Chapter 3 – Organic Compounds: Alkanes and Their Stereochemistry

Chapter Outline

I. Functional Groups (Section 3.1).
  A. Functional groups are groups of atoms within a molecule that have a characteristic chemical behavior.
  B. The chemistry of every organic molecule is determined by its functional groups.
  C. Functional groups described in this text can be grouped into three categories:
    1. Functional groups with carbon–carbon multiple bonds.
    2. Groups in which carbon forms a single bond to an electronegative atom.
    3. Groups with a carbon-oxygen double bond.

II. Alkanes (Sections 3.2 – 3.5).
  A. Alkanes and alkane isomers (Section 3.2).
    1. Alkanes are formed by overlap of carbon sp^3 orbitals.
    2. Alkanes are described as saturated hydrocarbons.
      a. They are hydrocarbons because they contain only carbon and hydrogen.
      b. They are saturated because all bonds are single bonds.
      c. The general formula for alkanes is C_nH_{2n+2}.
    3. For alkanes with four or more carbons, the carbons can be connected in more than one way.
      a. If the carbons are in a row, the alkane is a straight-chain alkane.
      b. If the carbon chain has a branch, the alkane is a branched-chain alkane.
    4. Alkanes with the same molecular formula are isomers.
      a. Isomers whose atoms are connected differently are constitutional isomers.
        Constitutional isomers are always different compounds with different properties but with the same molecular formula.
      b. A given alkane can be drawn in many ways.
    5. Straight-chain alkanes are named according to the number of carbons in their chain.
  B. Alkyl groups (Section 3.3).
    1. An alkyl group is the partial structure that results from the removal of a hydrogen atom from an alkane.
      a. Alkyl groups are named by replacing the -ane of an alkane by -yl.
      b. *n*-Alkyl groups are formed by removal of an end carbon of a straight-chain alkane.
      c. Branched-chain alkyl groups are formed by removal of a hydrogen atom from an internal carbon.
        The prefixes *sec*- and *tert*- refer to the degree of substitution at the branching carbon atom.
    2. There are four possible degrees of alkyl substitution for carbon.
      a. A primary carbon is bonded to one other carbon.
      b. A secondary carbon is bonded to two other carbons.
      c. A tertiary carbon is bonded to three other carbons.
      d. A quaternary carbon is bonded to four other carbons.
      e. The symbol **R** refers to the rest of the molecule.
    3. Hydrogens are also described as primary, secondary and tertiary.
      a. Primary hydrogens are bonded to primary carbons (RCH_3).
      b. Secondary hydrogens are bonded to secondary carbons (R_2CH_2).
      c. Tertiary hydrogens are bonded to tertiary carbons (R_3CH).

- C. Naming alkanes (Section 3.4).
  - 1. The system of nomenclature used in this book is the IUPAC system.
    In this system, a chemical name has a prefix, a parent and a suffix.
    - i. The parent shows the number of carbons in the principal chain.
    - ii. The suffix identifies the functional group family.
    - iii. The prefix shows the location of functional groups.
  - 2. Naming an alkane:
    - a. Find the parent hydrocarbon.
      - i. Find the longest continuous chain of carbons, and use its name as the parent name.
      - ii. If two chains have the same number of carbons, choose the one with more branch points.
    - b. Number the atoms in the parent chain.
      - i. Start numbering at the end nearer the first branch point.
      - ii. If branching occurs an equal distance from both ends, begin numbering at the end nearer the second branch point.
    - c. Identify and number the substituents.
      - i. Give each substituent a number that corresponds to its position on the parent chain.
      - ii. Two substituents on the same carbon receive the same number.
    - d. Write the name as a single word.
      - i. Use hyphens to separate prefixes and commas to separate numbers.
      - ii. Use the prefixes, *di-*, *tri-*, *tetra-* if necessary, but don't use them for alphabetizing.
    - e. Name a complex substituent as if it were a compound, and set it off in parentheses.
      - i. Some simple branched-chain alkyl groups have common names.
      - ii. The prefix *iso* is used for alphabetizing, but *sec-* and *tert-* are not.
- D. Properties of alkanes (Section 3.5).
  - 1. Alkanes are chemically inert to most laboratory reagents.
  - 2. Alkanes react with O_2 and Cl_2.
  - 3. The boiling points and melting points of alkanes increase with increasing molecular weight.
    - a. This effect is due to weak dispersion forces.
    - b. The strength of these forces increases with increasing molecular weight.
  - 4. Increased branching lowers an alkane's boiling point.

III. Conformations of straight-chain alkanes (Sections 3.6 – 3.7).

- A. Conformations of ethane (Section 3.6).
  - 1. Rotation about a single bond produces isomers that differ in conformation.
    These isomers have the same connections of atoms and can't be isolated.
  - 2. These isomers can be represented in two ways:
    - a. Sawhorse representations view the C–C bond from an oblique angle.
    - b. Newman projections represent the two carbons as a circle.
  - 3. There is a barrier to rotation that makes some conformers of lower energy than others.
    - a. The lowest energy conformer (staggered conformation) occurs when all C–H bonds are as far from each other as possible.
    - b. The highest energy conformer (eclipsed conformation) occurs when all C–H bonds are as close to each other as possible.
    - c. Between these two conformations lie an infinite number of other conformations.

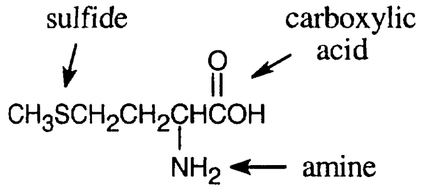
4. The staggered conformation is 12 kJ/mol lower in energy than the eclipsed conformation.
    a. This energy difference is due to torsional strain from interactions between C–H bonding orbitals on one carbon and C–H antibonding orbitals on an adjacent carbon, which stabilize the staggered conformer.
    b. The torsional strain resulting from a single C–H interaction is 4.0 kJ/mol.
    c. The barrier to rotation can be represented on a graph of potential energy vs. angle of rotation.

B. Conformations of other alkanes (Section 3.7).
1. Conformations of propane.
    a. Propane also shows a barrier to rotation that is 14 kJ/mol.
    b. The eclipsing interaction between a C–C bond and a C–H bond is 6.0 kJ/mol.
2. Conformations of butane.
    a. Not all staggered conformations of butane have the same energy; not all eclipsed conformations have the same energy.
        i. In the lowest energy conformation (anti) the two large methyl groups are as far from each other as possible.
        ii. The eclipsed conformation that has two methyl–hydrogen interactions and a H–H interaction is 16 kJ/mol higher in energy than the anti conformation.
        iii. The conformation with two methyl groups 60° apart (gauche conformation) is 3.8 kJ/mol higher in energy than the anti conformation.
            This energy difference is due to steric strain – the repulsive interaction that results from forcing atoms to be closer together than their atomic radii allow.
        iv. The highest energy conformations occur when the two methyl groups are eclipsed.
            This conformation is 19 kJ/mol less stable than the anti conformation.
            The value of a methyl–methyl eclipsing interaction is 11 kJ/mol.
    b. The most favored conformation for any straight-chain alkane has carbon–carbon bonds in staggered arrangements and large substituents anti to each other.
    c. At room temperature, bond rotation occurs rapidly, but a majority of molecules adopt the most stable conformation.

Solutions to Problems

3.1 Notice that certain functional groups have different designations if other functional groups are present in a molecule. For example, a molecule containing a carbon–carbon double bond and no other functional group is an alkene; if other groups are present, the group is referred to as a carbon–carbon double bond. Similarly, a compound containing a benzene ring, and only carbon- and hydrogen-containing substituents, is an arene; if other groups are present, the ring is labeled an aromatic ring.

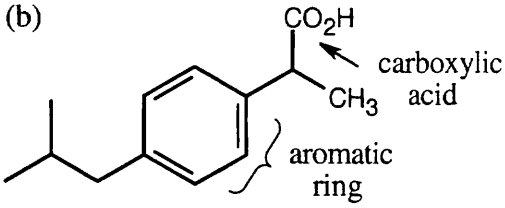
(a)



$CH_3SCH_2CH_2\underset{NH_2}{CH}\overset{O}{\overset{\|}{C}}OH$

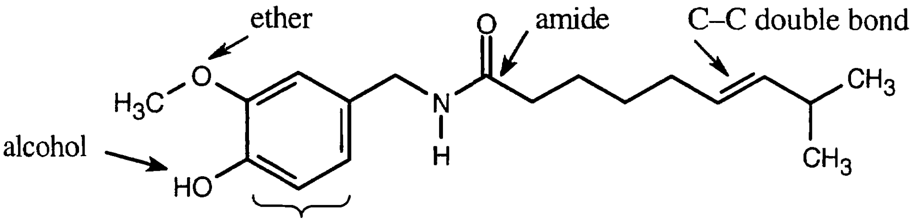
Methionine

(b)



Ibuprofen

(c)

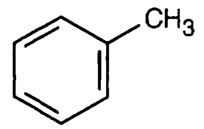


Capsaicin

3.2

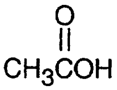
(a) CH_3OH **Methanol**

(b)



Toluene

(c)

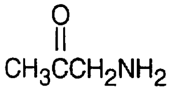


$CH_3\overset{O}{\overset{\|}{C}}OH$

Acetic acid

(d) CH_3NH_2 **Methylamine**

(e)



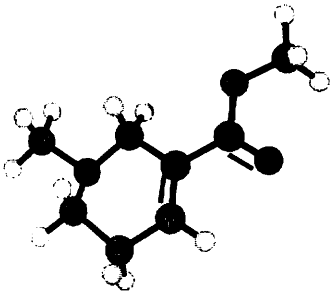
$CH_3\overset{O}{\overset{\|}{C}}CH_2NH_2$

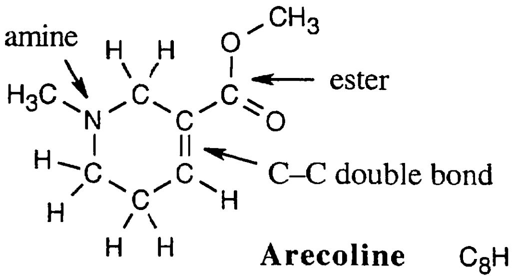
Aminoacetone

(f)

1,3-Butadiene

3.3



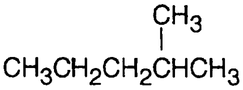


Arecoline $C_8H_{13}NO_2$

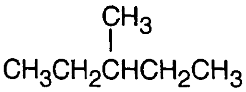
3.4 **Strategy:** We know that carbon forms four bonds and hydrogen forms one bond. Thus, draw all possible six-carbon skeletons and add hydrogens so that all carbons have four bonds. To draw all possible skeletons in this problem: (1) Draw the six-carbon straight-chain skeleton. (2) Draw a five-carbon chain, identify the different types of carbon atoms on the chain, and add a $-CH_3$ group to each of the different types of carbons, generating two skeletons. (3) Repeat the process with the four-carbon chain to give rise to the last two skeletons. Add hydrogens to the remaining carbons to complete the structures.

Solution:

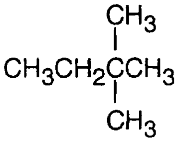
$CH_3CH_2CH_2CH_2CH_2CH_3$



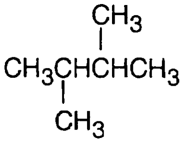
$\mathrm{CH_3CH_2CH_2\overset{\overset{CH_3}{|}}{C}HCH_3}$



$\mathrm{CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_3}$

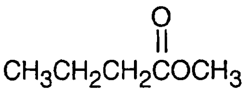


$\mathrm{CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_3}$

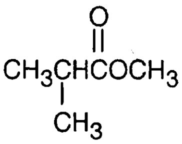


$\mathrm{CH_3\underset{\underset{CH_3}{|}}{C}H\overset{\overset{CH_3}{|}}{C}HCH_3}$

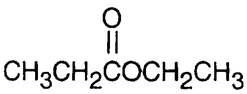
3.5 (a) Nine isomeric esters of formula $C_5H_{10}O_2$ can be drawn.



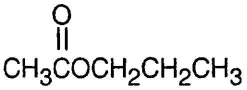
$\mathrm{CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}OCH_3}$



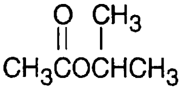
$\mathrm{CH_3\underset{\underset{CH_3}{|}}{C}H\overset{\overset{O}{\|}}{C}OCH_3}$



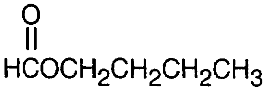
$\mathrm{CH_3CH_2\overset{\overset{O}{\|}}{C}OCH_2CH_3}$



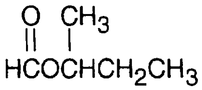
$\mathrm{CH_3\overset{\overset{O}{\|}}{C}OCH_2CH_2CH_3}$



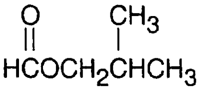
$\mathrm{CH_3\overset{\overset{O}{\|}}{C}O\overset{\overset{CH_3}{|}}{C}HCH_3}$



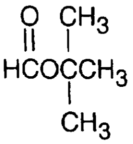
$\mathrm{H\overset{\overset{O}{\|}}{C}OCH_2CH_2CH_2CH_3}$



$\mathrm{H\overset{\overset{O}{\|}}{C}O\overset{\overset{CH_3}{|}}{C}HCH_2CH_3}$



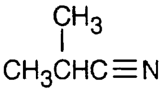
$\mathrm{H\overset{\overset{O}{\|}}{C}OCH_2\overset{\overset{CH_3}{|}}{C}HCH_3}$



$\mathrm{H\overset{\overset{O}{\|}}{C}O\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_3}$

(b)

$CH_3CH_2CH_2C{\equiv}N$ and

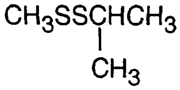


$\mathrm{CH_3\overset{\overset{CH_3}{|}}{C}HC{\equiv}N}$

(c)

$CH_3CH_2SSCH_2CH_3$

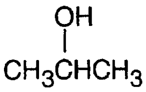
$CH_3SSCH_2CH_2CH_3$



$\mathrm{CH_3SS\underset{\underset{CH_3}{|}}{C}HCH_3}$

3.6 (a) Two alcohols have the formula C_3H_8O.

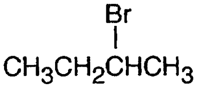
$CH_3CH_2CH_2OH$ and



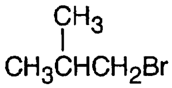
$CH_3\overset{OH}{C}HCH_3$

(b) Four bromoalkanes have the formula C_4H_9Br.

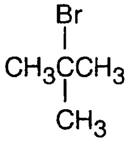
$CH_3CH_2CH_2CH_2Br$



$CH_3CH_2\overset{Br}{C}HCH_3$

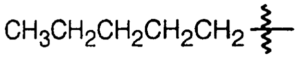


$CH_3\overset{CH_3}{C}HCH_2Br$

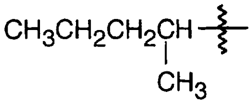


$CH_3\overset{Br}{\underset{CH_3}{C}}CH_3$

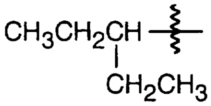
3.7



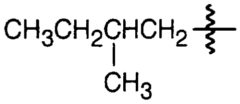
$CH_3CH_2CH_2CH_2CH_2\text{-}\wr$



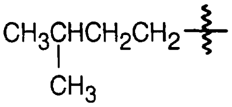
$CH_3CH_2CH_2\underset{CH_3}{C}H\text{-}\wr$



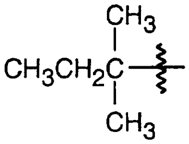
$CH_3CH_2\underset{CH_2CH_3}{C}H\text{-}\wr$



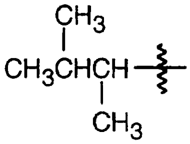
$CH_3CH_2\underset{CH_3}{C}HCH_2\text{-}\wr$



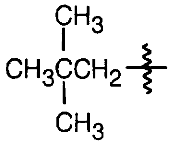
$CH_3\underset{CH_3}{C}HCH_2CH_2\text{-}\wr$



$CH_3CH_2\overset{CH_3}{\underset{CH_3}{C}}\text{-}\wr$



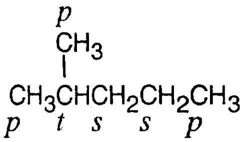
$CH_3\overset{CH_3}{C}H\underset{CH_3}{C}H\text{-}\wr$



$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\text{-}\wr$

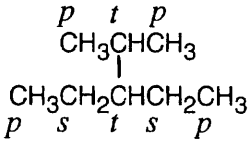
3.8

(a)



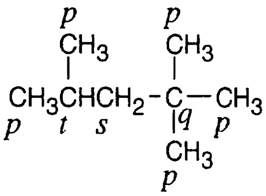
$\underset{p}{CH_3}\overset{\overset{p}{CH_3}}{\underset{t}{C}}H\underset{s}{CH_2}\underset{s}{CH_2}\underset{p}{CH_3}$

(b)



$\underset{p}{CH_3}\underset{s}{CH_2}\overset{\overset{p}{CH_3}\overset{t}{C}H\overset{p}{CH_3}}{\underset{t}{C}}H\underset{s}{CH_2}\underset{p}{CH_3}$

(c)

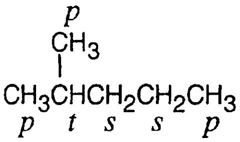


$\underset{p}{CH_3}\overset{\overset{p}{CH_3}}{\underset{t}{C}}H\underset{s}{CH_2}\text{-}\overset{\overset{p}{CH_3}}{\underset{\underset{p}{CH_3}}{\underset{q}{C}}}\text{—}\underset{p}{CH_3}$

p = primary; s = secondary; t = tertiary; q = quaternary

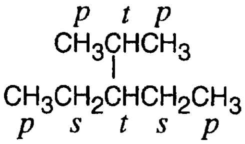
3.9

(a)



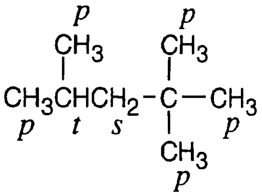
$\underset{p}{CH_3}\overset{\overset{p}{CH_3}}{\underset{t}{C}}H\underset{s}{CH_2}\underset{s}{CH_2}\underset{p}{CH_3}$

(b)



$\underset{p}{CH_3}\underset{s}{CH_2}\overset{\overset{p}{CH_3}\overset{t}{C}H\overset{p}{CH_3}}{\underset{t}{C}}H\underset{s}{CH_2}\underset{p}{CH_3}$

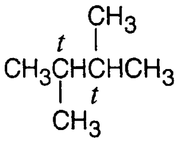
(c)



$\underset{p}{CH_3}\overset{\overset{p}{CH_3}}{\underset{t}{C}}H\underset{s}{CH_2}\text{-}\overset{\overset{p}{CH_3}}{\underset{\underset{p}{CH_3}}{C}}\text{—}\underset{p}{CH_3}$

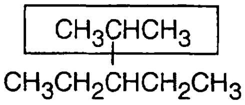
3.10

(a)



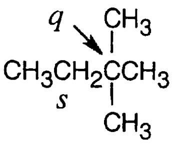
$CH_3\overset{CH_3}{\overset{t}{C}}H\underset{CH_3}{\underset{t}{C}}HCH_3$

(b)



$CH_3CH_2\overset{\boxed{CH_3CHCH_3}}{C}HCH_2CH_3$

(c)



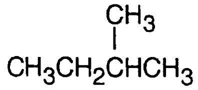
$CH_3\underset{s}{CH_2}\overset{\overset{q}{}CH_3}{\underset{CH_3}{C}}CH_3$

3.11

(a)

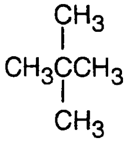
$CH_3CH_2CH_2CH_2CH_3$

Pentane



$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_3$

2-Methylbutane



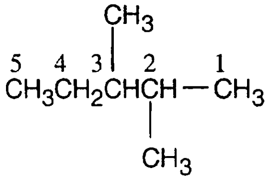
$CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_3$

2,2-Dimethylpropane

(b) **Strategy:**

Step 1: Find the longest continuous carbon chain and use it as the parent name. In (b), the longest chain is a pentane.
Step 2: Identify the substituents. In (b), both substituents are methyl groups.
Step 3: Number the substituents. In (b), numbering can start from either end of the carbon chain, and the methyl groups are in the 2- and 3- positions.
Step 4: Name the compound. Remember that the prefix *di*- must be used when two substituents are the same. The IUPAC name is 2,3-dimethylpentane.

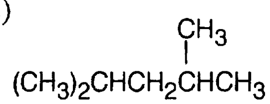
Solution:



$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{\underset{\underset{CH_3}{|}}{C}}H\overset{\overset{CH_3}{|}}{\overset{2}{C}}H-\overset{1}{C}H_3$

2,3-Dimethylpentane

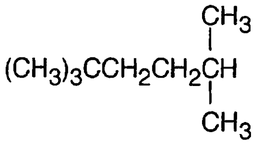
(c)



$(CH_3)_2CHCH_2\overset{\overset{CH_3}{|}}{C}HCH_3$

2,4-Dimethylpentane

(d)



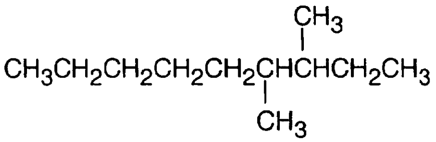
$(CH_3)_3CCH_2CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}H$

2,2,5-Trimethylhexane

3.12 **Strategy:** When you are asked to draw the structure corresponding to a given name, draw the parent carbon chain, attach the specified groups to the proper carbons, and fill in the remaining hydrogens.

Solution:

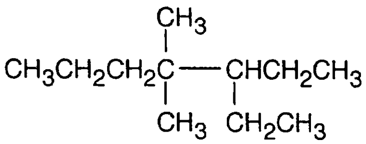
(a)



$CH_3CH_2CH_2CH_2CH_2\overset{\overset{CH_3}{|}}{C}H\underset{\underset{CH_3}{|}}{C}HCH_2CH_3$

3,4-Dimethylnonane

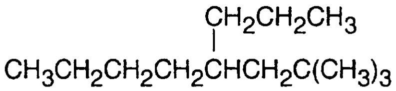
(b)



$CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CH_2CH_3}{|}}{C}HCH_2CH_3$

3-Ethyl-4,4-dimethylheptane

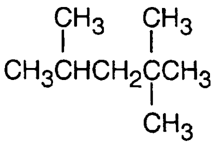
(c)



$CH_3CH_2CH_2CH_2\overset{\overset{CH_2CH_2CH_3}{|}}{C}HCH_2C(CH_3)_3$

2,2-Dimethyl-4-propyloctane

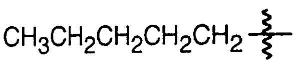
(d)



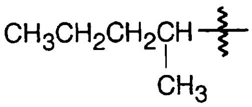
$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_3$

2,2,4-Trimethylpentane

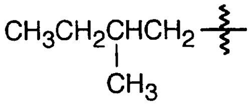
3.13


$\mathrm{CH_3CH_2CH_2CH_2CH_2}$–

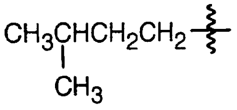
Pentyl


$\mathrm{CH_3CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H}$–

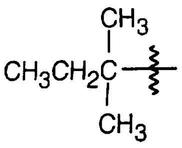
1-Methylbutyl


$\mathrm{CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2}$–

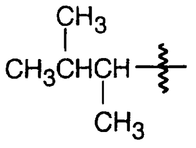
2-Methylbutyl


$\mathrm{CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2}$–

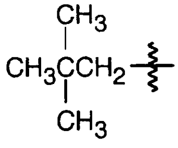
3-Methylbutyl


$\mathrm{CH_3CH_2\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}}$–

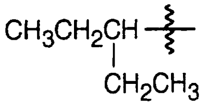
1,1-Dimethylpropyl


$\mathrm{CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}H\underset{\displaystyle CH_3}{\underset{|}{C}}H}$–

1,2-Dimethylpropyl

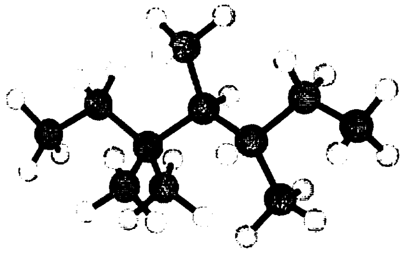

$\mathrm{CH_3\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}CH_2}$–

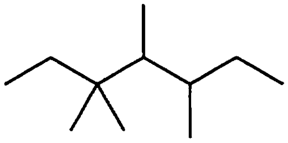
2,2-Dimethylpropyl


$\mathrm{CH_3CH_2\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}H}$–

1-Ethylpropyl

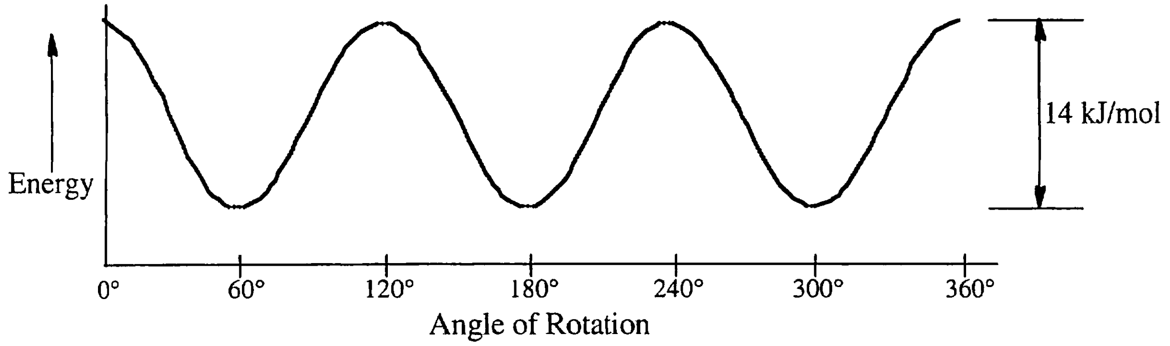
3.14

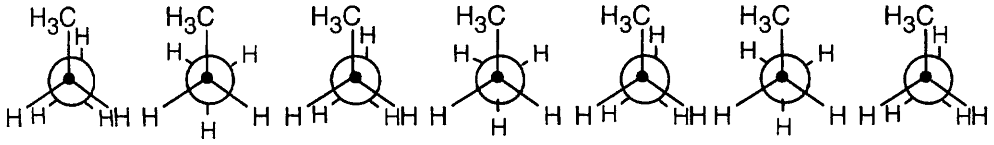




3,3,4,5-Tetramethylheptane

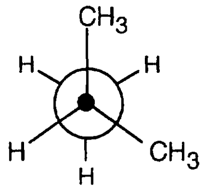
3.15





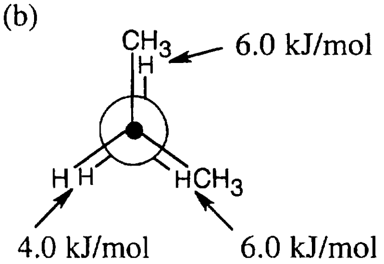
3.16

(a)



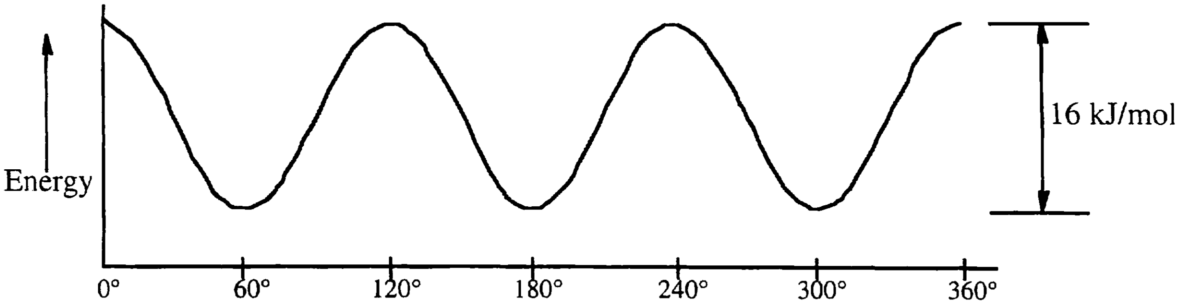
The *most stable* conformation is staggered and occurs at 60°, 180°, and 300°.

(b)

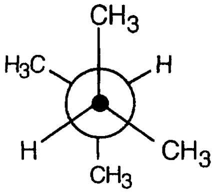


The *least stable* conformation is eclipsed and occurs at 0°, 120°, 240°, and 360°.

(c),(d)

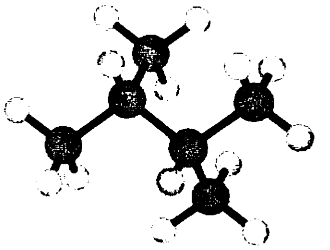


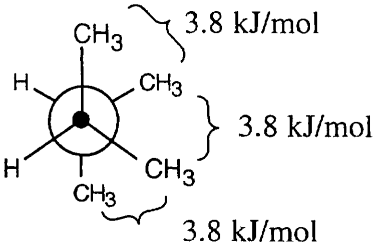
3.17



This conformation of 2,3-dimethylbutane is the most stable because it is staggered and has the fewest CH_3–CH_3 gauche interactions.

3.18 The conformation is a staggered conformation in which the hydrogens on carbons 2 and 3 are 60° apart. Draw the Newman projection.



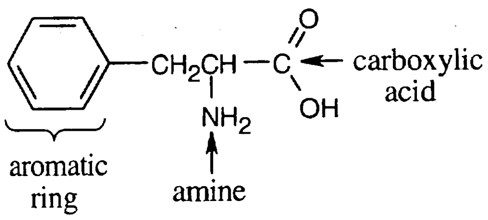


The Newman projection shows three gauche interactions, each of which has an energy cost of 3.8 kJ/mol. The total strain energy is 11.4 kJ/mol.

Visualizing Chemistry

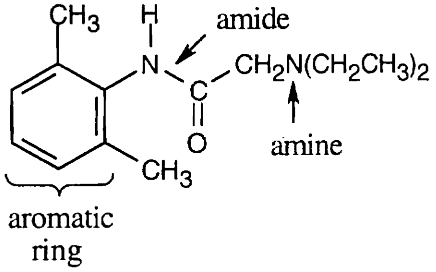
3.19

(a)



Phenylalanine $C_9H_{11}NO_2$

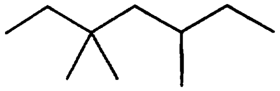
(b)



Lidocaine $C_{14}H_{22}N_2O$

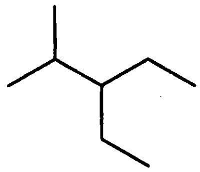
3.20

(a)



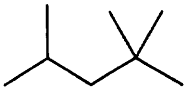
3,3,5-Trimethylheptane

(b)



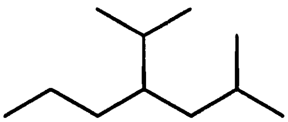
3-Ethyl-2-methylpentane

(c)



2,2,4-Trimethylpentane

(d)

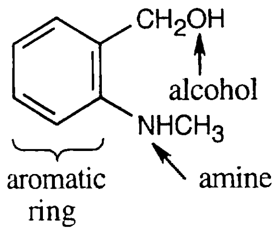


4-Isopropyl-2-methylheptane

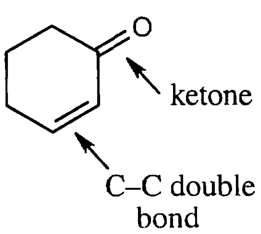
Additional Problems

3.21

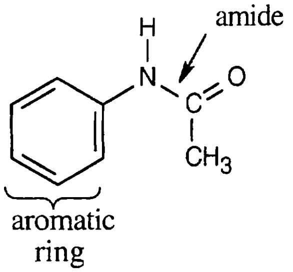
(a)



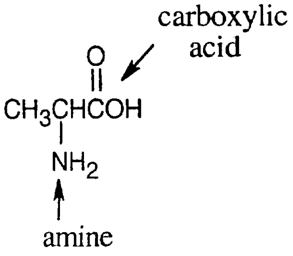
(b)



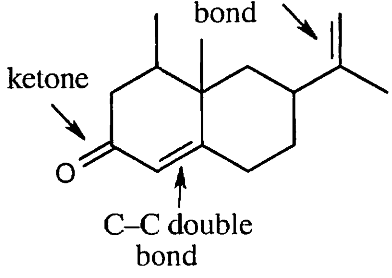
(c)



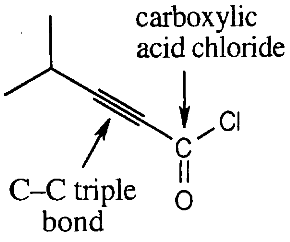
(d)



(e)

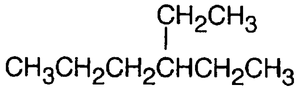


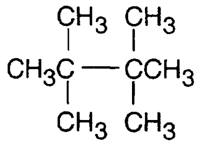
(f)



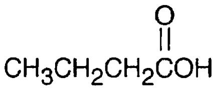
3.22 (a) Eighteen isomers have the formula C_8H_{18}. Three are pictured.

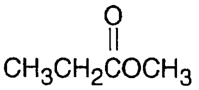
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$


$CH_3CH_2CH_2\overset{CH_2CH_3}{\overset{|}{C}}HCH_2CH_3$


$CH_3\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}CH_3$

(b) Structures with the formula $C_4H_8O_2$ may represent esters, carboxylic acids or many other complicated molecules. Three possibilities:


$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}OH$

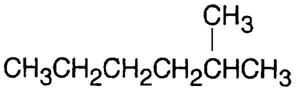

$CH_3CH_2\overset{O}{\overset{\|}{C}}OCH_3$

$HOCH_2CH=CHCH_2OH$

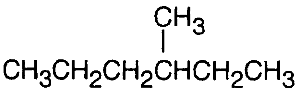
3.23

$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$

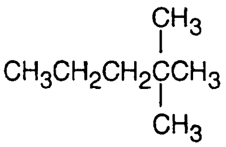
Heptane


$CH_3CH_2CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_3$

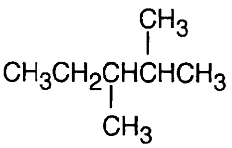
2-Methylhexane


$CH_3CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$

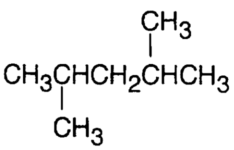
3-Methylhexane


$CH_3CH_2CH_2\underset{CH_3}{\overset{CH_3}{C}}CH_3$

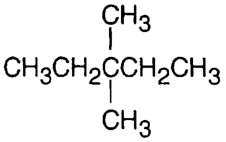
2,2-Dimethylpentane


$CH_3CH_2\overset{CH_3}{\overset{|}{C}}H\underset{CH_3}{\underset{|}{C}}HCH_3$

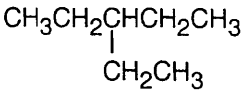
2,3-Dimethylpentane


$CH_3\underset{CH_3}{\underset{|}{C}}HCH_2\overset{CH_3}{\overset{|}{C}}HCH_3$

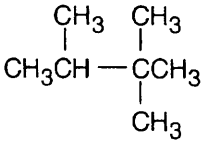
2,4-Dimethylpentane


$CH_3CH_2\underset{CH_3}{\overset{CH_3}{C}}CH_2CH_3$

3,3-Dimethylpentane


$CH_3CH_2\underset{CH_2CH_3}{\underset{|}{C}}HCH_2CH_3$

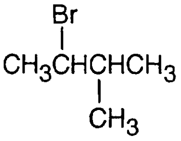
3-Ethylpentane


$CH_3\overset{CH_3}{\overset{|}{C}}H-\underset{CH_3}{\overset{CH_3}{C}}CH_3$

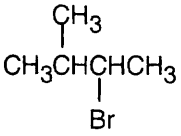
2,2,3-Trimethylbutane

3.24

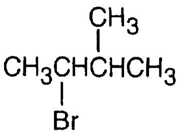
(a)


$CH_3\overset{Br}{\overset{|}{C}}H\underset{CH_3}{\underset{|}{C}}HCH_3$

same

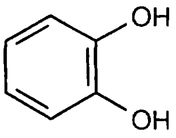

$CH_3\overset{CH_3}{\overset{|}{C}}H\underset{Br}{\underset{|}{C}}HCH_3$

same

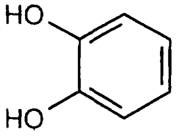

$CH_3\underset{Br}{\underset{|}{C}}H\overset{CH_3}{\overset{|}{C}}HCH_3$

same

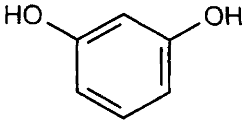
(b)



same

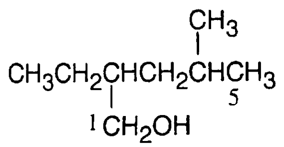


same



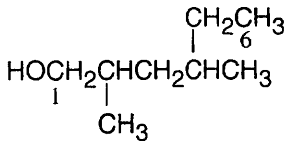
different

(c)



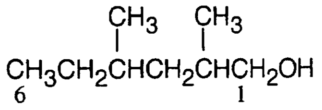
$CH_3CH_2\underset{{}^1CH_2OH}{\overset{}{C}}HCH_2\overset{CH_3}{\underset{5}{C}}HCH_3$

different



$HO\underset{1}{C}H_2\underset{CH_3}{C}HCH_2\overset{CH_2\overset{6}{C}H_3}{C}HCH_3$

same



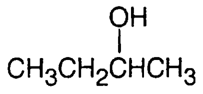
$\underset{6}{CH_3}CH_2\overset{CH_3}{C}HCH_2\overset{CH_3}{C}H\underset{1}{C}H_2OH$

same

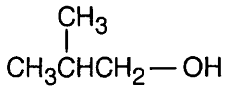
Give the number "1" to the carbon bonded to –OH, and count to find the longest chain containing the –OH group.

3.25 The isomers may be either alcohols or ethers.

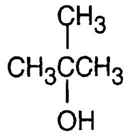
$CH_3CH_2CH_2CH_2—OH$



$CH_3CH_2\overset{OH}{C}HCH_3$

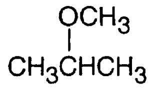


$CH_3\overset{CH_3}{C}HCH_2—OH$



$CH_3\underset{OH}{\overset{CH_3}{C}}CH_3$

$CH_3CH_2CH_2—OCH_3$

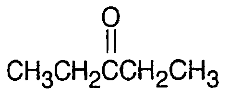


$CH_3\overset{OCH_3}{C}HCH_3$

$CH_3CH_2—OCH_2CH_3$

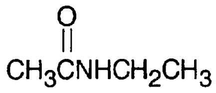
3.26 Different answers to this problem and to Problem 3.27 are acceptable.

(a)



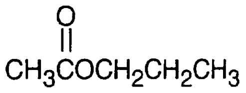
$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$

(b)



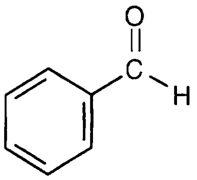
$CH_3\overset{O}{\overset{\|}{C}}NHCH_2CH_3$

(c)

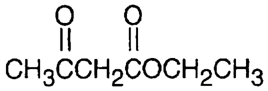


$CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_2CH_3$

(d)



(e)



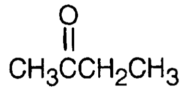
$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3$

(f)

$H_2NCH_2CH_2OH$

3.27

(a)

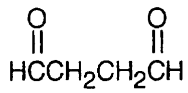


C_4H_8O: $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$

(b)

C_5H_9N: $CH_3CH_2CH_2CH_2C{\equiv}N$

(c)



$C_4H_6O_2$: $H\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}H$

(d)

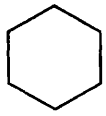
$C_6H_{11}Br$: $CH_3CH_2CH{=}CHCH_2CH_2Br$

(e)

C_6H_{14}: $CH_3CH_2CH_2CH_2CH_2CH_3$

(f)

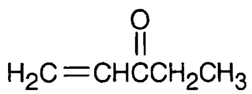
C_6H_{12}:



(g)

C_5H_8: $CH_3CH{=}CHCH{=}CH_2$

(h)

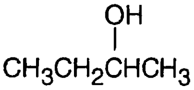


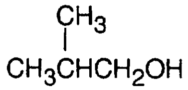
C_5H_8O: $H_2C{=}CH\overset{O}{\overset{\|}{C}}CH_2CH_3$

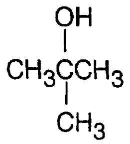
3.28 First, draw all straight-chain isomers. Then proceed to the simplest branched structure.

(a) There are four alcohol isomers with the formula $C_4H_{10}O$.

$CH_3CH_2CH_2CH_2OH$

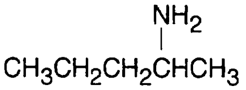

$CH_3CH_2\overset{\overset{OH}{|}}{C}HCH_3$

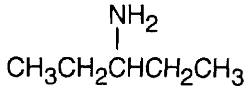

$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2OH$

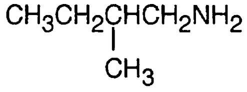

$CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}CH_3$

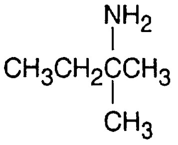
(b) There are 17 isomers of $C_5H_{13}N$. Nitrogen can be bonded to one, two or three alkyl groups.

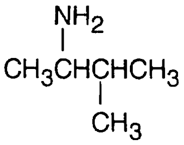
$CH_3CH_2CH_2CH_2CH_2NH_2$

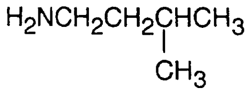

$CH_3CH_2CH_2\overset{\overset{NH_2}{|}}{C}HCH_3$

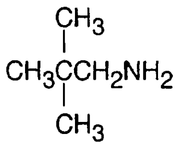

$CH_3CH_2\overset{\overset{NH_2}{|}}{C}HCH_2CH_3$


$CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCH_2NH_2$

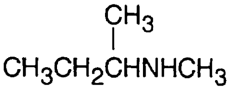

$CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{NH_2}{|}}{C}}CH_3$

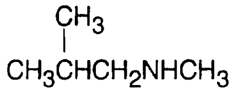

$CH_3\overset{\overset{NH_2}{|}}{C}H\underset{\underset{CH_3}{|}}{C}HCH_3$

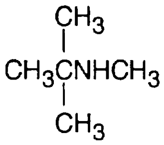

$H_2NCH_2CH_2\underset{\underset{CH_3}{|}}{C}HCH_3$


$CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_2NH_2$

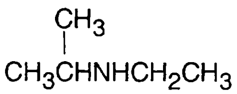
$CH_3CH_2CH_2CH_2NHCH_3$

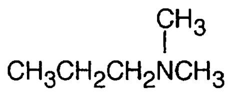

$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HNHCH_3$

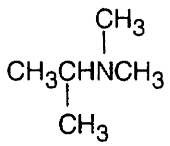

$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2NHCH_3$

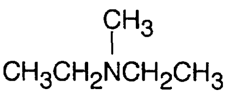

$CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}NHCH_3$

$CH_3CH_2CH_2NHCH_2CH_3$

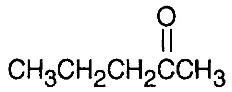

$CH_3\overset{\overset{CH_3}{|}}{C}HNHCH_2CH_3$

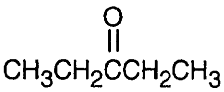

$CH_3CH_2CH_2\overset{\overset{CH_3}{|}}{N}CH_3$

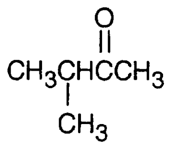

$CH_3\underset{\underset{CH_3}{|}}{C}H\overset{\overset{CH_3}{|}}{N}CH_3$


$CH_3CH_2\overset{\overset{CH_3}{|}}{N}CH_2CH_3$

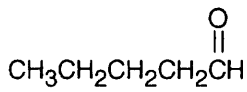
(c) There are 3 ketone isomers with the formula $C_5H_{10}O$.

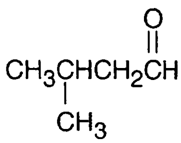

$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$

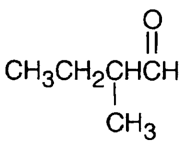

$CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3$

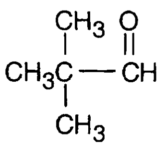

$CH_3\underset{\underset{CH_3}{|}}{C}H\overset{\overset{O}{\|}}{C}CH_3$

(d) There are 4 isomeric aldehydes with the formula $C_5H_{10}O$. Remember that the aldehyde functional group can occur only at the end of a chain.

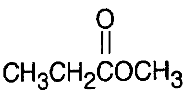

$CH_3CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}H$

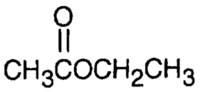

$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2\overset{\overset{O}{\|}}{C}H$

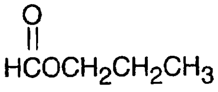

$CH_3CH_2\underset{\underset{CH_3}{|}}{C}H\overset{\overset{O}{\|}}{C}H$

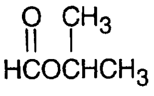

$CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{O}{\|}}{C}H$

(e) There are 4 esters with the formula $C_4H_8O_2$.


$CH_3CH_2\overset{O}{\overset{\|}{C}}OCH_3$

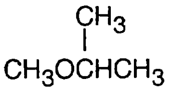

$CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3$


$H\overset{O}{\overset{\|}{C}}OCH_2CH_2CH_3$


$H\overset{O}{\overset{\|}{C}}O\overset{CH_3}{\overset{|}{C}}HCH_3$

(f) There are 3 ethers with the formula $C_4H_{10}O$.

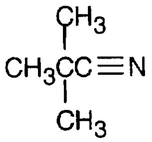
$CH_3CH_2OCH_2CH_3$ $CH_3OCH_2CH_2CH_3$


$CH_3O\overset{CH_3}{\overset{|}{C}}HCH_3$

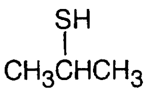
3.29

(a) CH_3CH_2OH

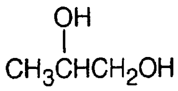
(b)


$CH_3\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}C\equiv N$

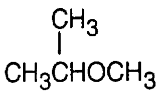
(c)


$CH_3\overset{SH}{\overset{|}{C}}HCH_3$

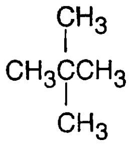
(d)


$CH_3\overset{OH}{\overset{|}{C}}HCH_2OH$

(e)


$CH_3\overset{CH_3}{\overset{|}{C}}HOCH_3$

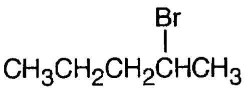
(f)


$CH_3\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}CH_3$

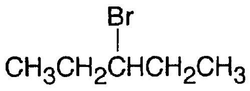
3.30

$CH_3CH_2CH_2CH_2CH_2Br$

1-Bromopentane

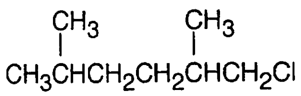

$CH_3CH_2CH_2\overset{Br}{\overset{|}{C}}HCH_3$

2-Bromopentane

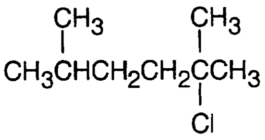

$CH_3CH_2\overset{Br}{\overset{|}{C}}HCH_2CH_3$

3-Bromopentane

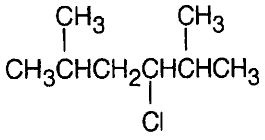
3.31


$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_2Cl$

1-Chloro-2,5-dimethylhexane


$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2\underset{\underset{Cl}{|}}{\overset{CH_3}{\overset{|}{C}}}CH_3$

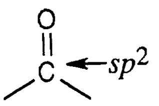
2-Chloro-2,5-dimethylhexane


$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2\underset{\underset{Cl}{|}}{C}H\overset{CH_3}{\overset{|}{C}}HCH_3$

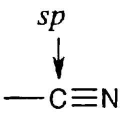
3-Chloro-2,5-di methylhexane

3.32

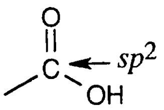
(a)



(b)

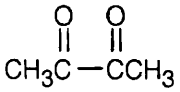


(c)



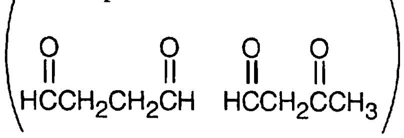
3.33 (a) Although it is stated that biacetyl contains no rings or carbon–carbon double bonds, it is obvious from the formula for biacetyl that some sort of multiple bond must be present. The structure for biacetyl contains two carbon–oxygen double bonds.
(b) Ethyleneimine contains a three-membered ring.
(c) Glycerol contains no multiple bonds or rings.

(a)

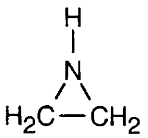

$CH_3\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}CH_3$

Biacetyl

also possible:

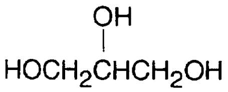

$H\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}H \quad H\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3$

(b)



Ethyleneimine

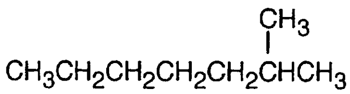
(c)


$HOCH_2\overset{OH}{\overset{|}{C}}HCH_2OH$

Glycerol

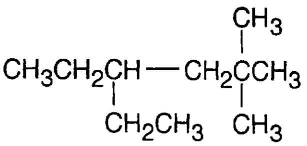
3.34

(a)


$CH_3CH_2CH_2CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_3$

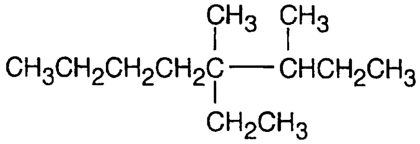
2-Methylheptane

(b)


$CH_3CH_2\underset{\underset{CH_2CH_3}{|}}{C}H-CH_2\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}CH_3$

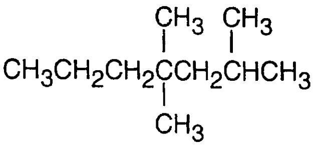
4-Ethyl-2,2-dimethylhexane

(c)


$CH_3CH_2CH_2CH_2\overset{CH_3}{\overset{|}{\underset{\underset{CH_2CH_3}{|}}{C}}}-\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$

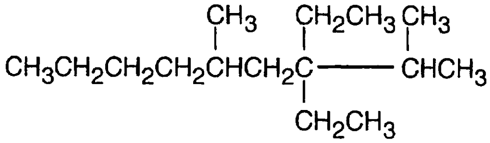
4-Ethyl-3,4-dimethyloctane

(d)


$CH_3CH_2CH_2\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}CH_2\overset{CH_3}{\overset{|}{C}}HCH_3$

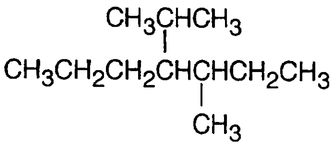
2,4,4-Trimethylheptane

(e)


$CH_3CH_2CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_2\overset{CH_2CH_3}{\overset{|}{\underset{\underset{CH_2CH_3}{|}}{C}}}-\overset{CH_3}{\overset{|}{C}}HCH_3$

3,3-Diethyl-2,5-dimethylnonane

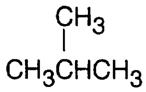
(f)


$CH_3CH_2CH_2\overset{CH_3CHCH_3}{\overset{|}{C}}H\underset{\underset{CH_3}{|}}{C}HCH_2CH_3$

4-Isopropyl-3-methylheptane

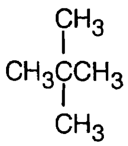
3.35

(a)


$CH_3\overset{CH_3}{\overset{|}{C}}HCH_3$

2-Methylpropane

(b)


$CH_3\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}CH_3$

2,2-Dimethylpropane

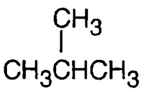
(c)

$CH_3CH_2CH_2CH_2CH_2CH_3$

Hexane

3.36

(a)


$CH_3\overset{CH_3}{\overset{|}{C}}HCH_3$

2-Methylpropane

(b)

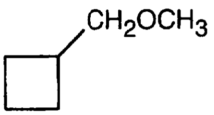
CH_3CH_3

Ethane

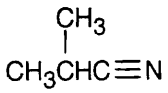
3.37

(a) $CH_3CH_2CH_2CH_2CH_2Br$

(b)

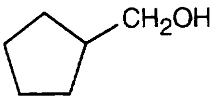


(c)

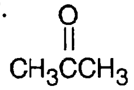


$CH_3\overset{\overset{CH_3}{|}}{C}HC\equiv N$

(d)

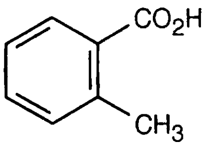


(e) There are no aldehyde isomers. However, the structure below is a ketone isomer.



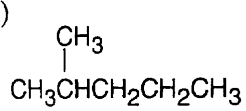
$CH_3\overset{\overset{O}{\|}}{C}CH_3$

(f)



3.38

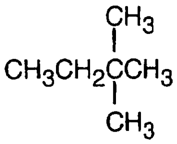
(a)



$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_3$

2-Methylpentane

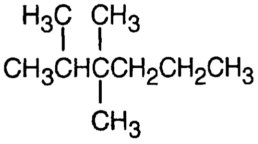
(b)



$CH_3CH_2\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_3$

2,2-Dimethylbutane

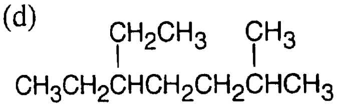
(c)



$CH_3\overset{\overset{H_3C}{|}}{C}H\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2CH_2CH_3$

2,3,3-Trimethylhexane

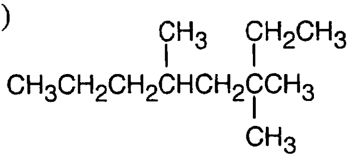
(d)



$CH_3CH_2\overset{\overset{CH_2CH_3}{|}}{C}HCH_2CH_2\overset{\overset{CH_3}{|}}{C}HCH_3$

5-Ethyl-2-methylheptane

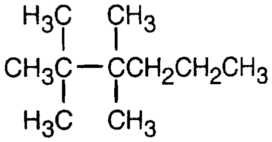
(e)



$CH_3CH_2CH_2\overset{\overset{CH_3}{|}}{C}HCH_2\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_3$

3,3,5-Trimethyloctane

(f)



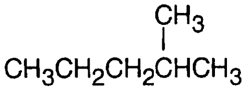
$CH_3\overset{\overset{H_3C}{|}}{\underset{\underset{H_3C}{|}}{C}}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2CH_2CH_3$

2,2,3,3-Tetramethylhexane

3.39

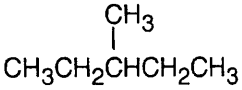
$CH_3CH_2CH_2CH_2CH_2CH_3$

Hexane



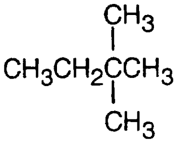
$CH_3CH_2CH_2\overset{\overset{CH_3}{|}}{C}HCH_3$

2-Methylpentane



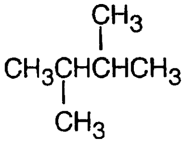
$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_3$

3-Methylpentane



$CH_3CH_2\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_3$

2,2-Dimethylbutane

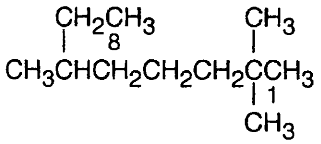


$CH_3\underset{\underset{CH_3}{|}}{C}H\overset{\overset{CH_3}{|}}{C}HCH_3$

2,3-Dimethylbutane

3.40 *Structure and Correct Name* *Error*

(a)

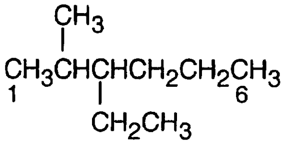


$$\overset{CH_2CH_3\ 8}{CH_3CH}CH_2CH_2CH_2\overset{CH_3}{\underset{1\ CH_3}{C}}CH_3$$

Correct name: 2,2,6-Trimethyloctane

The longest chain is an octane.

(b)

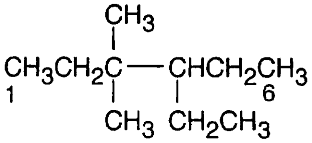


$$\underset{1}{CH_3}\overset{CH_3}{CH}\underset{CH_2CH_3}{CH}CH_2CH_2\underset{6}{CH_3}$$

Correct name: 3-Ethyl-2-methylhexane

The longest chain is a hexane. Numbering should start from the opposite end of the carbon chain, nearer the first branch.

(c)

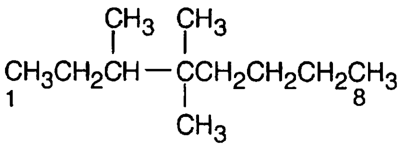


$$\underset{1}{CH_3}CH_2\overset{CH_3}{\underset{CH_3}{C}}-\underset{CH_2CH_3}{CH}CH_2\underset{6}{CH_3}$$

Correct name: 4-Ethyl-3,3-dimethylhexane

Numbering should start from the opposite end of the carbon chain. See step 2(b) in Section 3.4.

(d)

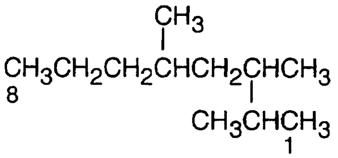


$$\underset{1}{CH_3}CH_2\overset{CH_3}{CH}-\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2CH_2\underset{8}{CH_3}$$

Correct name: 3,4,4-Trimethyloctane

Numbering should start from the opposite end of the carbon chain.

(e)



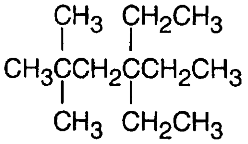
$$\underset{8}{CH_3}CH_2CH_2\overset{CH_3}{CH}CH_2\underset{CH_3CH\underset{1}{CH_3}}{CH}CH_3$$

Correct name: 2,3,5-Trimethyloctane

The longest chain is an octane.

3.41

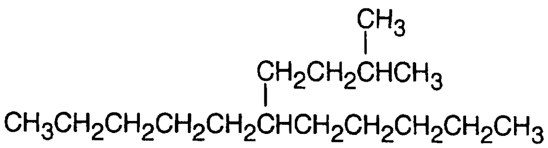
(a)



$$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\overset{CH_2CH_3}{\underset{CH_2CH_3}{C}}CH_2CH_3$$

4,4-Diethyl-2,2-dimethylhexane

(b)



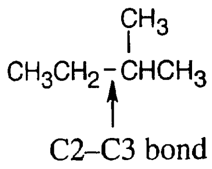
$$CH_3CH_2CH_2CH_2CH_2\overset{CH_2CH_2\overset{CH_3}{CH}CH_3}{CH}CH_2CH_2CH_2CH_2CH_3$$

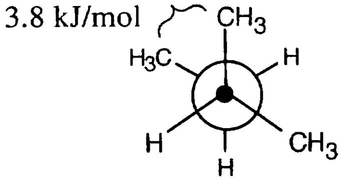
6-(3-Methylbutyl)-undecane

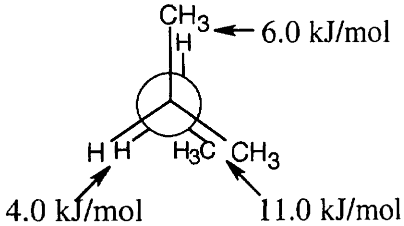
Remember that you must choose an alkane whose principal chain is long enough so that the substituent does not become part of the principal chain.

3.42

(a), (b)



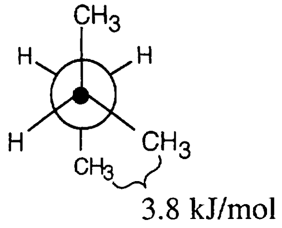


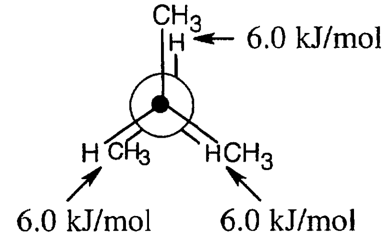


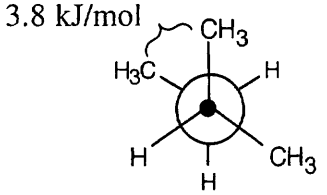
2-Methylbutane Most stable conformation Least stable comformation

The energy difference between the two conformations is (11.0 + 6.0 + 4.0) kJ/mol – 3.8 kJ/mol = 17.2 kJ/mol.

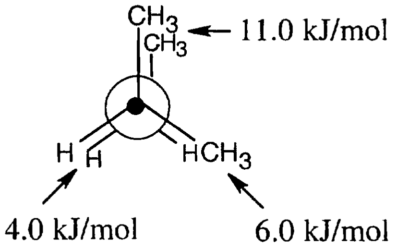
(c) Consider the least stable conformation to be at zero degrees. Keeping the front of the projection unchanged, rotate the back by 60° to obtain each conformation.

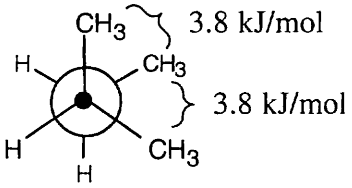






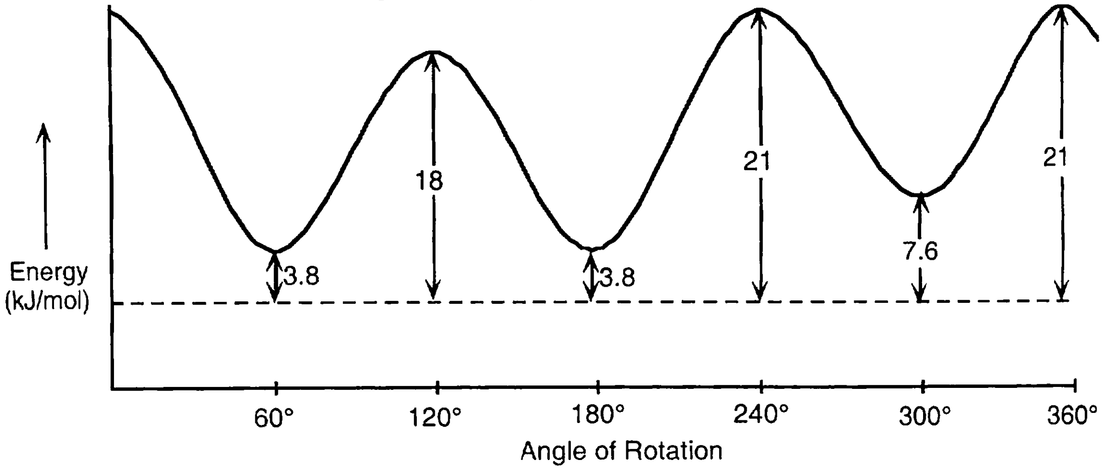
at 60°: energy = 3.8 kJ/mol at 120°: energy = 18.0 kJ/mol at 180°: energy = 3.8 kJ/mol



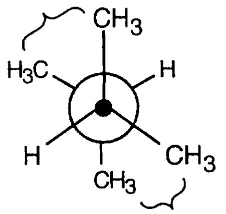


at 240°: energy = 21.0 kJ/mol at 300°: energy = 7.6 kJ/mol

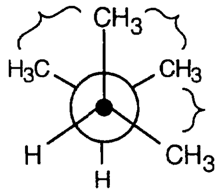
Use the lowest energy conformation as the energy minimum. The highest energy conformation is 17.2 kJ/mol higher in energy than the lowest energy conformation.



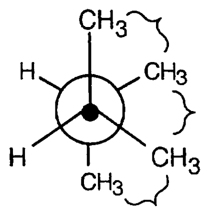
3.43



2 $CH_3 \leftrightarrow CH_3$ gauche
= 2 x 3.8 kJ/mol
= 7.6 kJ/mol

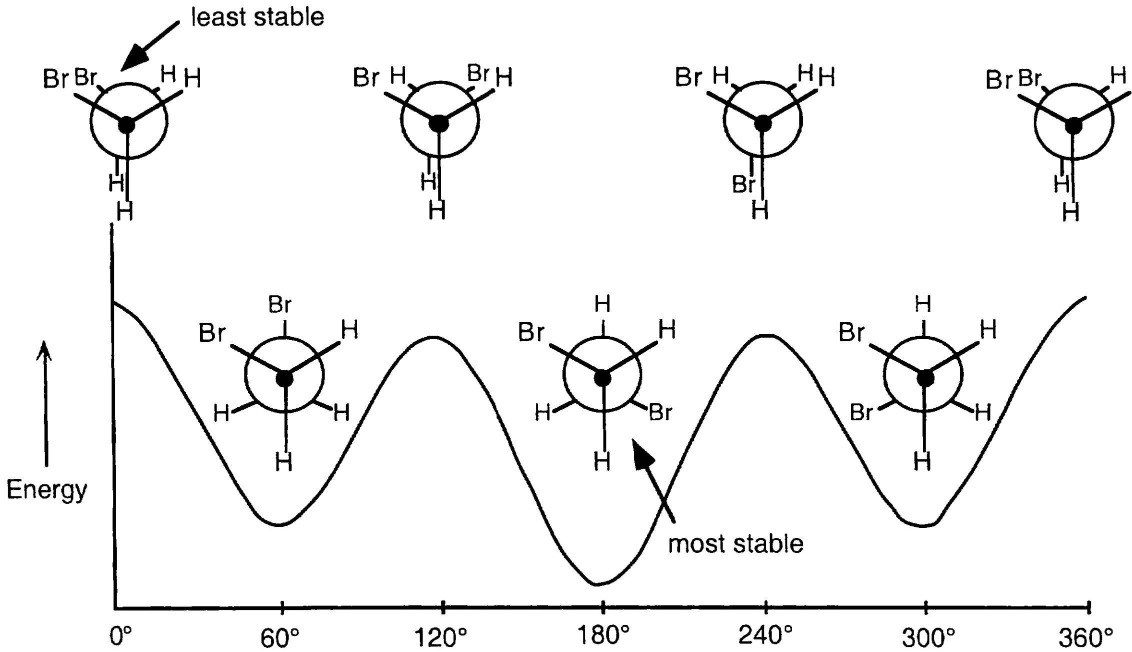


3 $CH_3 \leftrightarrow CH_3$ gauche
= 3 x 3.8 kJ/mol
= 11.4 kJ/mol



3 $CH_3 \leftrightarrow CH_3$ gauche
= 3 x 3.8 kJ/mol
= 11.4 kJ/mol

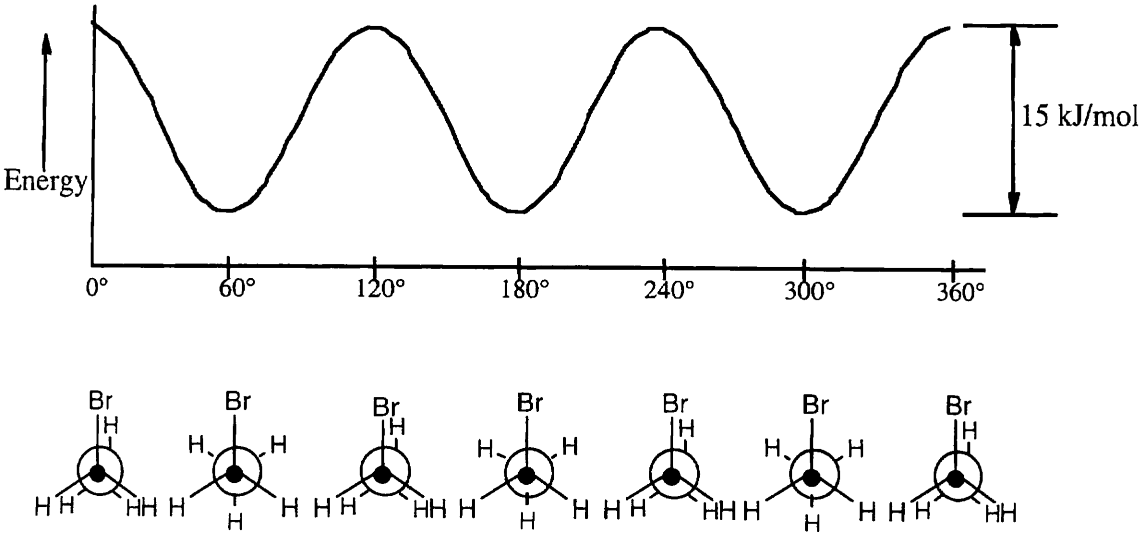
3.44 Since we are not told the values of the interactions for 1,2-dibromoethane, the diagram can only be qualitative.



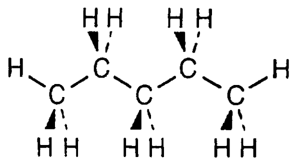
The anti conformation is at 180°.
The gauche conformations are at 60°, 300°.′

3.45 The anti conformation has no net dipole moment because the polarities of the individual bonds cancel. The gauche conformation, however, has a dipole moment. Because the observed dipole moment is 1.0 D at room temperature, a mixture of conformations must be present.

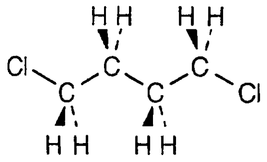
3.46 The highest energy conformation of bromoethane has a strain energy of 15 kJ/mol. Because this includes two H–H eclipsing interactions of 4.0 kJ/mol each, the value of an H–Br eclipsing interaction is 15 kJ/mol – 2(4.0 kJ/mol) = 7.0 kJ/mol.



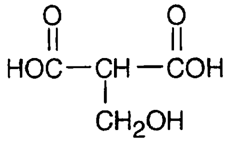
3.47 The best way to draw pentane is to make a model and to copy it onto the page. A model shows the relationship among atoms, and its drawing shows how these relationships appear in two dimensions. From your model, you should be able to see that all atoms are staggered in the drawing.



3.48

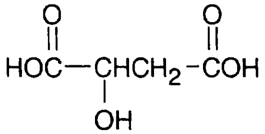


3.49 **Strategy:** (a) Because malic acid has two $-CO_2H$ groups, the formula for the rest of the molecule is C_2H_4O. Possible structures for malic acid are:



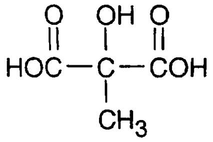
$$HO\overset{O}{\overset{\|}{C}}-\underset{CH_2OH}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}OH$$

primary alcohol



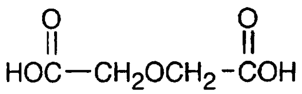
$$HO\overset{O}{\overset{\|}{C}}-\underset{OH}{\underset{|}{C}}HCH_2-\overset{O}{\overset{\|}{C}}OH$$

secondary alcohol

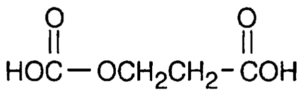


$$HO\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}OH$$

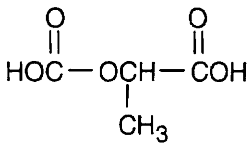
tertiary alcohol



$$HO\overset{O}{\overset{\|}{C}}-CH_2OCH_2-\overset{O}{\overset{\|}{C}}OH$$



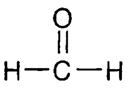
$$HO\overset{O}{\overset{\|}{C}}-OCH_2CH_2-\overset{O}{\overset{\|}{C}}OH$$



$$HO\overset{O}{\overset{\|}{C}}-O\underset{CH_3}{\underset{|}{C}}H-\overset{O}{\overset{\|}{C}}OH$$

(b) Because only one of these compounds (the second one) is also a secondary alcohol, it must be malic acid.

3.50 **Strategy:** To solve this type of problem, read the problem carefully, word for word. Then try to interpret parts of the problem. For example:

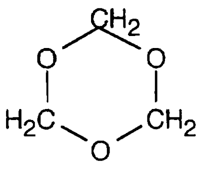
1) Formaldehyde is an aldehyde,  $H-\overset{O}{\overset{\|}{C}}-H$

2) It trimerizes – that is, 3 formaldehydes come together to form a compound $C_3H_6O_3$. Because no atoms are eliminated, all of the original atoms are still present.

3) There are no carbonyl groups. This means that trioxane cannot contain any $-C{=}O$ functional groups. If you look back to Table 3.1, you can see that the only oxygen-containing functional groups that can be present are either ethers or alcohols.

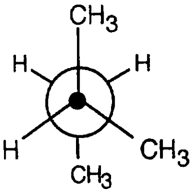
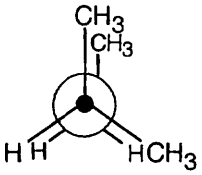
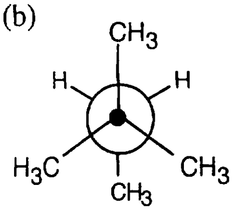
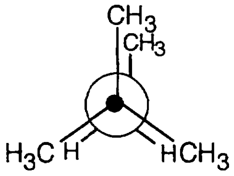
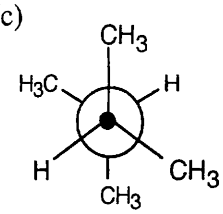
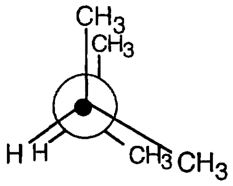
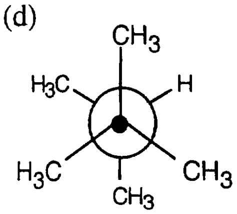
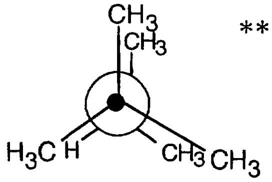
4) A monobromo derivative is a compound in which one of the –H's has been replaced by a –Br. Because only one monobromo derivative is possible, we know that there can only be one type of hydrogen in trioxane. The only possibility for trioxane is:

Solution:



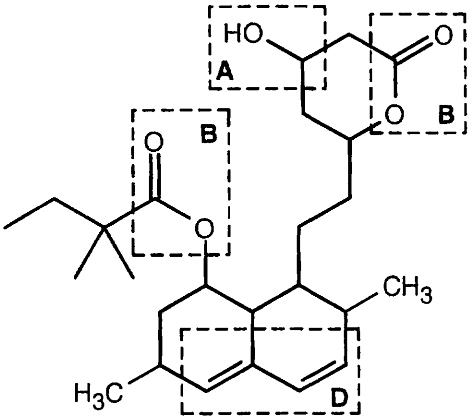
Trioxane

3.51

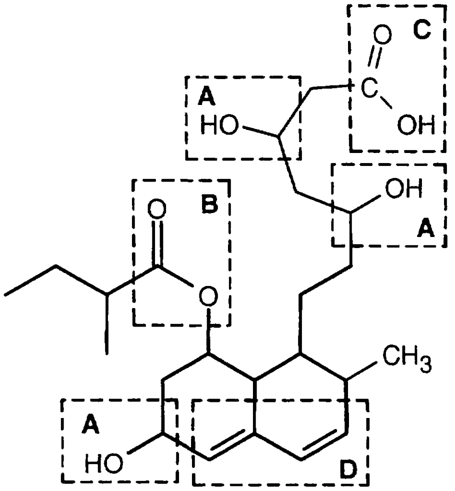
	Most stable	*Strain energy*	*Least stable*	*Strain energy*
(a)		* 3.8 kJ/mol		21 kJ/mol
(b)		7.6 kJ/mol		23 kJ/mol
(c)		7.6 kJ/mol		26 kJ/mol
(d)		15.2 kJ/mol		** 28 kJ/mol

*most stable overall (least strain)
**least stable overall (most strain)

3.52



Zocor $C_{25}H_{38}O_5$

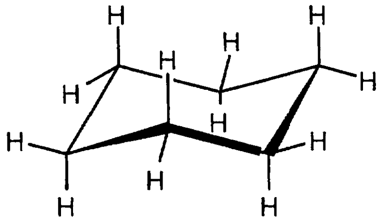


Pravachol $C_{23}H_{36}O_7$

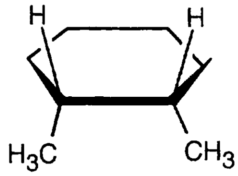
A	alcohol	**B**	ester
C	carboxylic acid	**D**	C–C double bond (alkene)

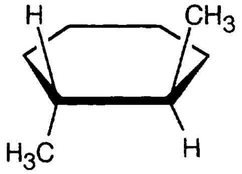
The carboxylic acid group in Pravachol is an ester group in Zocor.
The alcohol at the bottom left of Pravachol is a methyl group in Zocor.

3.53 A puckered ring allows all the bonds in the ring to have a nearly tetrahedral bond angle. (If the ring were flat, C–C–C bond angles would be 120°.)



3.54





In one of the 1,2-dimethylcyclohexanes the two methyl groups are on the same side of the ring, and in the other isomer the methyl groups are on opposite sides.