

## Chapter 2: Three-Dimensional Geometry, Intermolecular Interactions, and Physical Properties

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### LEARNING OBJECTIVES

Determine the number of groups around a central atom.

Determine an atom's molecular geometry.

Determine an atom's electronic geometry.

Apply VSEPR theory to understand organic structure and geometry.

Use molecular geometry to predict bond angles.

Relate polarity to molecular geometry and physical properties.

Correctly depict the three-dimensional structure of a molecule using dash-wedge notation.

Understand the influence of ring strain on organic structure.

Execute a prescribed rotation and draw the molecule in its new orientation.

Differentiate between polar and nonpolar organic molecules.

Identify the relative strength of the common intermolecular forces as they apply to organic molecules.

Identify the intermolecular forces in which a functional group engages.

Utilize knowledge of chemical structure to identify solubility properties of an organic compound.

Deduce the intermolecular forces that are possible between specified molecules.

Evaluate the solvation of an ion or molecule by a protic or an aprotic solvent.

Predict the solubility of an organic species during a chemical reaction and/or extraction.

Explain how and why soaps and detergents work as cleaning agents.

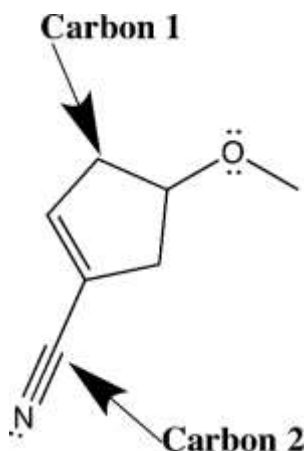
Diagram a micelle to identify the intermolecular forces that are present.

Identify biomolecules by their structure.

Identify the isoprene units in a polyisoprenoid.

## MULTIPLE CHOICE

1. When applying VSEPR theory to determine the geometry about a central atom, it is important to count the number of electron groups. Separately consider the two atoms highlighted with an arrow in the molecule shown below. How many electron groups must be considered for each of these central atoms?



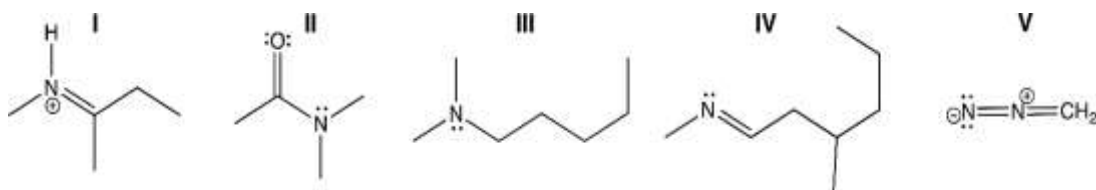
- $C_1$  has two groups;  $C_2$  has two groups.
- $C_1$  has three groups;  $C_2$  has four groups.
- $C_1$  has four groups;  $C_2$  has two groups.
- $C_1$  has four groups;  $C_2$  has three groups.
- $C_1$  has four groups;  $C_2$  has four groups.

ANS: C                      DIF: Moderate                      REF: 2.1

OBJ: Determine the number of groups around a central atom.

MSC: Understanding

2. Which of the following molecules contains a nitrogen atom that has bent molecular geometry?



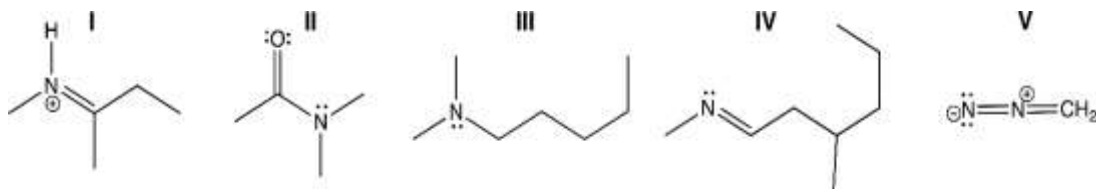
- I
- II
- III
- IV
- V

ANS: D                      DIF: Moderate                      REF: 2.1

OBJ: Determine an atom's molecular geometry.

MSC: Understanding

3. Which of the following molecules contain(s) a nitrogen atom that has trigonal pyramidal molecular geometry?



- I only
- II only
- III only
- I and II
- II and III

ANS: C                      DIF: Moderate                      REF: 2.1

OBJ: Determine an atom's molecular geometry.

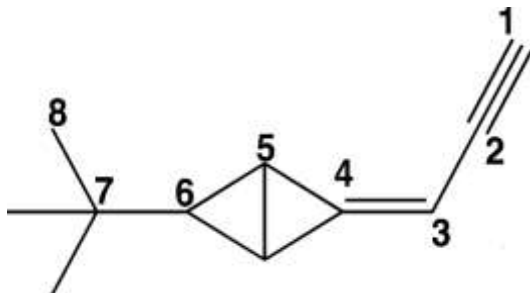
MSC: Understanding

4. Which cycloalkane contains a C—C—C bond angle that deviates from the ideal tetrahedral bond angle by approximately  $20^\circ$ ?

- a. a seven-membered cycloalkane
- b. a six-membered cycloalkane
- c. a five-membered cycloalkane
- d. a four-membered cycloalkane
- e. a three-membered cycloalkane

ANS: D                      DIF: Moderate                      REF: 2.1  
 OBJ: Understand the influence of ring strain on organic structure.  
 MSC: Understanding

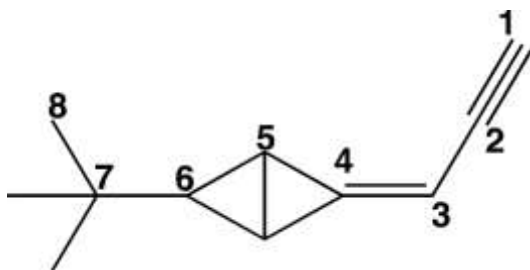
5. The carbon atoms in the molecule below are labeled 1–8. Which C—C—C bond angle in the molecule would be approximately 120°?



- a. C<sub>1</sub>—C<sub>2</sub>—C<sub>3</sub>
- b. C<sub>2</sub>—C<sub>3</sub>—C<sub>4</sub>
- c. C<sub>4</sub>—C<sub>5</sub>—C<sub>6</sub>
- d. C<sub>5</sub>—C<sub>6</sub>—C<sub>7</sub>
- e. C<sub>6</sub>—C<sub>7</sub>—C<sub>8</sub>

ANS: B                      DIF: Moderate                      REF: 2.1  
 OBJ: Use molecular geometry to predict bond angles. MSC: Understanding

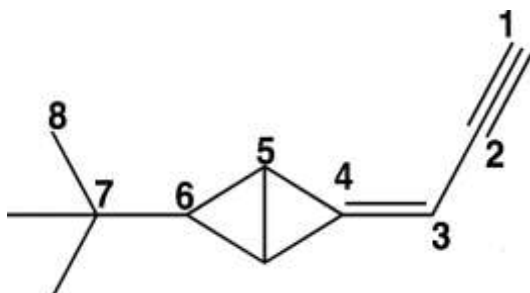
6. The carbon atoms in the molecule below are labeled 1–8. Which C—C—C bond angle in the molecule would be approximately 180°?



- a. C<sub>1</sub>—C<sub>2</sub>—C<sub>3</sub>
- b. C<sub>2</sub>—C<sub>3</sub>—C<sub>4</sub>
- c. C<sub>4</sub>—C<sub>5</sub>—C<sub>6</sub>
- d. C<sub>5</sub>—C<sub>6</sub>—C<sub>7</sub>
- e. C<sub>6</sub>—C<sub>7</sub>—C<sub>8</sub>

ANS: A                      DIF: Easy                      REF: 2.1  
 OBJ: Use molecular geometry to predict bond angles. MSC: Applying

7. The carbon atoms in the molecule below are labeled 1–8. Which C—C—C bond angle in the molecule would be approximately 109.5°?

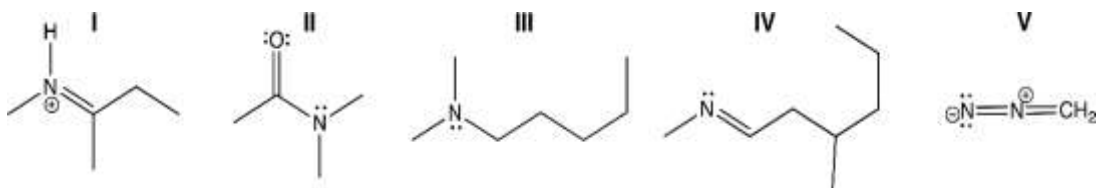


- a. C<sub>1</sub>—C<sub>2</sub>—C<sub>3</sub>
- b. C<sub>2</sub>—C<sub>3</sub>—C<sub>4</sub>
- d. C<sub>5</sub>—C<sub>6</sub>—C<sub>7</sub>
- e. C<sub>6</sub>—C<sub>7</sub>—C<sub>8</sub>

c. C<sub>4</sub>—C<sub>5</sub>—C<sub>6</sub>

ANS: E                  DIF: Easy                  REF: 2.1  
OBJ: Use molecular geometry to predict bond angles. MSC: Applying

8. Which of the following molecules contains a nitrogen atom with linear geometry?



- a. I                                                  d. IV  
b. II                                                 e. V  
c. III

ANS: E                  DIF: Moderate                  REF: 2.1  
OBJ: Determine an atom's molecular geometry. MSC: Applying

9. Which cycloalkane has the greatest ring strain per-CH<sub>2</sub>-unit?  
a. a seven-membered cycloalkane                          d. a four-membered cycloalkane  
b. a six-membered cycloalkane                              e. a three-membered cycloalkane  
c. a five-membered cycloalkane

ANS: E                  DIF: Moderate                  REF: 2.1  
OBJ: Understand the influence of ring strain on organic structure.  
MSC: Analyzing

10. Which cycloalkane contains a C—C—C bond angle that deviates from the ideal tetrahedral bond angle by approximately 50°?  
a. a seven-membered cycloalkane                          d. a four-membered cycloalkane  
b. a six-membered cycloalkane                              e. a three-membered cycloalkane  
c. a five-membered cycloalkane

ANS: E                  DIF: Moderate                  REF: 2.1  
OBJ: Understand the influence of ring strain on organic structure.  
MSC: Analyzing

11. Which of the following cycloalkanes contains a C—C—C bond angle of approximately 90°?  
a. a seven-membered cycloalkane                          d. a four-membered cycloalkane  
b. a six-membered cycloalkane                              e. a three-membered cycloalkane  
c. a five-membered cycloalkane

ANS: D                  DIF: Easy                          REF: 2.1  
OBJ: Understand the influence of ring strain on organic structure.  
MSC: Understanding

12. What is the molecular geometry for the carbon atom in COCl<sub>2</sub>?  
a. linear                                                              d. trigonal planar  
b. tetrahedral                                                         e. bent  
c. trigonal pyramidal

ANS: D                  DIF: Moderate                  REF: 2.1  
OBJ: Determine an atom's molecular geometry. MSC: Understanding

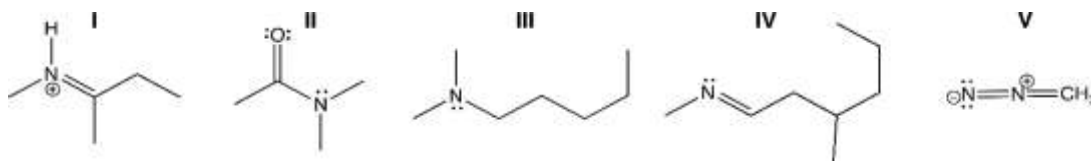
13. What is the molecular geometry for any carbon atom in an aryl ring?  
a. linear                                                                 d. trigonal planar  
b. tetrahedral                                                           e. bent  
c. trigonal pyramidal

ANS: D                  DIF: Moderate                  REF: 2.1

OBJ: Determine an atom's molecular geometry.

MSC: Understanding

14. Which of the following molecules contains a trigonal planar nitrogen atom connected to one tetrahedral carbon atom?



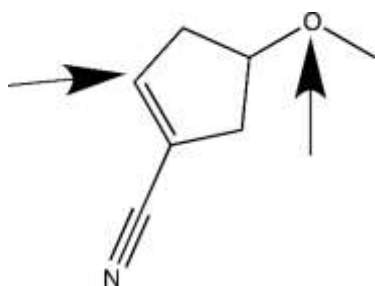
- a. I  
b. II  
c. III  
d. IV  
e. V

ANS: A                      DIF: Moderate                      REF: 2.1

OBJ: Determine an atom's molecular geometry.

MSC: Understanding

15. When applying VSEPR theory to determine the geometry about a central atom, it is important to count the total number of bonded and nonbonded electron groups. Separately consider the two atoms highlighted with an arrow in the molecule shown below. How many bonded electron groups must be considered for each of these central atoms?



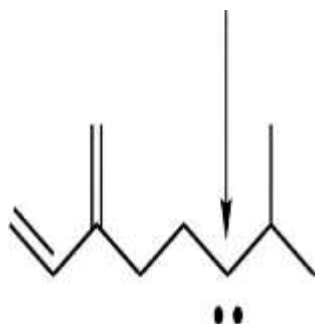
- a. C has two groups; O has two groups.  
b. C has three groups; O has four groups.  
c. C has three groups; O has two groups.  
d. C has three groups; O has three groups.  
e. C has four groups; O has four groups.

ANS: B                      DIF: Moderate                      REF: 2.1

OBJ: Determine the number of groups around a central atom.

MSC: Understanding

16. What is the electronic geometry for the indicated atom?



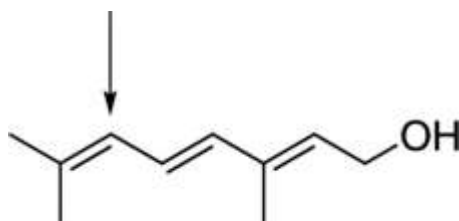
- a. linear  
b. trigonal planar  
c. trigonal pyramidal  
d. tetrahedral  
e. bent

ANS: D                      DIF: Moderate                      REF: 2.1

OBJ: Determine an atom's electronic geometry.

MSC: Understanding

17. What is the electronic geometry for the indicated atom?



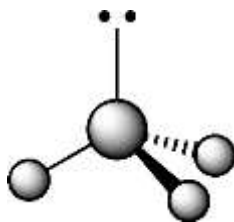
- a. linear  
 b. trigonal planar  
 c. trigonal pyramidal  
 d. tetrahedral  
 e. bent

ANS: B DIF: Easy REF: 2.1

OBJ: Determine an atom's electronic geometry.

MSC: Understanding

18. How does the presence of the lone pair affect the geometry of the central atom in the following molecule?



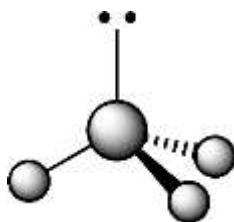
- I. The lone pair is attracted to the nuclei of the three substituents, creating larger bond angles.  
 II. The lone pair repels the three sets of covalently bonded electrons.  
 III. The lone pair has no bearing whatsoever on the VSEPR geometry at the central atom.  
 IV. The bond angles are smaller than a traditional tetrahedral bond angle due to lone pair repulsion.
- a. I  
 b. II  
 c. III  
 d. IV  
 e. II and IV

ANS: E DIF: Difficult REF: 2.1

OBJ: Apply VSEPR theory to understand organic structure and geometry.

MSC: Understanding

19. What are the approximate H—C—H bond angles expected for the carbanion whose structure is given in the ball-and-stick representation below?



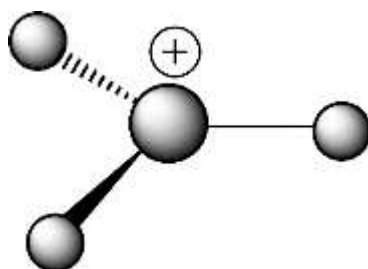
- a. 180°  
 b. 150°  
 c. 109.5°  
 d. 107°  
 e. 90°

ANS: D DIF: Moderate REF: 2.1 | 2.2

OBJ: Use molecular geometry to predict bond angles.

MSC: Understanding

20. Which of the following choices correctly describes the structure of the ball-and-stick representation with the formula  $\text{H}_3\text{C}^+$ ?

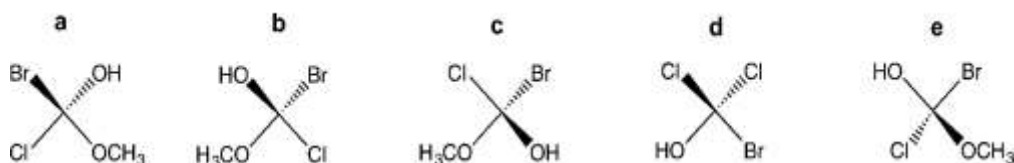
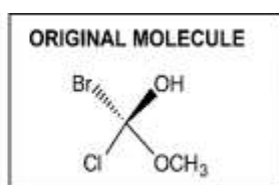


- a carbocation with a tetrahedral carbon
- a carbocation with trigonal planar geometry
- a carbocation with unknown geometry
- a carbanion with a tetrahedral carbon
- a carbanion with trigonal planar geometry

ANS: B                      DIF: Moderate                      REF: 2.1 | 2.2  
 OBJ: Determine an atom's molecular geometry.

MSC: Analyzing

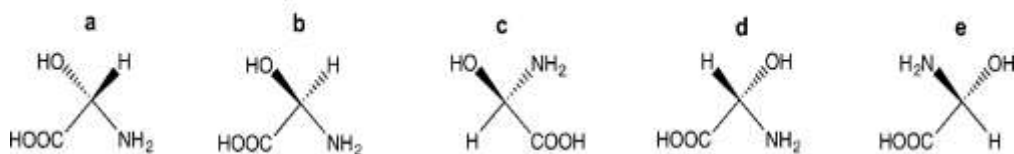
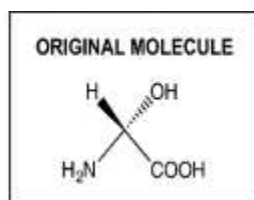
21. Turn the original molecule shown below  $90^\circ$  in a clockwise direction on the plane of this paper. Which choice represents the product of this manipulation?



- structure a
- structure b
- structure c
- structure d
- structure e

ANS: C                      DIF: Moderate                      REF: 2.2  
 OBJ: Execute a prescribed rotation and draw the molecule in its new orientation.  
 MSC: Applying

22. Rotate the molecule below horizontally  $180^\circ$ , in the same way you would flip a pancake or an egg during cooking. Which choice represents the product of the manipulation?



- structure a
- structure b
- structure c
- structure d
- structure e

ANS: B                    DIF: Moderate            REF: 2.2  
OBJ: Execute a prescribed rotation and draw the molecule in its new orientation.  
MSC: Applying

23. Which of the following molecules possesses at least one polar covalent bond but does not have an overall net molecular dipole?
- a. CH<sub>4</sub>
  - b. CHCl<sub>3</sub>
  - c. CH<sub>2</sub>Cl<sub>2</sub>
  - d. CCl<sub>4</sub>
  - e. CH<sub>3</sub>CH<sub>3</sub>

ANS: D                    DIF: Moderate            REF: 2.4  
OBJ: Differentiate between polar and nonpolar organic molecules.  
MSC: Remembering

24. Which of the following intermolecular forces is responsible for the boiling-point trends in alkanes?
- a. hydrogen bond
  - b. ion–dipole
  - c. ion–ion
  - d. dipole-induced dipole
  - e. induced dipole–induced dipole

ANS: E                    DIF: Easy                    REF: 2.6  
OBJ: Identify the intermolecular forces in which a functional group engages.  
MSC: Analyzing

25. Which functional group will engage in dipole–dipole interactions, but will NOT serve as a hydrogen-bond acceptor?
- a. nitrile
  - b. ketone
  - c. alkyl bromide
  - d. carboxylic acid
  - e. amine

ANS: C                    DIF: Moderate            REF: 2.6  
OBJ: Identify the intermolecular forces in which a functional group engages.  
MSC: Analyzing

26. Which of the following functional groups contains *both* a hydrogen-bond donor and a hydrogen-bond acceptor?
- a. alkyl fluoride
  - b. epoxide
  - c. carboxylic acid
  - d. nitrile
  - e. ketone

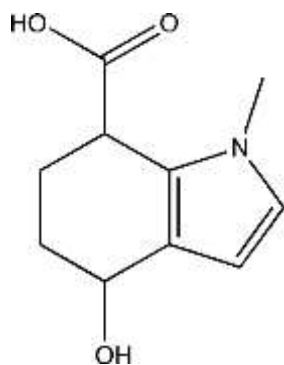
ANS: C                    DIF: Easy                    REF: 2.6  
OBJ: Identify the intermolecular forces in which a functional group engages.  
MSC: Applying

27. Identify the strongest intermolecular force.
- a. hydrogen bond
  - b. ion–dipole
  - c. ion–ion
  - d. dipole-induced dipole
  - e. induced dipole–induced dipole

ANS: C                    DIF: Easy                    REF: 2.6  
OBJ: Identify the relative strength of the common intermolecular forces as they apply to organic molecules.  
MSC: Remembering

28. How many hydrogen-bond donors and acceptors are present in the following molecule?





- a. one donor and four acceptors  
 b. two donors and four acceptors  
 c. two donors and three acceptors  
 d. one donor and three acceptors  
 e. two donors and two acceptors

ANS: B                      DIF: Easy                      REF: 2.6

OBJ: Identify the intermolecular forces in which a functional group engages.

MSC: Applying

29. Identify the weakest intermolecular force.

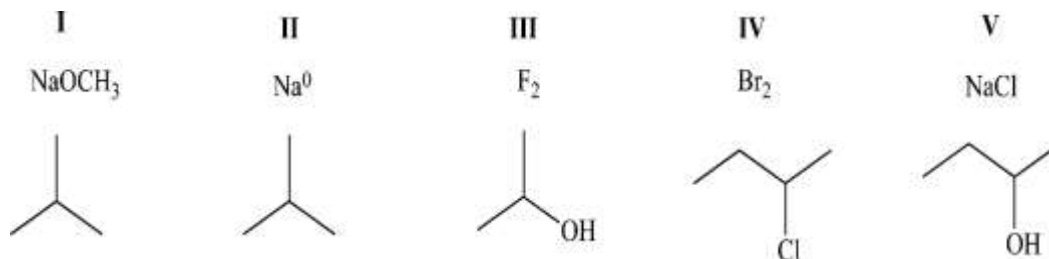
- a. hydrogen bond  
 b. ion-dipole  
 c. ion-ion  
 d. dipole-induced dipole  
 e. induced dipole-induced dipole

ANS: E                      DIF: Easy                      REF: 2.6

OBJ: Identify the relative strength of the common intermolecular forces as they apply to organic molecules.

MSC: Remembering

30. When mixed, which of the following pairs of compounds will exhibit *both* ion-dipole and ion-ion intermolecular attractive forces?



- a. I  
 b. II  
 c. III  
 d. IV  
 e. V

ANS: E                      DIF: Easy                      REF: 2.6

OBJ: Deduce the intermolecular forces that are possible between specified molecules.

MSC: Analyzing

31. What is the strongest intermolecular attractive force between an alcohol and a ketone?

- a. hydrogen bond  
 b. ion-dipole  
 c. ion-ion  
 d. dipole-induced dipole  
 e. induced dipole-induced dipole

ANS: A                      DIF: Moderate                      REF: 2.6

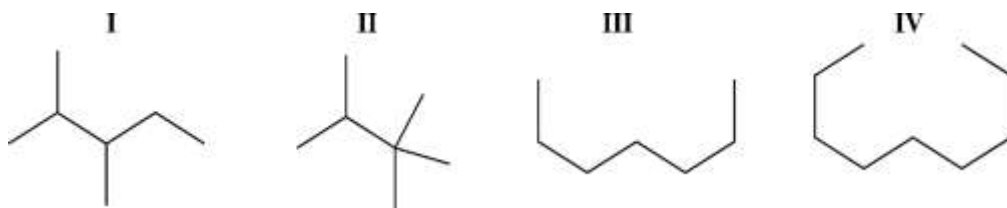
OBJ: Identify the relative strength of the common intermolecular forces as they apply to organic molecules.

MSC: Analyzing

32. What is the strongest intermolecular attractive force possible between an alkyl chloride and an alkane?

- a. hydrogen bond  
 b. ion-dipole  
 c. ion-ion  
 d. dipole-induced dipole  
 e. induced dipole-induced dipole





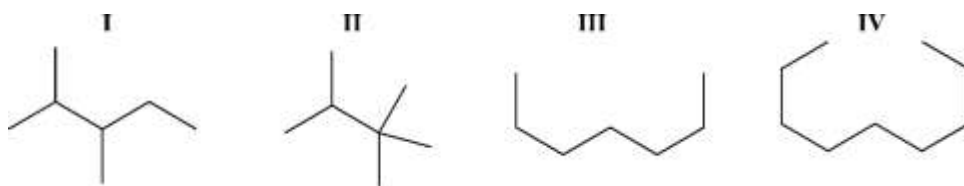
- a.  $I < II < III < IV$   
 b.  $II < I < III < IV$   
 c.  $IV < III < I < II$   
 d.  $II < III < IV < I$   
 e.  $IV < III < II < I$

ANS: B                      DIF: Easy                      REF: 2.8

OBJ: Identify the relative strength of the common intermolecular forces as they apply to organic molecules.

MSC: Evaluating

38. Rank the following molecules based on *decreasing* boiling point (highest boiling point to lowest boiling point).



- a.  $I > II > III > IV$   
 b.  $II > I > III > IV$   
 c.  $I > III > IV > II$   
 d.  $IV > III > I > II$   
 e.  $IV > III > II > I$

ANS: D                      DIF: Easy                      REF: 2.8

OBJ: Identify the relative strength of the common intermolecular forces as they apply to organic molecules.

MSC: Evaluating

39. Select a phrase to complete this sentence: “\_\_\_\_\_ are induced dipole–induced dipole interactions common to nonpolar molecules such as hydrocarbons.”

- a. Electromotive forces  
 b. Hydrogen bonds  
 c. Ionic attractions  
 d. London dispersion forces  
 e. Mechanical forces

ANS: D                      DIF: Easy                      REF: 2.8

OBJ: Deduce the intermolecular forces that are possible between specified molecules.

MSC: Remembering

40. Which of the following statements is true about carbon tetrachloride,  $CCl_4$ ?

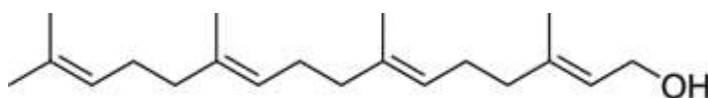
- a. It is polar protic with tetrahedral geometry.  
 b. The carbon has trigonal planar geometry.  
 c. None of the C–Cl bonds has a dipole.  
 d. It is miscible in water with  $109.5^\circ$  bond angles.  
 e. It is polar aprotic with tetrahedral geometry at C.

ANS: E                      DIF: Easy                      REF: 2.9

OBJ: Relate polarity to molecular geometry and physical properties.

MSC: Evaluating

41. How many isoprene units are in the given molecule?



- a. one  
 b. two  
 c. three  
 d. four  
 e. five

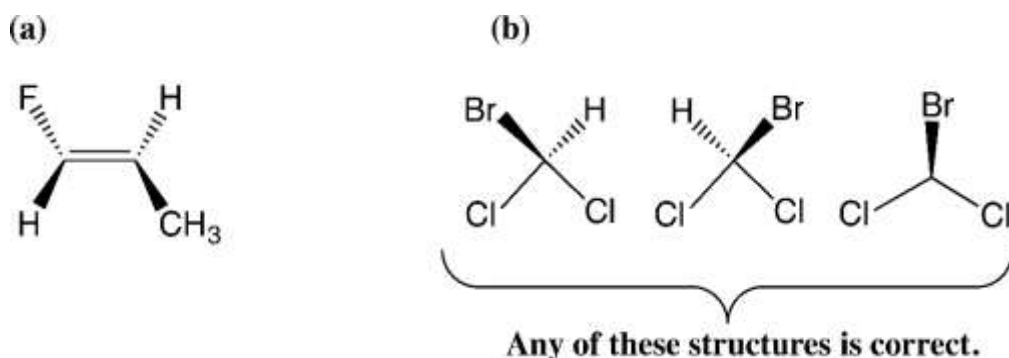
ANS: D                      DIF: Easy                      REF: 2.10

OBJ: Identify the isoprene units in a polyisoprenoid. MSC: Understanding

### SHORT ANSWER

1. Add substituents using dash-wedge notation to achieve the structure specified.
  - a. An alkene that has a fluorine atom pointing back on the leftmost carbon and a methyl group coming out on the rightmost carbon. Assume that hydrogen fills the valence of carbon.
  - b. A tetrahedral carbon with two chlorine atoms pointing down on the plane of the paper, a bromine atom pointing out, and a hydrogen atom pointing back.

ANS:

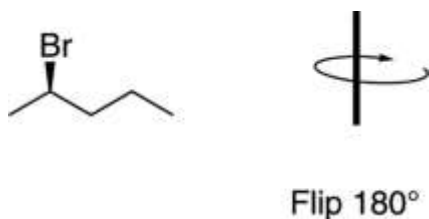


DIF: Moderate REF: 2.2

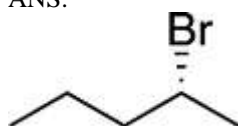
OBJ: Correctly depict the three-dimensional structure of a molecule using dash-wedge notation.

MSC: Creating

2. Redraw the following molecule after flipping it 180° in the identified direction.



ANS:

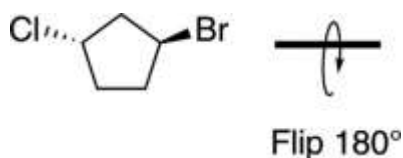


DIF: Easy REF: 2.2

OBJ: Execute a prescribed rotation and draw the molecule in its new orientation.

MSC: Understanding

3. Redraw the following molecule after flipping it 180° in the identified direction.



ANS:

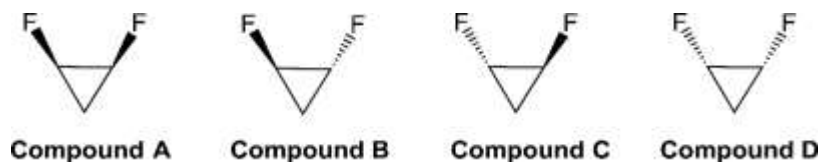


DIF: Moderate REF: 2.2

OBJ: Execute a prescribed rotation and draw the molecule in its new orientation.

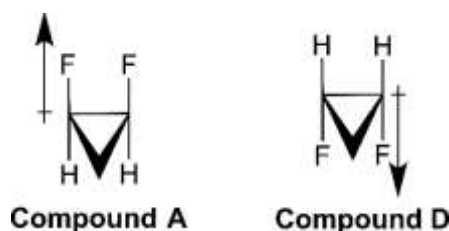
MSC: Understanding

4. Are any of the 1,2-difluorocyclopropane isomers drawn below polar? Indicate the direction of the net molecular dipole, if one is present.



ANS:

All molecules are polar. Compounds A and D have the greatest net dipole because the fluorines are *cis* to one another. Compounds B and C have dipoles of equal magnitude projecting in opposite directions. Although it appears that the C-F bond dipoles in Compounds B and C would each sum to zero, the geometry of the ring carbon atom prevents this from happening. Literature suggests that the sum of the C-F bond dipoles in both Compounds B and C is nonzero, leading to these two compounds being polar.



DIF: Moderate REF: 2.4

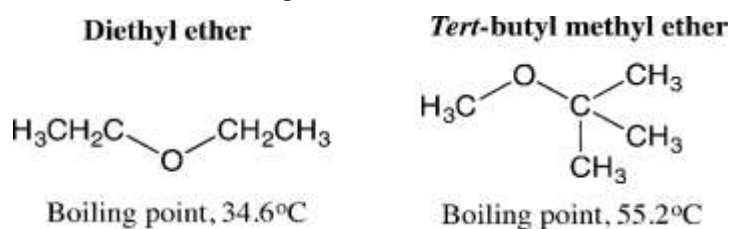
OBJ: Relate polarity to molecular geometry and physical properties.

MSC: Understanding

5. The solvent *tert*-butyl methyl ether (MTBE) is used as a “greener” replacement for the organic solvent diethyl ether, because it has less propensity to form peroxides upon standing. Draw the line structures of both diethyl ether and MTBE. Look up the physical properties (boiling point and flash point) of both solvents. Explain why the boiling point of diethyl ether is lower.

ANS:

Diethyl ether has a smaller molecular weight and thus fewer intermolecular attractive forces when equal amounts of the two ethers are compared.



DIF: Easy REF: 2.6

OBJ: Identify the relative strength of the common intermolecular forces as they apply to organic molecules.

MSC: Understanding

6. Winter gasoline mixes for cold climates require 10% ethanol, or 1 gallon of ethanol for every 9 gallons of gasoline, in part to help prevent water in the gas from freezing and causing engine trouble. List the intermolecular forces between water and ethanol, and between ethanol and octane. Why are the intermolecular forces relevant in winter-mix gasoline?

ANS:

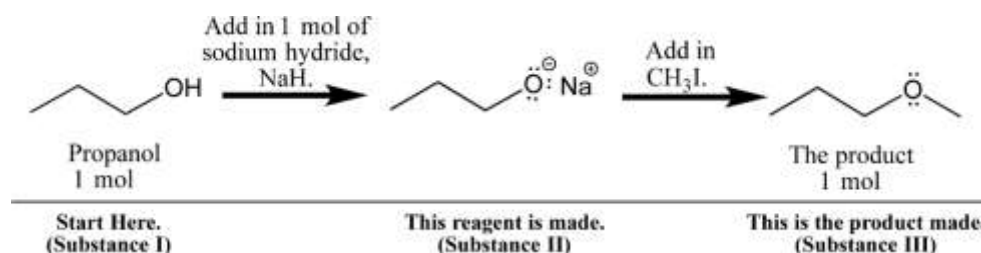
Octane (a major component to gasoline) interacts with the hydrocarbon chain of ethanol via induced dipole forces and can also interact with the OH group via dipole-induced dipole interactions. Ethanol interacts with water via H bonding, which is a special type of dipole-dipole force. H bonds are stronger than induced dipole forces, and thus help stop water from freezing in the gas.

DIF: Moderate REF: 2.6

OBJ: Deduce the intermolecular forces that are possible between specified molecules.

MSC: Analyzing

7. Propanol can be dissolved in diethyl ether and treated with sodium hydride, a base, to form a sodium alkoxide, as shown below.



Although this and related chemical reactions will be studied in later chapters, you can apply your knowledge of solubility to the process.

Fill in your solubility predictions using the following table. Do you expect propanol (I), sodium propoxide (II), and the new ether product (III) to be soluble in the reaction solvent, diethyl ether? If soluble, predict the intermolecular interactions that will exist in solution. Also, anticipate the physical appearance of the reaction at each point: Will the solution be transparent, or will a precipitate form?

Substance	Is the substance soluble in diethyl ether? (yes or no)	What intermolecular forces are present between the solvent, diethyl ether, and the organic substance?	Physical appearance (transparent or precipitate)
I			
II			
III			

ANS:

Substance	Is the substance soluble in diethyl ether? (yes or no)	What intermolecular forces are present between the solvent, diethyl ether, and the organic substance?	Physical appearance (transparent or precipitate)
I	Yes	H bonding	Transparent
II	No	Ion-dipole forces will exist between the diethyl ether solvent and the ions. However, the ion-ion forces of the salt dominate, and the precipitate forms.	Precipitate
III	Yes	Dipole-dipole	Transparent

DIF: Difficult REF: 2.6 | 2.7

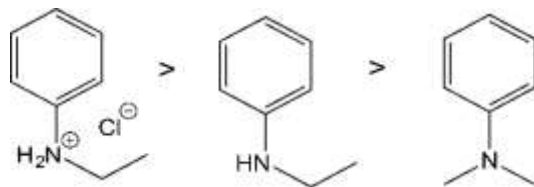
OBJ: Predict the solubility of an organic species during a chemical reaction and/or extraction.

MSC: Creating

8. Rank *N,N*-dimethylaniline, phenethylamine, and phenethylamine hydrochloride in order of decreasing boiling point. Explain your reasoning.

ANS:

The salt phenethylamine hydrochloride, a solid at room temperature with a melting point of 220–221°C, possesses the strongest intermolecular forces. This salt therefore has the highest boiling point of the three compounds. Both *N,N*-dimethylaniline (b.p. 193–194°C) and phenethylamine (b.p. 197–199°C) are also amines. Phenethylamine is more polar than *N,N*-dimethylaniline due to the strong dipole on the NH bond. *N,N*-dimethylaniline is also branched, with a lower surface area. Although both molecules engage in strong dipole–dipole attractions and induced dipole interactions, *N,N*-dimethylaniline has a slightly lower boiling point.



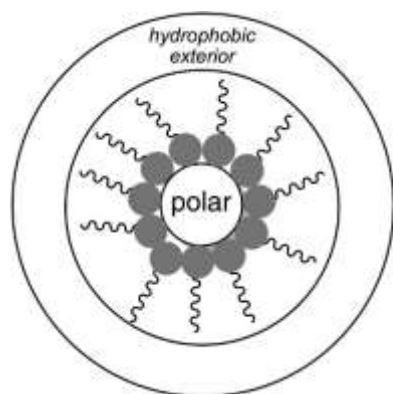
DIF: Moderate REF: 2.6 | 2.8

OBJ: Identify the relative strength of the common intermolecular forces as they apply to organic molecules.

MSC: Understanding

9. A reverse micelle can form when a polar substance dissolves in a nonpolar substance. Create a conceptual diagram of a reverse micelle. What intermolecular forces are driving the formation of the reverse micelle?

ANS:



Ion–dipole attractions between the encapsulated polar substance and the charged head groups favor formation of the micelle. Additionally, favorable induced dipole–induced dipole forces of the hydrophobic solvent and greasy tails are also present. Collectively, these forces outweigh the negative entropy of the system.

DIF: Moderate REF: 2.6 | 2.10

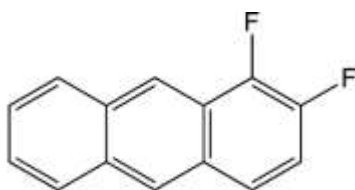
OBJ: Diagram a micelle to identify the intermolecular forces that are present.

MSC: Creating

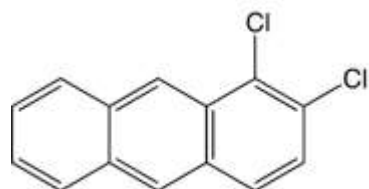
10. Which of the following benzene derivatives would be most soluble in benzene? Why?



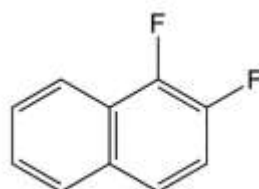
Compound A



Compound B



Compound C



Compound D

ANS:

Adding extra benzene rings to the molecule will increase solubility, although there will be an upper limit. Additionally, because chlorine is more polarizable and less electronegative than fluorine, Compound C is predicted to be most soluble in benzene.

DIF: Moderate REF: 2.7

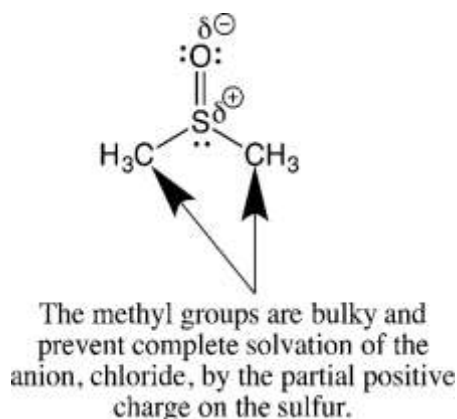
OBJ: Utilize knowledge of chemical structure to identify solubility properties of an organic compound.

MSC: Evaluating

11. Sodium chloride, an ionic compound, is highly water soluble but minimally soluble in the polar aprotic solvent dimethyl sulfoxide (DMSO). Why?

ANS:

Dimethyl sulfoxide possesses two methyl groups that are hydrophobic and bulky. Although it is expected that chloride will be highly solvated, steric hindrance prevents full solvation of the anion. In other words, the hydrophobic, bulky methyl groups make the partial positive charge of DMSO less accessible to the electrons of chloride. Refer to Figure 2.24 in the text for a full depiction.



DIF: Moderate REF: 2.7 | 2.9

OBJ: Evaluate the solvation of an ion or molecule by a protic or an aprotic solvent.

MSC: Evaluating

12. Explain why polar protic solvents (like butanol) solvate anions (like chloride) better than polar aprotic solvents (like *N,N*-dimethylformamide, DMF) do.

ANS:

Polar protic solvents interact with chloride via ion-dipole interactions. The partial positive charge on hydrogen from butanol's -OH is both significant and well exposed to foster attraction to the chloride. Another important point is that the aprotic solvent DMF has two bulky methyl groups that block full access to carbon's partial positive charge.

DIF: Moderate REF: 2.7 | 2.9

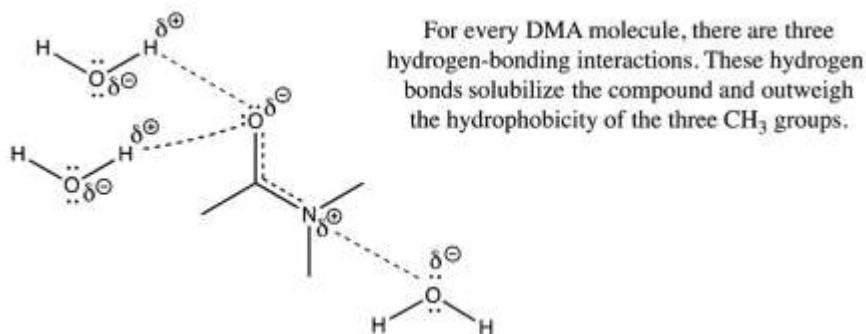
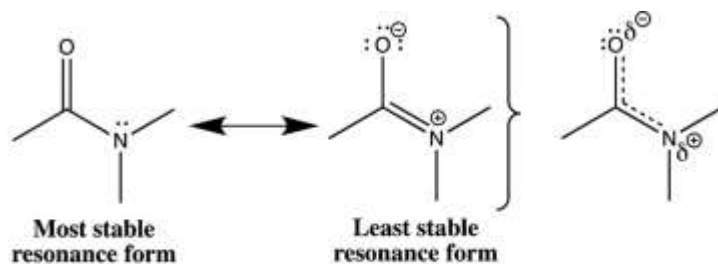
OBJ: Evaluate the solvation of an ion or molecule by a protic or an aprotic solvent.

MSC: Analyzing

13. Tertiary amides are typically insoluble in water. The solvent dimethyl acetamide, CH<sub>3</sub>CON(CH<sub>3</sub>)<sub>2</sub>, which is commonly called DMA, is an exception. Explain why the solvent DMA is soluble in water. Diagram the intermolecular forces that make DMA soluble in water.

ANS:





DIF: Difficult      REF: 2.7 | 2.9

OBJ: Evaluate the solvation of an ion or molecule by a protic or an aprotic solvent.

MSC: Creating

14. Rank 1,4-dimethylbenzene, phenol, and *N,N*-dimethylaniline in order of decreasing solubility in the organic solvent toluene.

ANS:

The molecule 1,4-dimethylbenzene is the most soluble, followed by *N,N*-dimethylaniline, followed by phenol. Following the “like dissolves like” rule, 1,4-dimethylbenzene is the most “like” toluene, having only induced dipole forces between molecules. *N,N*-dimethylaniline is aprotic and polar, with dipole–dipole and induced-dipole–dipole interactions. Phenol is the least soluble in toluene. The dipole–dipole interactions for phenol are likely stronger than the induced dipole forces found in a solution of toluene.

DIF: Moderate      REF: 2.7 | 2.9

OBJ: Utilize knowledge of chemical structure to identify solubility properties of an organic compound.

MSC: Understanding

15. Your lab partner disobeyed lab rules and poured table salt from lunch into your unknown organic white powder, which is aprotic and contains an ester functional group. What solvent might you add to the solid mixture to remove the table salt, leaving the ester? What solvent is appropriate to remove the unknown ester, leaving instead the salt? Explain your reasoning.

ANS:

The basic premise of “like dissolves like” applies here. In general, neutral, polar organic compounds will be soluble in a polar aprotic solvent. More specifically, you can complete an extraction using a separatory funnel or the appropriate microscale gear provided in your laboratory.

First, add water to the solid mixture; then add ether. Two layers will form, with the more dense solvent, water, on the bottom. Think carefully about which layer may contain each substance. To extract the salt, an ionic compound, and leave the organic ester, remove the water layer.

Alternatively, to remove the organic ester, remove the ether layer. As you will likely learn in your organic chemistry wet lab, three rounds of extraction are best to optimize efficiency in the extraction (i.e., ensure that all of the undesired compound is removed).

DIF: Difficult      REF: 2.7 | 2.9

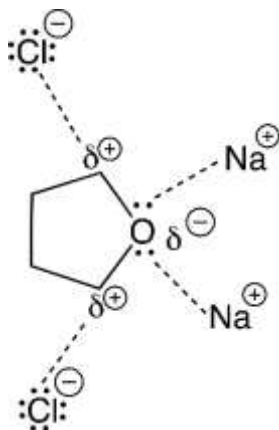
OBJ: Predict the solubility of an organic species during a chemical reaction and/or extraction.

MSC: Evaluating

16. Why do polar aprotic solvents solvate cations more strongly than anions? Using sodium chloride as the representative ionic compound, diagram the intermolecular interactions with tetrahydrofuran (THF).

ANS:

Polar aprotic solvents often have a partially negative oxygen atom, or another heteroatom, that is attracted to the cation's positive charge. The anion—in this case, chloride—is not solvated as strongly due to either steric repulsions of hydrocarbon groups or the weaker induced dipole polarization of hydrocarbons. An example of THF interacting with NaCl is given here.



DIF: Moderate REF: 2.7 | 2.9

OBJ: Evaluate the solvation of an ion or molecule by a protic or an aprotic solvent.

MSC: Understanding

17. (a) Group I cations are common ions found in organic salts. Write the electron configuration for the Group I cations below. In the fourth column, use circles to represent the relative size of each cation conceptually. Define the term ionic radius and label the ionic radius of each cation.

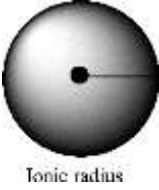
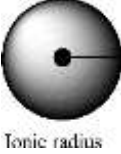

Cation	Electron configuration of cation	Ionic radius (nanometer)	Draw schematic of cation, and label ionic radius	Calculate ionic diameter (picometer [pm])
K <sup>+</sup>		0.138 nm		
Na <sup>+</sup>		0.102 nm		
Li <sup>+</sup>		0.076 nm		

- (b) Organic molecules called crown ethers (refer to the box titled “Phase Transfer Catalysts” in Chapter 2 of your text) can sequester a cation of specific size to make the organic anion more reactive. Charles Pedersen, in fact, shared the 1987 Nobel Prize in Chemistry for contributions to the synthesis of crown ethers. Suppose you wanted to use a crown ether to selectively remove each individual cation from a solution of sodium, lithium, and potassium. For each cation, which crown ether might you add?

Select cation (Na <sup>+</sup> , K <sup>+</sup> , Li <sup>+</sup> )	Crown ether cavity diameter (picometer [pm])	Crown ether
	260–320 pm	18-crown-6
	170–220 pm	15-crown-5
	120–140 pm	12-crown-4

ANS:

Cation	Electron configuration of cation	Ionic radius (picometer [pm])	Draw schematic of cation, and label ionic radius	Calculate ionic diameter (picometer [pm])

K <sup>+</sup>	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup>	138 pm		276 pm
Na <sup>+</sup>	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup>	102 pm		204 pm
Li <sup>+</sup>	1s <sup>2</sup>	70 pm		140 pm

Select cation (Na <sup>+</sup> , K <sup>+</sup> , Li <sup>+</sup> )	Crown ether cavity diameter (picometer [pm])	Crown ether
K <sup>+</sup>	260–320 pm	18-crown-6
Na <sup>+</sup>	170–220 pm	15-crown-5
Li <sup>+</sup>	120–140 pm	12-crown-4

DIF: Difficult      REF: 2.9

OBJ: Evaluate the solvation of an ion or molecule by a protic or an aprotic solvent.

MSC: Evaluating

18. Explain the chemical difference between a detergent and a soap. Provide one example of each in your answer.

ANS:

A detergent such as sodium dodecyl sulfate (SDS) is an anionic surfactant commonly used to break up noncovalent interactions in proteins such that the proteins' three-dimensional structure is disrupted (i.e., it denatures the protein). Detergents resemble soaps because both have a long hydrophobic chain and a charged head group. However, detergents differ because the larger head group does not bind as intensely to cations and thus is more suitable for use in biochemical experiments and in hard water. Soaps in general are salts of fatty acids and contain a carboxylate, RC(O)O<sup>-</sup>, where R is a long fatty acid chain. Sodium oleate is one example of a soap.

DIF: Easy      REF: 2.10

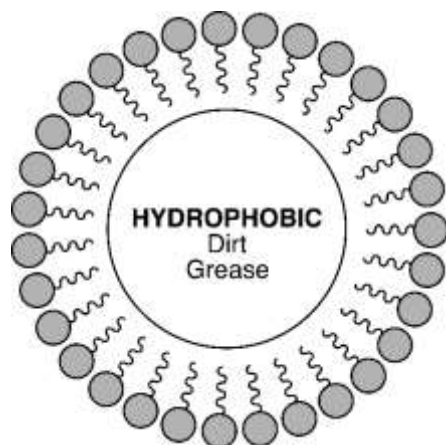
OBJ: Explain how and why soaps and detergents work as cleaning agents.

MSC: Understanding

19. A micelle is formed when soap dissolves in water. What intermolecular forces govern the formation of the micelle? Explain.

ANS:

Soaps contain a hydrophobic tail that solubilizes nonpolar hydrocarbons, with a polar head group that is hydrophilic (water loving). The "grease-loving" hydrocarbon chain of the soap relies on induced dipole interactions to remove dirt. These temporary dipoles are often called London dispersion forces. In contrast, the hydrophilic head group relies on dipole–dipole forces and hydrogen bonding. Ion–dipole attractive forces are also possible. The hydrophilic "heads" of the soap molecules that are replaced by gray spheres interact with water on the exterior via "ion–dipole" interactions.

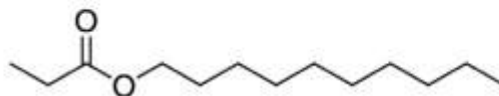
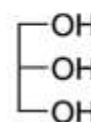
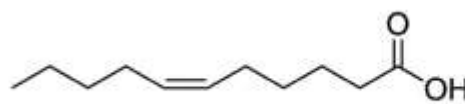
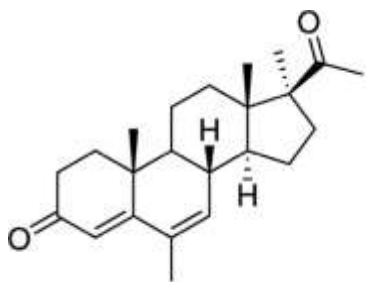


DIF: Easy REF: 2.10

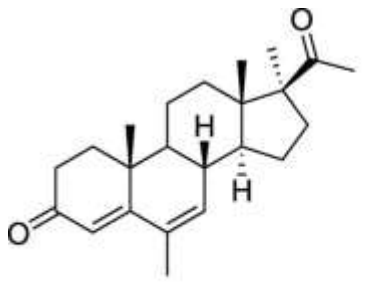
OBJ: Diagram a micelle to identify the intermolecular forces that are present.

MSC: Analyzing

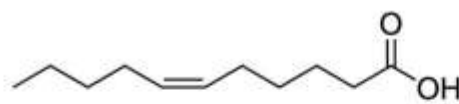
20. Label each of the following compounds as a detergent, glycerol, fatty acid, DNA base, triacylglycerol, steroid, phospholipid, wax, or isoprenoid.



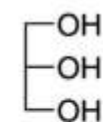
ANS:



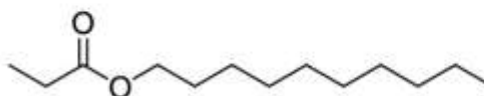
**steroid**



**fatty acid**



**glycerol**



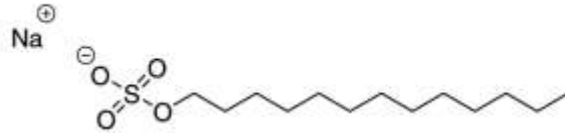
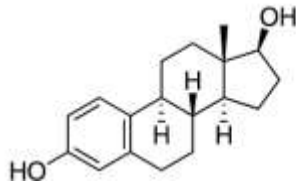
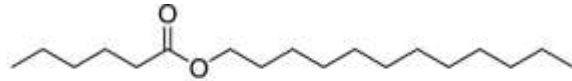
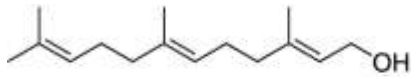
**wax**

DIF: Easy REF: 2.11

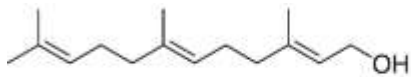
OBJ: Identify biomolecules by their structure.

MSC: Understanding

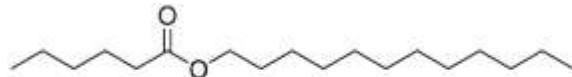
21. Label each of the following compounds as a soap, glycerol, fatty acid, DNA base, triacylglycerol, steroid, phospholipid, wax, or isoprenoid.



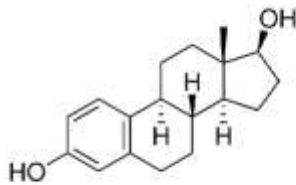
ANS:



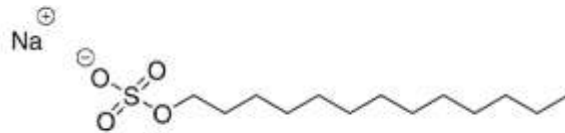
**isoprenoid**



**wax**



**steroid**



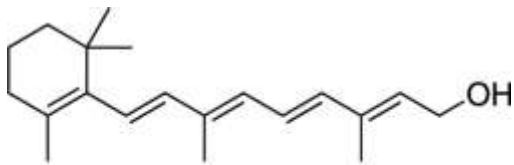
**detergent**

DIF: Easy  
MSC: Understanding

REF: 2.11

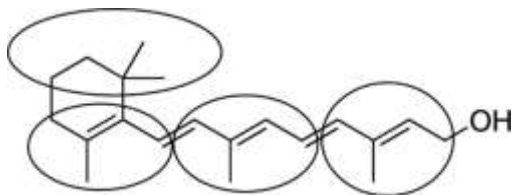
OBJ: Identify biomolecules by their structure.

22. Circle the isoprene units in the vitamin A.



**Vitamin A**

ANS:



DIF: Difficult  
MSC: Analyzing

REF: 2.11

OBJ: Identify the isoprene units in a polyisoprenoid.

