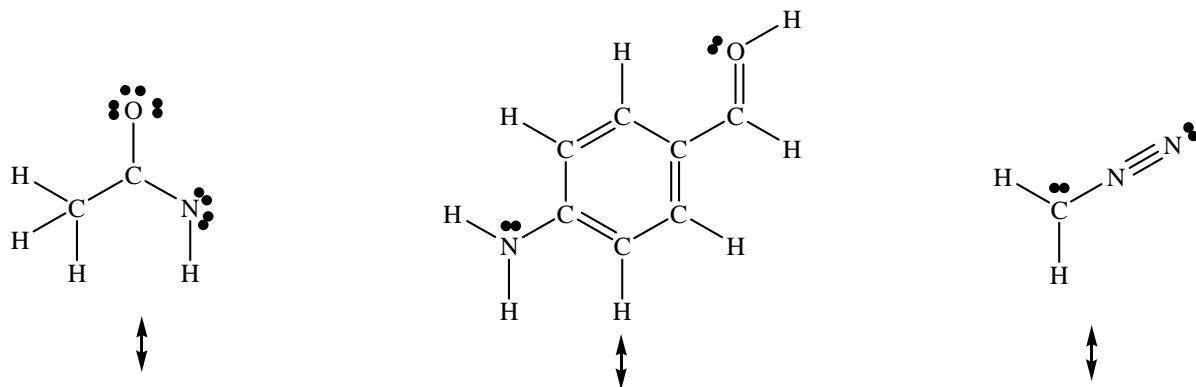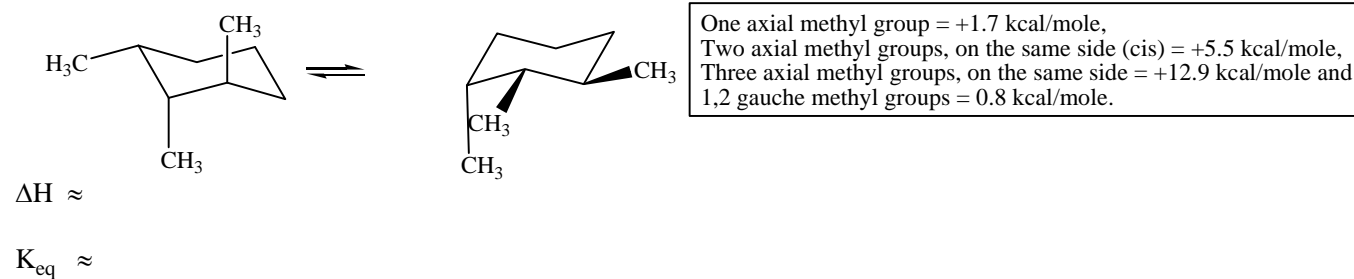
3. Draw all possible chair conformations of trans-1- bromo-3-isopropyllcyclohexane. Make the left most ring carbon C1 and number towards the front. Show **all** axial and equatorial groups in the first chair. Which conformation is more stable? Provide a reason for your answer. Draw a Newman projections of the least stable conformation using the $C_2 \rightarrow C_1$ and $C_4 \rightarrow C_5$ bonds to sight along. Point out any gauche interactions shown in your Newman projection. If the axial energy of a isopropyl group is 2.1 kcal/mole and the axial energy of bromo group is 0.5 kcal/mole and a isopropyl/bromo gauche interaction is 0.6 kcal/mole, what is the ratio of the two conformations at equilibrium? Show your work. 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. (X pts)

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

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

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.

One axial methyl group = +1.7 kcal/mole,
Two axial methyl groups, on the same side (cis) = +5.5 kcal/mole,
Three axial methyl groups, on the same side = +12.9 kcal/mole and
1,2 gauche methyl groups = 0.8 kcal/mole.

ΔH ≈

K_{eq} ≈

4. Use a Newman projection of the C3→C4 bond of 2,2-dibromo-3-methyllhexane to **show the most stable conformation first**. Rotate through all of the eclipsed and staggered conformations. Using the energy values provided in the table 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. (X pts)

2D Structure

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	3.0	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	4.0	10.0	3.8	3.1
i-Pr	1.6	3.0	4.0	7.8	13.0	8.1	3.6
t-Bu	3.0	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	1.6	3.0	1.5	1.3
i-Pr	0.2	1.1	1.6	2.0	4.1	2.1	1.6
t-Bu	0.5	2.7	3.0	4.1	8.2	3.9	3.3
Ph	0.2	1.4	1.5	2.1	3.9	2.3	1.9
Br	0.1	1.0	1.3	1.6	3.3	1.9	1.1

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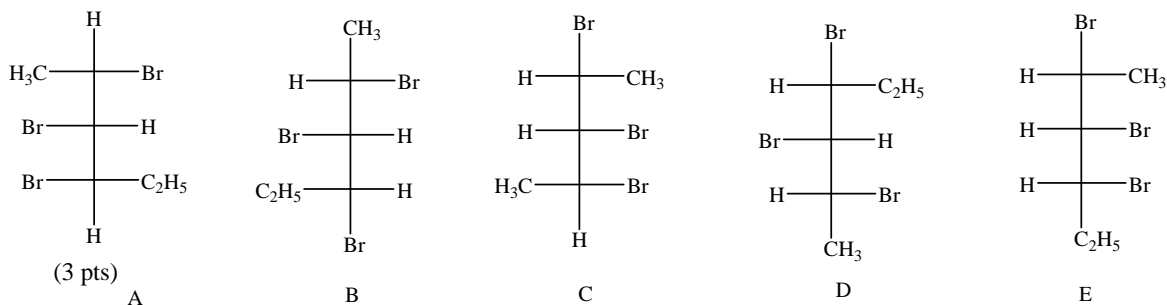
$$K_{eq} = 10^{\frac{-\Delta H}{2.3RT}}$$

Newman projections:

lowest PE
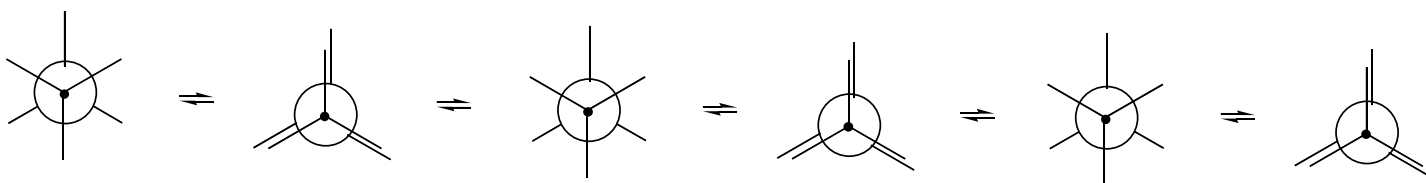
K_eq calculation

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. (X pts)

A
```
        H
        |
H₃C ——— Br
        |
Br  ———  H
        |
Br  ——— C₂H₅
        |
        H
     (3 pts)
```

B
```
       CH₃
        |
H  ———  Br
        |
Br  ———  H
        |
C₂H₅ ——— H
        |
       Br
```

C
```
       Br
        |
H  ——— CH₃
        |
H  ———  Br
        |
H₃C ——— Br
        |
        H
```

D
```
       Br
        |
H  ——— C₂H₅
        |
Br  ———  H
        |
H  ———  Br
        |
       CH₃
```

E
```
       Br
        |
H  ——— CH₃
        |
H  ———  Br
        |
H  ———  Br
        |
       C₂H₅
```

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   AB   AC   AD   AE   BC   BD   BE   CD   CE   DE
   will not rotate plane polarized light?

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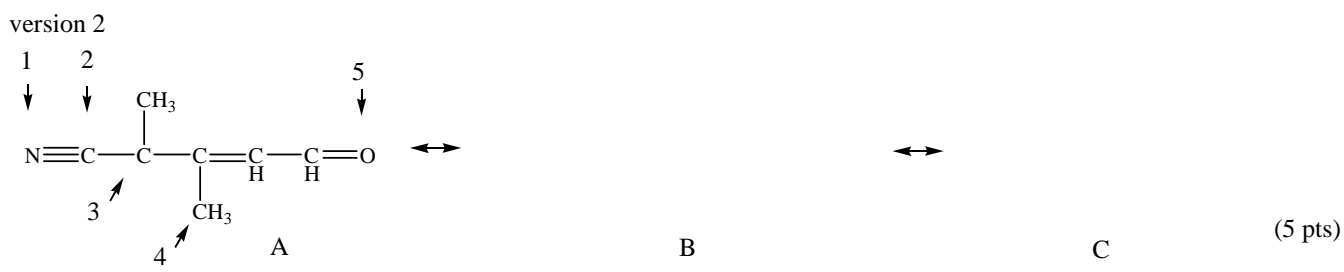   If there are none, indicate this. (5 pts)

i. Lanosterol is constantly being made in your body. It about 19 steps away from cholesterol, which is the precursor for all of the other steroids in your body. Circle all of the chiral centers. How many stereoisomers are possible? Show work. (5 pts)

Lanosterol
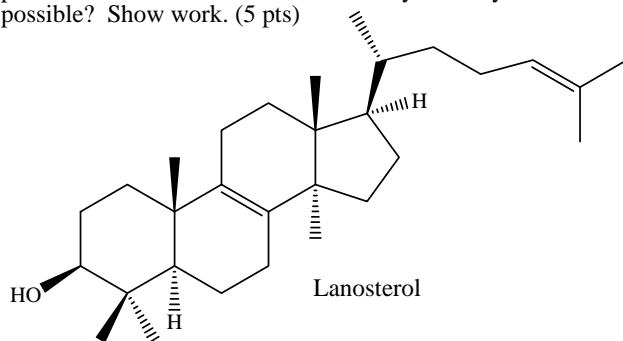
chiral centers = _____

possible stereoisomers _____

6. Draw two additional "**better**" 2D resonance structures of the given structure. Assume all nonhydrogen atoms have full octets except for + carbon. Add in any necessary lone pairs and use proper curved arrows. 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. (X pts)

version 1

1   2   3   4   5
↓   ↓   H   ↓   ↓   ↓

⊕
H—N═C—C═C—O—CH₃

A   CH₃   B   C   (5 pts)

version 2

1   2   5
↓   ↓   CH₃   ↓

N≡C—C—C═C—C═O   ↔   ↔

3   CH₃   A   B   C
4   (5 pts)
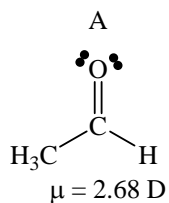
(X pts)

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

Atom	Shape	Hybridization	Bond Angles	# sigma bonds	# pi bonds	# lone pairs
1						
2						
3						
4						
5						

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

A   B

—NH₂   —NH₂

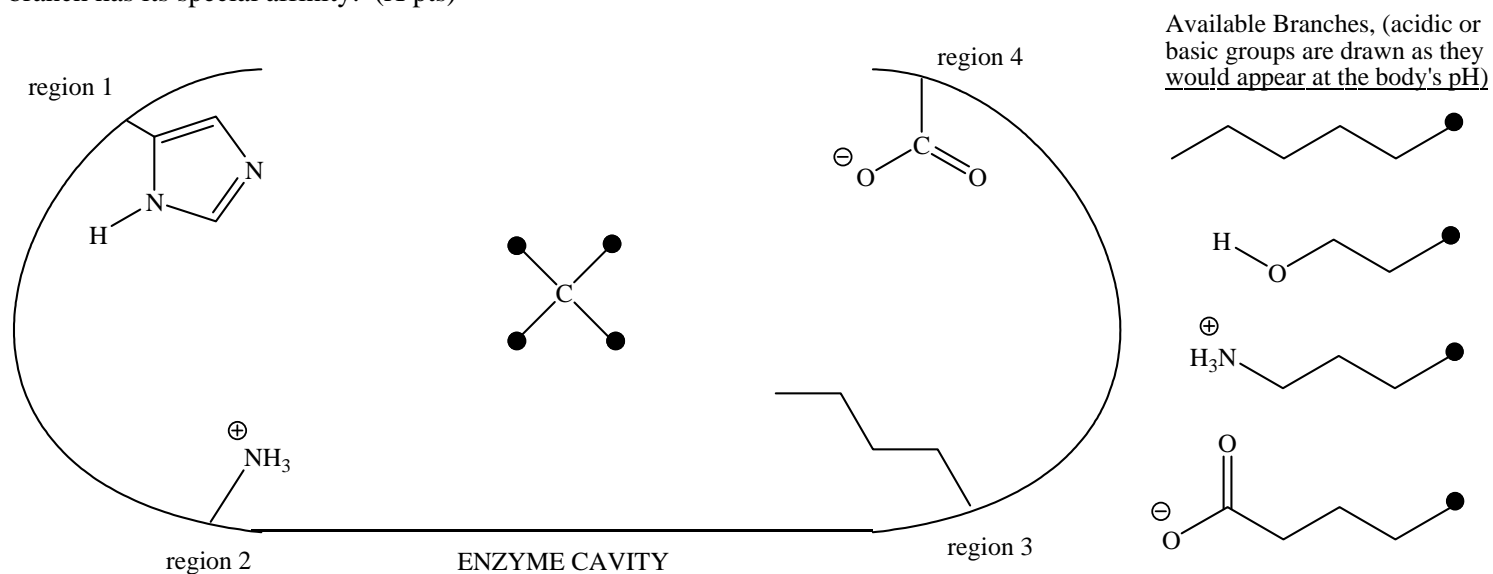82 kcal/mole   102 kcal/mole
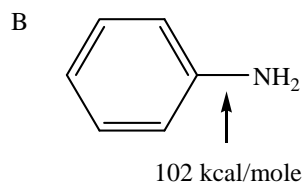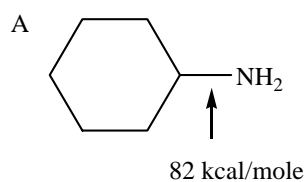
7. Explain what the following dipole moments suggest about inductive effects and resonance effects. You will need to draw additional structures to help your explanation. (X pts)

A

H_3C — C(=O) — H

$\mu = 2.68$ D

B

H_3C — C(=O) — CH_3

$\mu = 2.9$ D

C

H — N(H) — C(=O) — H

$\mu = 3.71$ D
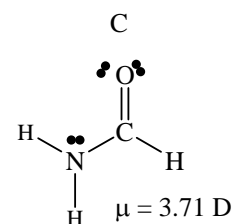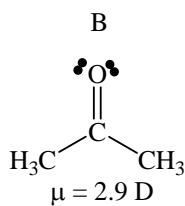
8. Use the formula $C_6H_{12}O_2$ to draw examples for each type of isomerism indicated. This will require that you draw at least two structures to show these differences. What is the degree of unsaturation? (X pts)

skeletal isomers	positional isomers	functional group isomers
conformational isomers	enantiomers	diasteromers

9. a. The active site of an important liver enzyme has just been discovered. Four key regions are shown in the enzyme cavity, 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. You have a variety of branches that you can attach to a central sp^3 carbon atom. Pick appropriate branches and show how your molecule will sit in the enzyme cavity. Give a very brief explanation (1-2 words) for why each branch has its special affinity. (X pts)
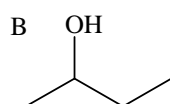
Available Branches, (acidic or basic groups are drawn as they would appear at the body's pH)

region 1

region 4

region 2

ENZYME CAVITY

region 3

b. Match the compounds with their boiling points with a brief explanation. (X pts)

boiling points: 1420°C, 100°C, 80°C, 36°C, -1°C, -12°C

A   B   OH   C   D   E   F
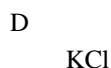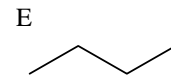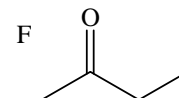
KCl
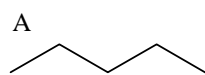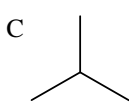
MW = 72 g/mol   MW = 74 g/mol   MW = 58 g/mol   MW = 74 g/mol   MW = 58 g/mol   MW = 72 g/mol

10. Draw an acceptable Lewis structure (2D) for each of the following. Show all 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. Identify any functional groups by name (i.e. ketone, amide, etc.) (X pts)

$\left[\text{OHC(CH}_3\text{)}_2\text{NCH(COCl)CCCHCHCO}_2\text{CH}_2\text{COC}_6\text{H}_4\text{CHCH}_3\text{CHOHCHNH}_2\text{CONHCH(OCH}_3\text{)CH(NO}_2\text{)CH(CONH}_2\text{)CH(COCH}_3\text{)CHCNCO}_2 \right]$

11. Draw an example molecule that has the indicated functional groups. Name each functional group.   (X pts)

functional groups: carboxylic acid, anhydride, thiol, sulfide, 3° amide, 2° amine, alcohol, ether, alkene, alkyne, cyclic alkane, bromo, aromatic, acid chloride, ester, aldehyde, ketone

Use the given molecular formula to calculate the degree of unsaturation. $C_{25}H_{27}BrClNO_7S_2$,

12. a. Which atom has the higher first ionization potential and why? (Na or Cl)   (X pts)

b. Which neutral atom has the larger atomic radius and why? (Si or Ar)

c. Which anion has the larger radius and why? (N^{-3} or O^{-2})

d. Which cation has the larger radius and why? (Mg^{+2} or Al^{+3})

13. Match the arrows with the terms. Some arrows may be associated with more than one term. (X pts)

1. vinyl _____

2. allyl _____

3. propargyl _____

4. phenyl _____

5. benzyl _____

6. primary amine _____

7. quarternary _____

8. isopropyl _____

9. isobutyl _____

10. secondary amine _____

11. tertiary amine _____

12. neopentyl _____

13. methyl _____

14. methylene _____

15. methine _____

16. primary _____

17. secondary _____

18. tertiary _____

19. sec-butyl _____

20. t-butyl _____

21. quaternary ammonium

ion _____