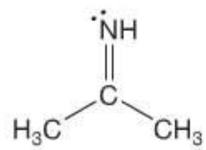
Chapter 2 – Three-Dimensional Geometry, Intermolecular Interactions, and Physical Properties

SOLVED problem 2.1 Imines, which are characterized by a C═N double bond, are commonly used as intermediates in organic synthesis. Use VSEPR theory to predict the electron and molecular geometries about the nitrogen atom in the acetone imine molecule below.



Think How many electron groups surround the N atom? Are any of them lone pairs?

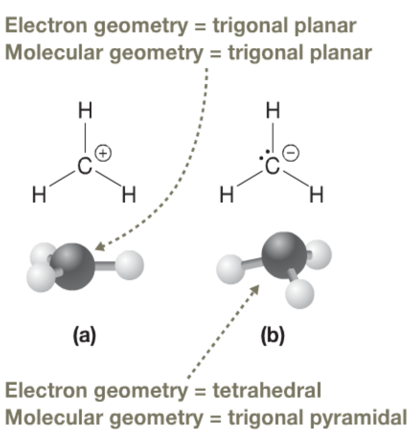
problem 2.2 Prop-2-yn-1-ol (propargyl alcohol) is used as an intermediate in organic synthesis and can be polymerized to make poly(propargyl alcohol). Use VSEPR theory to predict the electron and molecular geometries about each nonhydrogen atom in the molecule.

Prop-2-yn-1-ol
(Propargyl alcohol)

YOUR TURN 2.1

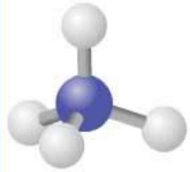
Circle each electron group in the Lewis structures of CH_3^+ and CH_3^- in Figure 2-3.

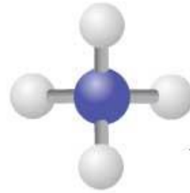
Answers to Your Turns are in the back of the book.



YOUR TURN 2.2

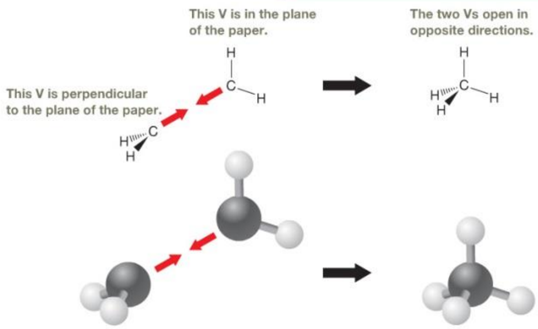
Ball-and-stick representations of NH_4^+ from two different vantage points are provided. Next to each one, draw the corresponding cation using dash–wedge notation.

 ______________

 ______________

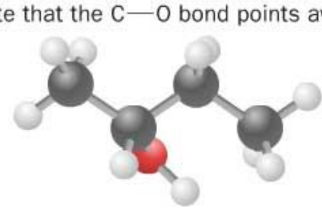
YOUR TURN 2.3

In the Lewis structure at the right of Figure 2-6, trace the V that is in the plane of the page and draw an arrow in the direction in which it opens. Do the same to the V that is perpendicular to the page.

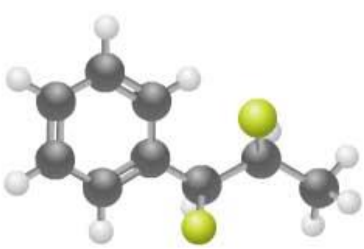


YOUR TURN 2.4

In the box provided, draw the line structure of butan-2-ol using dash–wedge notation. Note that the C—O bond points away from you.



problem 2.3 Draw line structures of each of the following molecules using dash–wedge notation. Assume that no atoms have formal charges. (*Note:* Black = carbon, white = hydrogen, green-yellow = chlorine, and blue = nitrogen.)

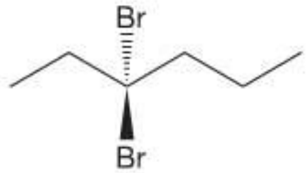


(a)

(b)

(c)

problem 2.4 The following is a common mistake made with dash–wedge notation. Explain what is incorrect about it and then fix it.



YOUR TURN 2.5

Construct the following molecule using a molecular modeling kit and then draw its structure using dash–wedge notation after each successive 180° flip.

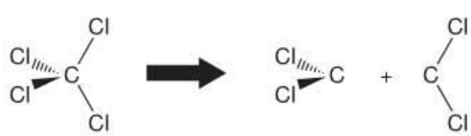
2.6 YOUR TURN

Like CO_2, BeH_2 is a linear nonpolar molecule. Using the structure of BeH_2 below, draw dipole arrows above each Be—H bond. (For electronegativities, see Fig. 1-16.)

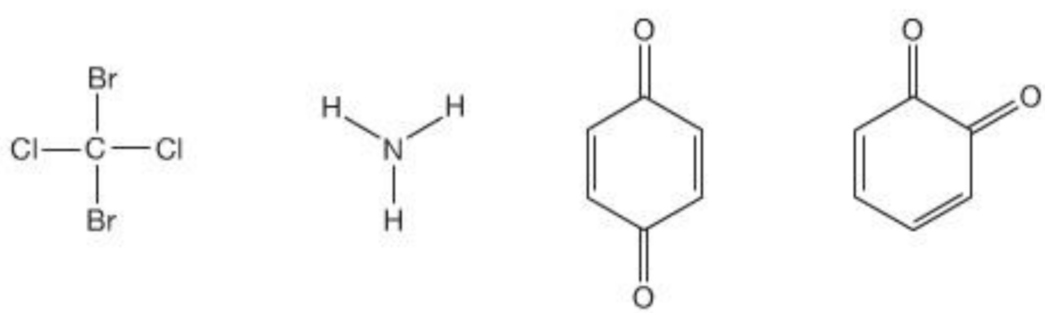
H—Be—H

2.7 YOUR TURN

A molecule of CCl_4 is decomposed into its two Vs below. Draw the bond dipoles along the two C—Cl bonds in each V and also draw the net dipole resulting from their vector addition.



problem 2.5 Which of the following molecules are polar? For those that are, draw a dipole arrow indicating the direction of the net molecular dipole.



(a) (b) (c) (d)

2.8 YOUR TURN

Identify the functional group that is present in each covalent compound in Table 2-4.

YOUR TURN 2.9

The boiling point of CH_3CH_2F is −37.1 °C. How does this compare to the boiling point of $CH_3CH{=}O$? Which compound has a greater dipole moment?

SOLVED problem 2.6 Which compound has a higher melting point, $NaOCH_2CH_3$ or $CH_3CH{=}O$?

Think What is the strongest intermolecular interaction in $NaOCH_2CH_3$? In $CH_3CH{=}O$? Which type of interaction is stronger? How does that affect the melting point?

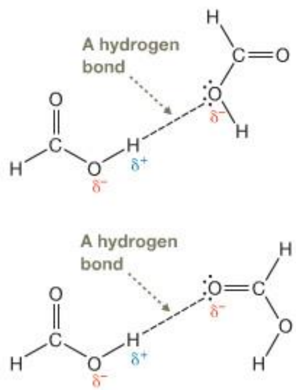
Solve $NaOCH_2CH_3$ is an ionic compound. It consists of $CH_3CH_2O^-$ and Na^+, which are held together by ion–ion interactions. $CH_3CH{=}O$, on the other hand, is a polar covalent compound, so it experiences dipole–dipole interactions. Because ion–ion interactions are stronger than dipole–dipole interactions, the melting point of $NaOCH_2CH_3$ is higher than the melting point of $CH_3CH{=}O$.

problem 2.7 Which compound has a higher boiling point, $NaOCH_2CH_3$ or $CH_3CH{=}O$?

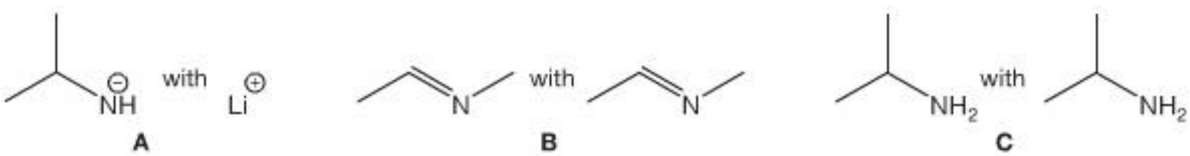
problem 2.8 Which compound has a higher boiling point, CH_4 or CH_3F?

YOUR TURN 2.10

Circle and label the H-bond donor and H-bond acceptor in *each* H bond shown in Figure 2-14b.

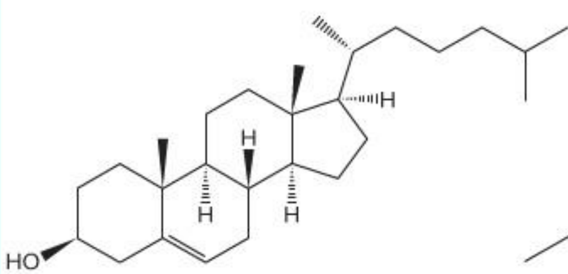


problem 2.9 Which pair of species will give rise to the strongest intermolecular interactions? The weakest?

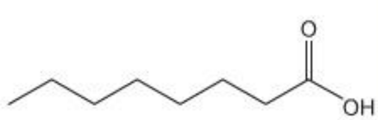


2.11 YOUR TURN

High levels of cholesterol, a naturally occurring steroid, have been linked to cardiovascular disease. Octanoic acid (caprylic acid) is a fatty acid found in milk and is used commercially to manufacture perfumes and dyes. Identify the number of *potential* H-bond donors and acceptors in each of these compounds.

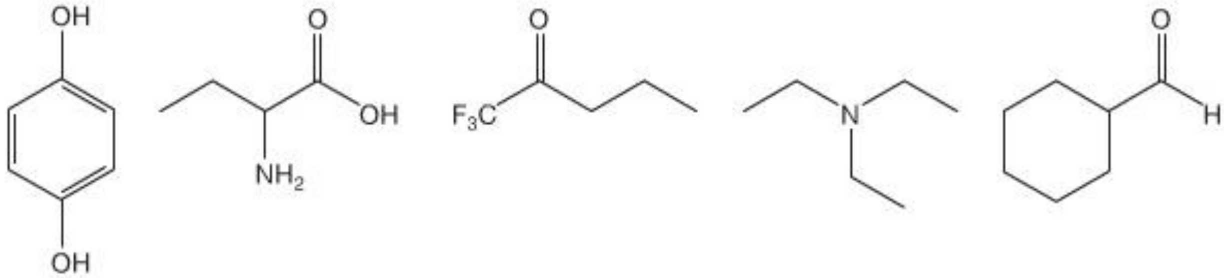


Cholesterol



Octanoic acid (Caprylic acid)

problem 2.10 How many potential H-bond donors and H-bond acceptors are there in each of the following molecules?

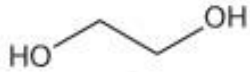


(a) (b) (c) (d) (e)

problem 2.11 Which functional groups in Table 1-6 possess at least one H-bond acceptor, but no H-bond donors? Which functional groups possess at least one H-bond donor and one H-bond acceptor? Which functional groups possess no H-bond donors and no H-bond acceptors?

One H-bond acceptor, no H-bond donors	One H-bond donor, one H-bond acceptor	No H-bond donor, no H-bond acceptor

SOLVED problem 2.12 1,2-Ethanediol (ethylene glycol, **A**) is historically used as an automotive antifreeze. Hydroxyacetaldehyde (**B**) is believed to be an intermediate in the metabolism of proteins and carbohydrates. Which of these compounds would you expect to have a higher boiling point? Why?



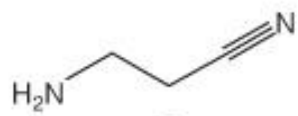
A

B

Think What is the most important intermolecular interaction that will occur between two molecules of **A**? Between two molecules of **B**? Which interaction is stronger, and how would it affect the boiling points of **A** and **B**?

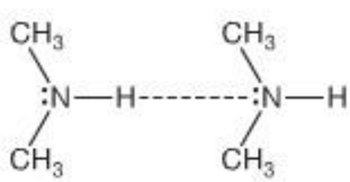
problem 2.13 Which compound, **C** or **D**, would you expect to have a higher boiling point? Why?

C



D

problem 2.14 Which H bond would you expect to be stronger? Why?

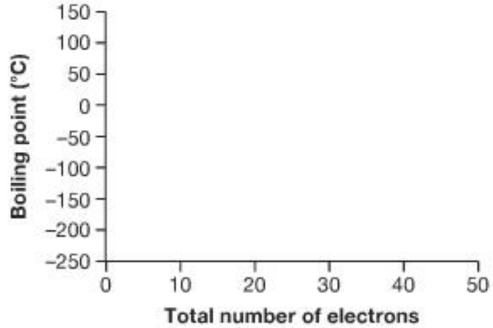


E

F

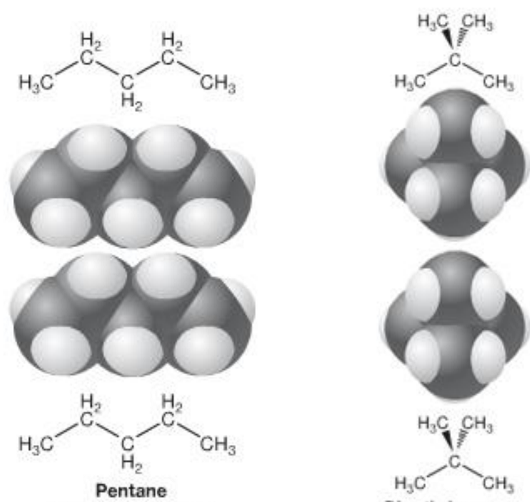
YOUR TURN 2.12

In the space provided, construct a rough plot of the boiling point as a function of total number of electrons for the straight-chain alkanes in Table 2-5 (i.e., methane, ethane, propane, butane, and pentane). What do you notice?



2.13 YOUR TURN

In Figure 2-18, shade in the contact surface area for each pair of molecules. Indicate which pair of molecules has greater contact surface area.



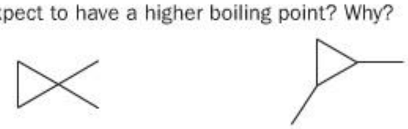
Pentane
Boiling point = 36 °C
(a)

Dimethylpropane
Boiling point = 10 °C
(b)

problem 2.15 For each pair of molecules, which would you expect to have a higher boiling point? Why?

2,2-Dimethylbutane **2-Methylpentane**

A



1,1-Dimethylcyclopropane **1,2-Dimethylcyclopropane**

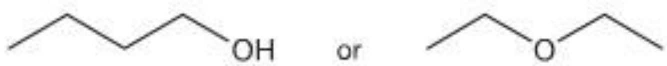
B

Which compound, **A** or **B**, do you expect to be more soluble in H_2O?

A **B**

2.14 YOUR TURN

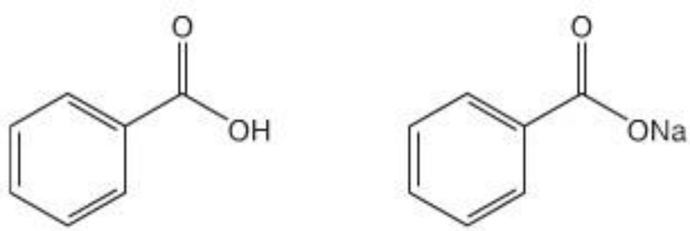
SOLVED problem 2.16 Which of the following compounds would you expect to be more soluble in toluene ($C_6H_5CH_3$)? Explain.



Butan-1-ol **Diethyl ether**

Think What are the relative strengths of the intermolecular interactions in the pure substances that would be disrupted upon mixing? How do these compare to the strengths of the intermolecular interactions that would be gained?

problem 2.17 Which compound, **C** or **D**, would you expect to be more soluble in toluene ($C_6H_5CH_3$)? Explain.



C **D**

SOLVED problem 2.18 In which solvent would you expect NaCl to be more soluble, dimethyl ether (CH_3OCH_3) or ethanal ($CH_3CH{=}O$)?

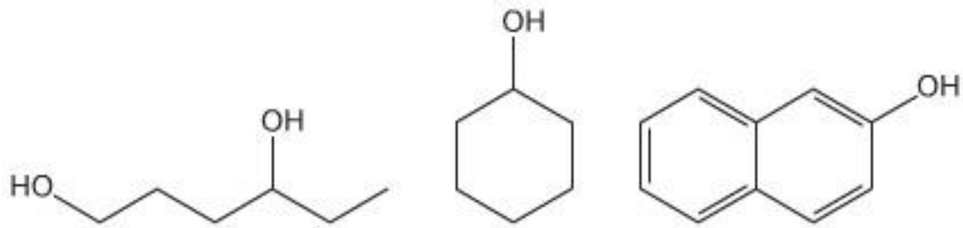
Think What are the most important intermolecular interactions that would be disrupted upon dissolution? What intermolecular interactions would be gained in the solution? In which solvent are those intermolecular interactions stronger?

problem 2.19 NaCl is more soluble in methanol (CH_3OH) than in propan-1-ol ($CH_3CH_2CH_2OH$). Which solvent is better at solvating ions?

problem 2.20 Which functional groups in Table 1-6 would be considered hydrophilic? Which would be considered hydrophobic?

hydrophilic functional groups	hydrophobic functional groups

SOLVED problem 2.21 Would you expect each of the following compounds to be soluble in water? Why or why not?

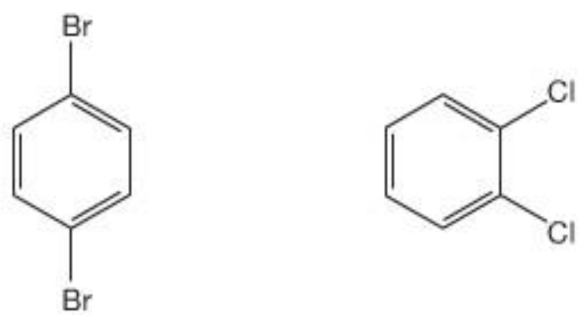


A B C

Think What is the ratio of alcohol groups to the number of carbon atoms of the hydrocarbon group?

problem 2.22 Like alcohols, aldehydes (R—CH═O) become less soluble in water as the number of carbon atoms in the alkyl group R increases. Do you think the maximum number of carbon atoms for water-soluble aldehydes will be greater than or less than that for water-soluble alcohols? Explain.

SOLVED problem 2.23 1,4-Dibromobenzene, a nonpolar compound, has a boiling point of 219 °C. The boiling point of 1,2-dichlorobenzene, a polar compound, is 181 °C. Explain.

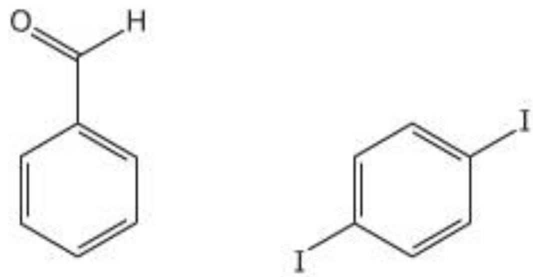


1,4-Dibromobenzene
Boiling point = 219 °C

1,2-Dichlorobenzene
Boiling point = 181 °C

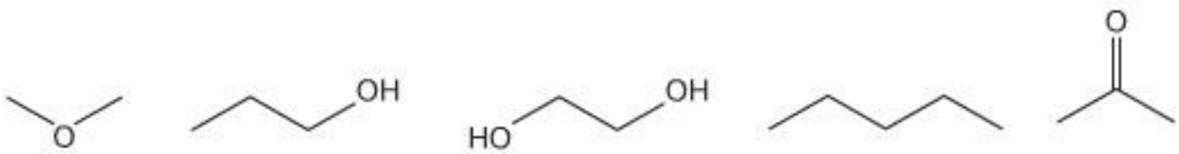
Think What intermolecular interactions are present in each compound? Are they of similar strength in each compound?

problem 2.24 Which of the following compounds do you think has a higher boiling point? Explain.



A B

SOLVED problem 2.25 Rank the following compounds from lowest solubility in hexane, $CH_3(CH_2)_4CH_3$, to highest solubility in hexane.



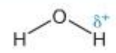
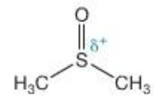
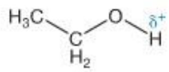
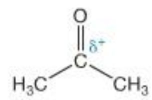
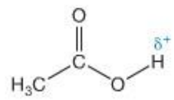
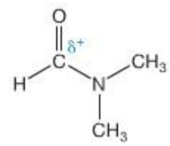
A B C D E

Think What are the most important intermolecular interactions that exist in the isolated substances and what are their relative strengths? What are the most important intermolecular interactions that exist in the solution?

problem 2.26 Rank the compounds in Solved Problem 2.25 in order from least soluble in water to most soluble.

2.16 YOUR TURN

In Table 2-7, circle and label each potential hydrogen-bond donor.

Polar Protic Solvents		Polar Aprotic Solvents	
Structure	**Name**	**Structure**	**Name**
	Water		Dimethyl sulfoxide (DMSO)
	Ethanol		Propanone (Acetone)
	Ethanoic acid (Acetic acid)		*N,N*-Dimethyl formamide (DMF)

problem 2.27 Will $KSCH_3$ be more soluble in ethanol or acetone? Explain.

YOUR TURN 2.17

On the electrostatic potential map in Figure 2-26, circle the hydrophilic region and label it. Circle the hydrophobic region and label it.

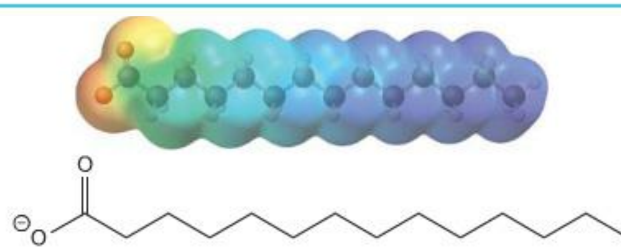
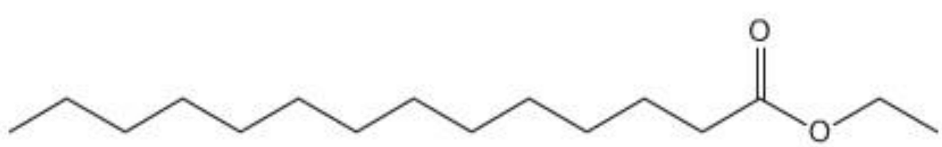
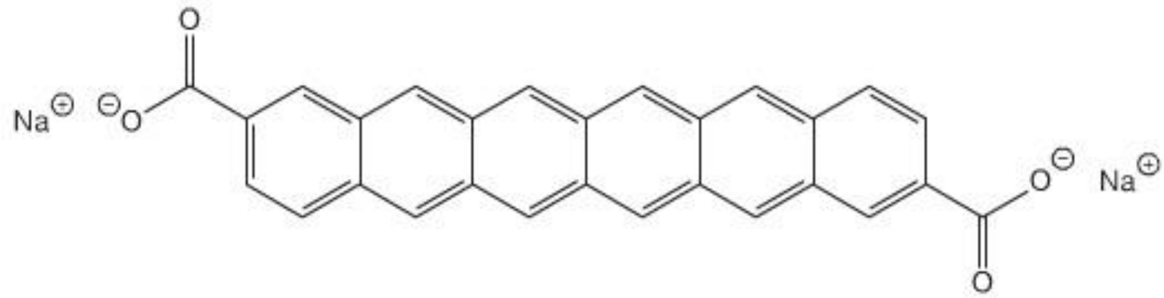


FIGURE 2-26 **Electrostatic potential map of a fatty acid carboxylate anion** A significant negative charge is located on the portion of the ion containing the $—CO_2^-$ group (the ionic head group), making it hydrophilic. At the same time, the hydrocarbon tail is very nonpolar, making it hydrophobic.

problem 2.28 Ethyl ethanoate (ethyl acetate, $CH_3CO_2CH_2CH_3$), a relatively small ester, is insoluble in water. Knowing this, would you expect the following compound to form micelles in water? Explain.

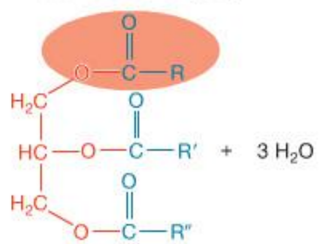


problem 2.29 Would you expect the following compound to act as a soap? Why or why not?



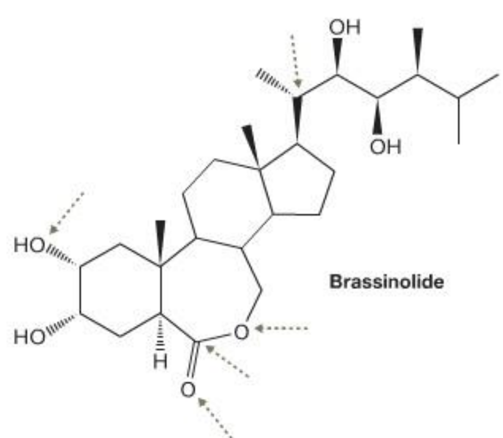
2.18 YOUR TURN

Circle and label the other two ester functional groups in the fat molecule in Equation 2-4.

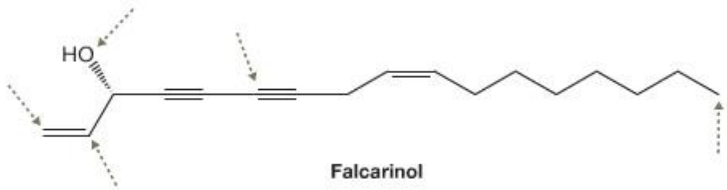


(2-4)

2.30 Brassinolide, a naturally occurring steroid derivative found in a wide variety of plants, is thought to promote plant growth. Identify the electron geometry for each atom indicated. Where applicable, describe the atom's molecular geometry and estimate the bond angle.

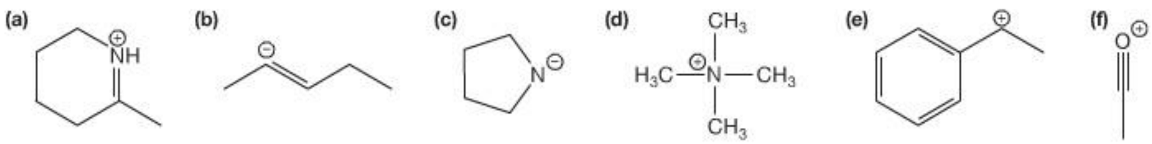


2.31 Falcarinol, a naturally occurring pesticide found in carrots, is being studied as an anticancer agent. Identify the electron geometry for each atom indicated. Where applicable, describe the atom's molecular geometry and estimate the bond angle.



Falcarinol

2.32 Identify the electron geometry about each charged atom. Where appropriate, indicate the molecular geometry and approximate bond angle as well.



2.33 Which molecule, **A** or **B**, has greater angle strain? Explain.

A **B**