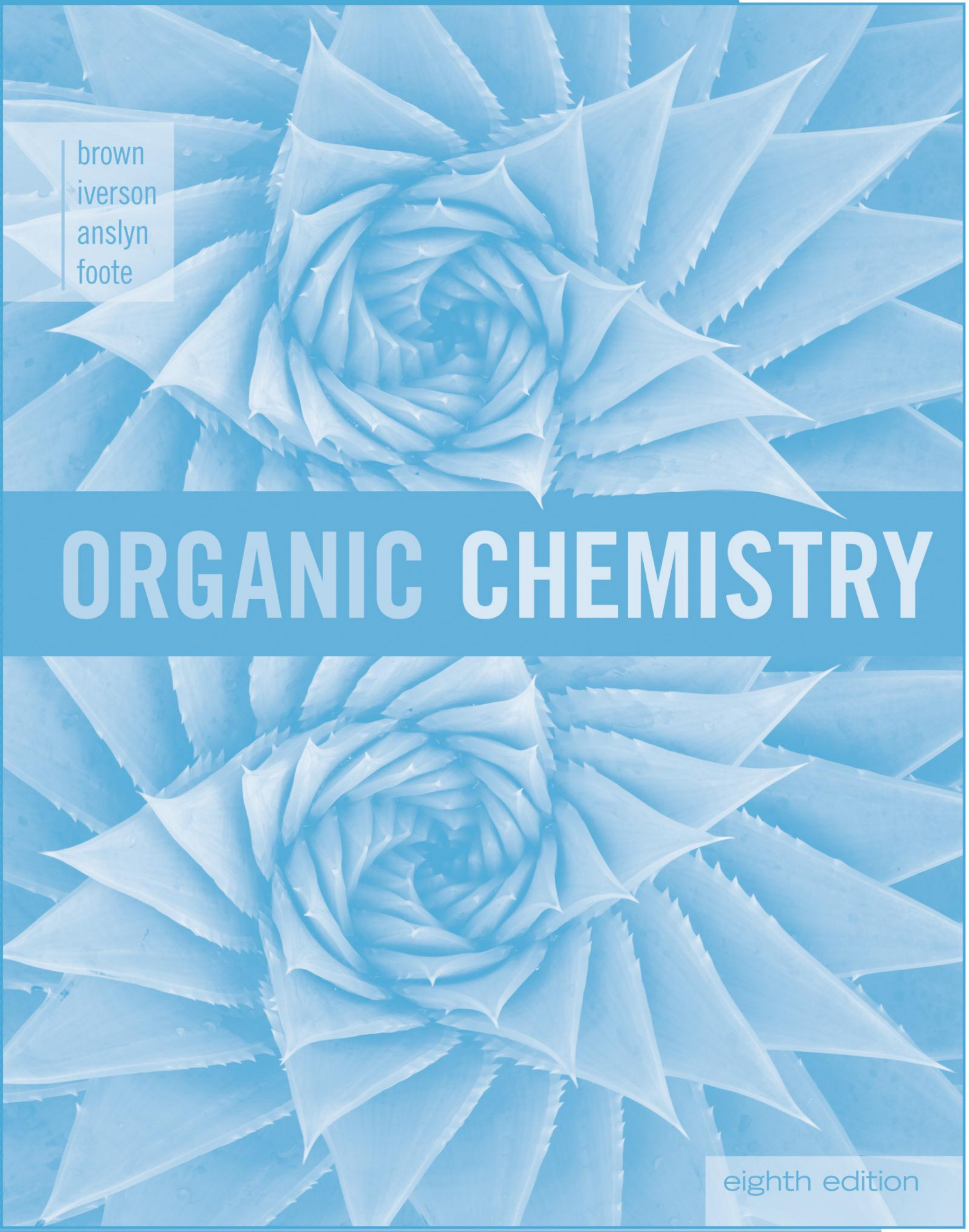
Student Study Guide and Solutions Manual



SHEILA IVERSON | BRENT IVERSON

Student Study Guide and Solutions Manual

Organic Chemistry

EIGHTH EDITION

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To Carina, Alexandra, Alanna, and Juliana
with love

This Student Study Guide and Solutions Manual is a companion to the eighth edition of *Organic Chemistry* by William Brown, Brent Iverson, Eric Anslyn and Christopher Foote. All of the problems from the text have been reprinted in this guide, so there is no need to flip back and forth between the text and the guide. Detailed, stepwise solutions to all of the problems are provided.

Molecules are three-dimensional and understanding the three-dimensionality of organic chemistry is important for any student. This Student Study Guide has placed special emphasis on stereochemistry, an important aspect of three-dimensional molecular structure. Throughout the problems and answers, many of the molecules with chiral centers have the configuration explicitly denoted using wedges and dashes to indicate location in space. When the configuration is not specifically given, chiral centers are indicated by an asterisk (*). In addition, the stereochemical outcome of every reaction is stated, whether the question calls for consideration of stereochemistry or not.

There are several innovative features of this Student Study Guide and Solutions Manual. First, *each* mechanistic step is identified as one of the relatively few fundamental mechanistic elements introduced in the "Things You Should Know III: Reaction Mechanisms" section immediately preceding Chapter 6. Providing such systematic and stepwise answers to all of the mechanism questions will help students more easily identify the similarities and thereby make connections between the mechanisms from different chapters. This revolutionary new approach will help students *understand* as opposed to just memorize organic chemistry. The second innovative feature of this Student Study Guide is the inclusion of organic chemistry roadmaps in all of the chapters that introduce new reactions (for an example see Problem 7.29). Roadmaps are effective study aides in which key functional groups are listed as locations, and specific reactions are shown as the routes between them. Roadmaps help students collect and organize the different reactions from multiple chapters in a two-dimensional format that is easy to understand and review. These roadmaps help students "navigate" synthesis questions that involve multiple sequential reactions, the type of problem that in our experience causes students the most difficulty. Immediately following an end of chapter problem asking students to update their roadmap, we have added new questions requiring students to utilize the roadmaps while navigating multi-step transformations (for an example see Problem 7.30).

If you have any comments or questions, please direct them to Professor Brent Iverson, Department of Chemistry, the University of Texas at Austin, Austin, Texas 78712. E-mail: iversonb@austin.utexas.edu.

Brent and Sheila Iverson
Austin, Texas
April, 2017

CHAPTER 1

Solutions to the Problems

Problem 1.1 Write and compare the ground-state electron configurations for each pair of elements:
(a) Carbon and silicon
C (6 electrons) $1s^2 2s^2 2p^2$
Si (14 electrons) $1s^2 2s^2 2p^6 3s^2 3p^2$
Both carbon and silicon have four electrons in their outermost (valence) shells.

(b) Oxygen and sulfur
O (8 electrons) $1s^2 2s^2 2p^4$
S (16 electrons) $1s^2 2s^2 2p^6 3s^2 3p^4$
Both oxygen and sulfur have six electrons in their outermost (valence) shells.

(c) Nitrogen and phosphorus
N (7 electrons) $1s^2 2s^2 2p^3$
P (15 electrons) $1s^2 2s^2 2p^6 3s^2 3p^3$
Both nitrogen and phosphorus have five electrons in their outermost (valence) shells.

Problem 1.2 Show how each chemical change leads to a stable octet.

(a) Sulfur forms S^{2-}.
S (16 electrons): $1s^2 2s^2 2p^6 3s^2 3p^4$
S^{2-} (18 electrons): $1s^2 2s^2 2p^6 3s^2 3p^6$

(b) Magnesium forms Mg^{2+}.
Mg (12 electrons): $1s^2 2s^2 2p^6 3s^2$
Mg^{2+} (10 electrons): $1s^2 2s^2 2p^6$

Problem 1.3 Judging from their relative positions in the Periodic Table, which element in each set is more electronegative?
(a) Lithium or potassium

In general, electronegativity increases from left to right across a row and from bottom to top of a column in the Periodic Table. This is because electronegativity increases with increasing positive charge on the nucleus and with decreasing distance of the valence electrons from the nucleus. Lithium is closer to the top of the Periodic Table and thus more electronegative than potassium.

(b) Nitrogen or phosphorus

Nitrogen is closer to the top of the Periodic Table and thus more electronegative than phosphorus.

(c) Carbon or silicon

Carbon is closer to the top of the Periodic Table and thus more electronegative than silicon.

Problem 1.4 Classify each bond as nonpolar covalent or polar covalent or state that ions are formed.
(a) S-H (b) P-H (c) C-F (d) C-Cl

Recall that bonds formed from atoms with an electronegativity difference of less than 0.5 are considered nonpolar covalent and with an electronegativity difference of 0.5 or above are considered a polar covalent bond.

Bond	Difference in electronegativity	Type of bond
S-H	**2.5 - 2.1 = 0.4**	**Nonpolar covalent**
P-H	**2.1 - 2.1 = 0**	**Nonpolar covalent**
C-F	**4.0 - 2.5 = 1.5**	**Polar covalent**
C-Cl	**3.0 - 2.5 = 0.5**	**Polar covalent**

Problem 1.5 Using the symbols δ- and δ+, indicate the direction of polarity in each polar covalent bond.

(a) C-N
δ+ δ-
C-N

Nitrogen is more electronegative than carbon

(b) N-O
δ+ δ-
N-O

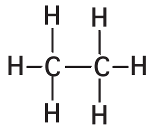
Oxygen is more electronegative than nitrogen

(c) C-Cl
δ+ δ-
C-Cl

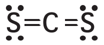
Chlorine is more electronegative than carbon

Problem 1.6 Draw Lewis structures, showing all valence electrons, for these molecules.

(a) C_2H_6



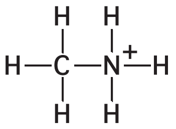
(b) CS_2



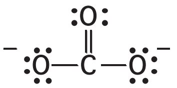
(c) HCN

Problem 1.7 Draw Lewis structures for these ions, and show which atom (or atoms) in each bears the formal charge.

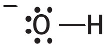
(a) $CH_3NH_3^+$
Methylammonium ion



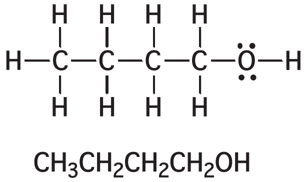
(b) CO_3^{2-}
Carbonate ion



(c) HO^-
Hydroxide ion

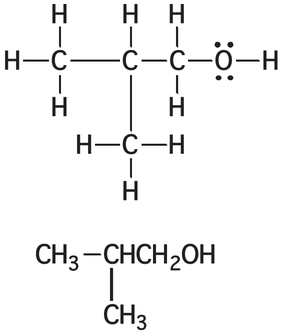


Problem 1.8 Draw Lewis structures and condensed structural formulas for the four alcohols with molecular formula $C_4H_{10}O$. Classify each alcohol as primary, secondary, or tertiary.



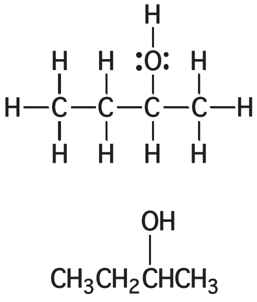
$CH_3CH_2CH_2CH_2OH$

Primary



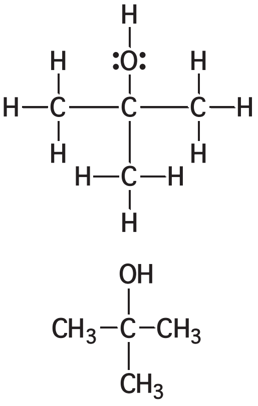
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH$

Primary



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

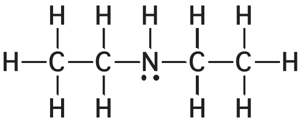
Secondary

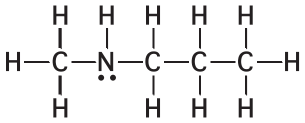


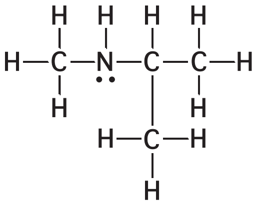
$CH_3-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$

Tertiary

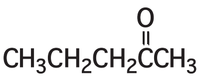
Problem 1.9 Draw structural formulas for the three secondary amines with molecular formula $C_4H_{11}N$.



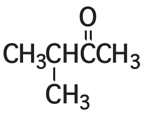




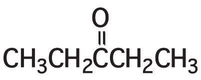
Problem 1.10 Draw condensed structural formulas for the three ketones with molecular formula $C_5H_{10}O$.



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



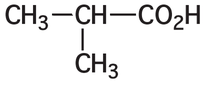
$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H\overset{\displaystyle O}{\overset{\|}{C}}CH_3$



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

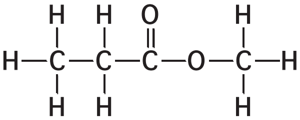
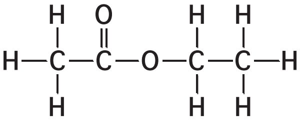
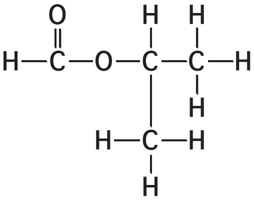
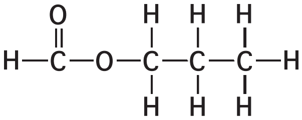
Problem 1.11 Draw condensed structural formulas for the two carboxylic acids with molecular formula $C_4H_8O_2$.

$CH_3-CH_2-CH_2-CO_2H$



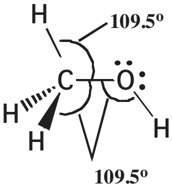
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CO_2H$

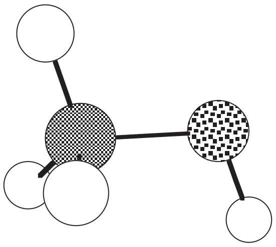
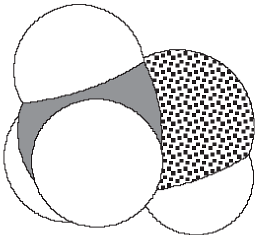
Problem 1.12 Draw structural formulas for the four esters with molecular formula $C_4H_8O_2$.

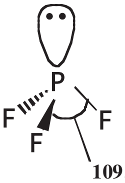
Problem 1.13 Predict all bond angles for these molecules.

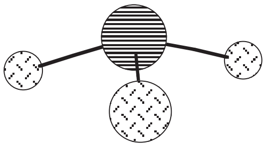
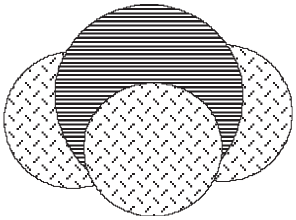
(a) CH_3OH



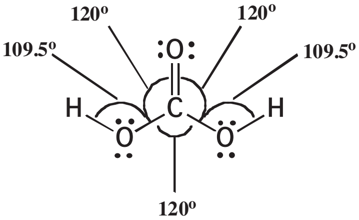



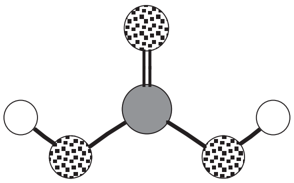
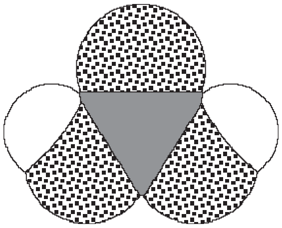
(b) PF_3



(c) H_2CO_3 (Carbonic Acid)



MCAT Practice: Questions

Fullerenes

A. The geometry of carbon in diamond is tetrahedral, while carbon's geometry in graphite is trigonal planar. What is the geometry of the carbons in C_{60}?

1. They are all tetrahedral.
2. They are all trigonal planar.
3. They are all pyramidal with bond angles near 109.5°.
4. **They are not perfectly trigonal planar but have an extent of pyramidalization. The curve of the buckyball surface is curved requiring some extent of pyramidilization.**

B. Because of their spherical shape, C_{60} moleclues are used as nanoscale ball bearings in grease and lubricants. We can estimate the size of these ball bearings by examining C-C bond distances. Carbon-carbon bond distances vary between approximately 120pm (pm = picometers) and 155pm. What is the approximate diameter of C_{60}?

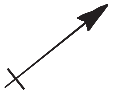
1. 10 pm
2. 100 pm
3. **1,000 pm C_{60} is approximately 8 bonds across so approximately 1,000 pm in diameter.**
4. 10,000 pm

C. What best describes the C-C-C bond angles in C_{60}?

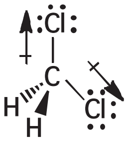
1. They are exactly 120°.
2. They are a bit larger than 120°.
3. **They are a bit smaller than 120°. The five-membered rings in the C_{60} structure reduce bond angles.**
4. They are near 109.5°.

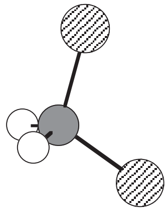
Problem 1.14 Which molecules are polar? For each molecule that is polar, specify the direction of its dipole moment.
(a) CH_2Cl_2

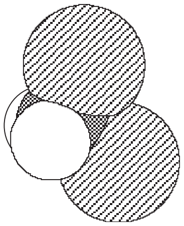
A molecular dipole moment is determined as the vector sum of the bond dipoles in three-dimensional space. Thus, by superimposing the bond dipoles on a three-dimensional drawing, the molecular dipole moment can be determined. Note that on the following diagrams, the dipole moments from the C-H bonds are ignored because they are small.



μ = 1.60 D

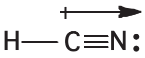


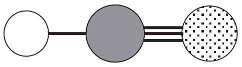


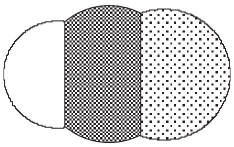


(b) HCN

μ = 2.98 D



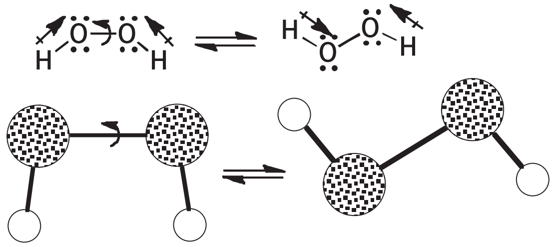




(c) H_2O_2

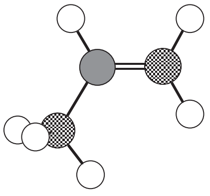
The H_2O_2 molecule can rotate around the O-O single bond, so we must consider the molecular dipole moments in the various possible conformations. Conformations such as the one on the left have a net molecular dipole moment, while conformations such as the one the right below do not. The presence of at least some conformations (such as that on the left) that have a molecular dipole moment means that the entire molecule must have an overall dipole moment, in this case μ = 2.2 D.

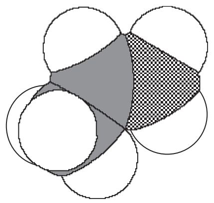
μ = 2.2 D



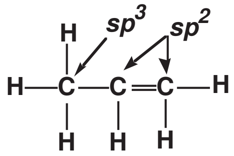
Problem 1.15 Describe the bonding in these molecules in terms of hybridization of C and N, and the types of bonds between carbon and nitrogen, and if there are any lone pairs, describe what type of orbital contains these electrons.

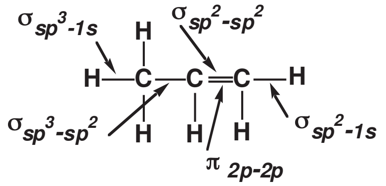
(a) CH_3-CH=CH_2

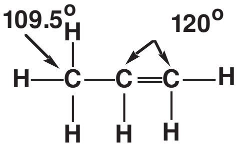




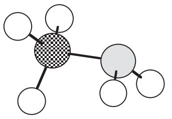
(a)

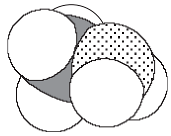




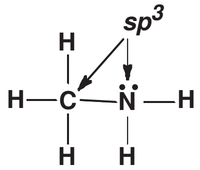


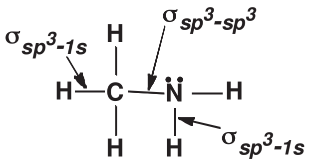
(b) CH_3-NH_2

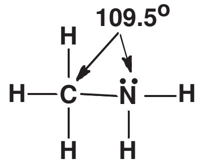




(b)

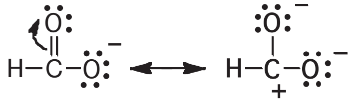




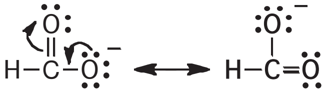


Problem 1.16 Draw the contributing structure indicated by the curved arrows. Show all valence electrons and all formal charges.

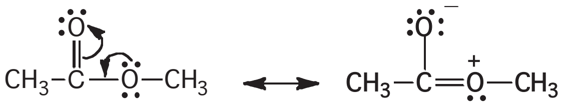
(a)



(b)

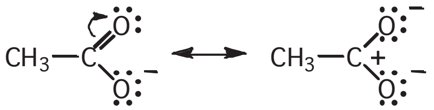


(c)

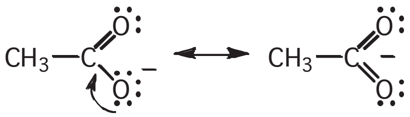


Problem 1.17 Which sets are valid pairs of contributing structures?

(a)



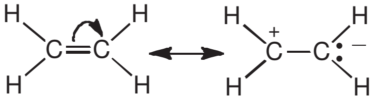
(b)



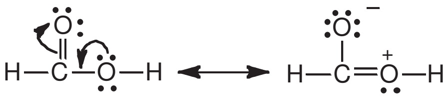
The set in (a) is a pair of contributing structures, while the set in (b) is not. The structure on the right in set (b) is not a viable contributing structure because there are five bonds to the carbon atom, implying 10 electrons in the valence shell, which can only hold a maximum of 8 electrons.

Problem 1.18 Estimate the relative contribution of the members in each set of contributing structures.

(a)

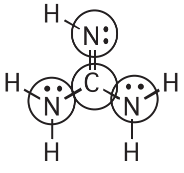


(b)

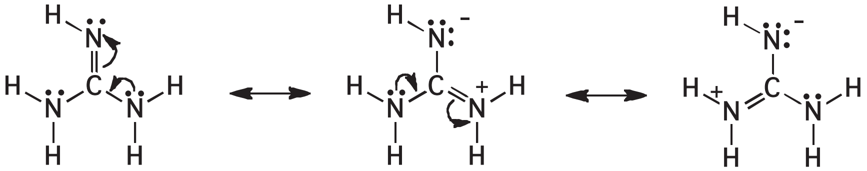


The first structure makes the greater contribution in (a) and (b). In both cases, the second contributing structure involves the disfavored creation and separation of unlike charges.

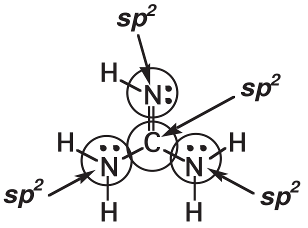
Problem 1.19 Draw three contributing structures of the following compound (called guanidine) and state the hybridization of the four highlighted atoms. In which orbitals do the three lone pairs drawn reside?

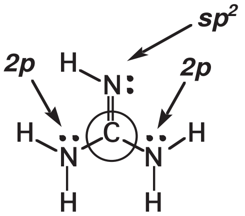


Guanidine

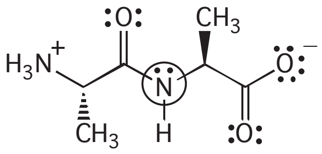


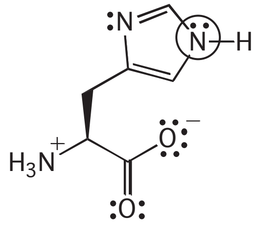
Remember that if any significant contributing structure contains a π bond, then the hybridization of that atom must be able to accommodate the π bond. Consideration of the three significant contributing structures indicates that all of the nitrogen atoms are sp^2 hybridized because of the π bonding. To be consistent with the contributing structures, two of the lone pairs on the original structure are in *2p* orbitals, while the third resides in an sp^2 orbital. Guanidine is one of many examples you will encounter in which the lone pair on nitrogen is delocalized into an adjacent π bond. Such delocalization of electron density in π orbitals is stabilizing and therefore favorable, a phenomenon that is best explained using quantum mechanical arguments (beyond the scope of this text).





MCAT Practice: Questions
VSEPR and Resonance





Histidine

A. What is the hybridization state of the circled nitrogens. What kind of orbital contains the lone pairs identified in these circles?

1. sp, $2p$
2. sp^2, sp^2
3. sp^3, $2p$
4. **sp^2, $2p$ The circled N atoms are each part of delocalized pi systems explaining their sp^2 hybridization. Write contributing structures to help understand this point. An sp^2 hybridized N atom with bonds to three other atoms must have the lone pair in $2p$ orbital.**

B. The molecule shown on the right in the example is the amino acid histidine, and the five-membered ring is known as aromatic. An aromatic ring has 2, 6, 10, or 14, etc. electrons placed in $2p$-orbitals around a ring. Indicate which statements must therefore also be true.

1. There are a total of 6 electrons in the pi system (defined as electrons in $2p$-orbitals), including the lone pair that is on the ring N that is not circled.
2. There are a total of 6 electrons in the pi system, including the lone pair that is on the ring N atom that is circled.
3. The lone pair on the ring N atom that is not circled resides in an sp^2 orbital on an sp^2 hybridized nitrogen atom.
4. **Both 2 and 3. A lone pair will be part of an aromatic pi system if it contributes to the aromatic number (in this case 6 pi electrons) like the circled N atom, while a lone pair will be in an sp^2 orbital of the N atom already has a pi bond without counting the lone pair like the non-circled N atom.**

C. Which of the following are reasonable contributing structures for the amide bond of the molecule shown on the left in the example above ?

Figure 1

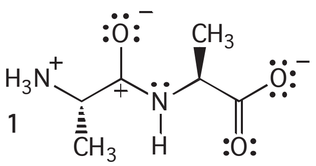


Figure 2

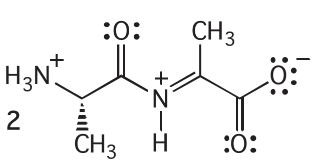
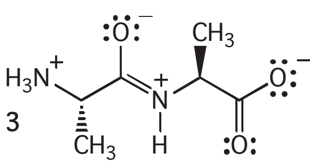
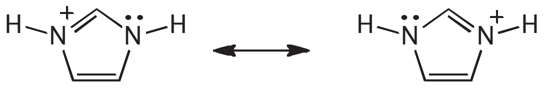


Figure 3



1. Figure 1
2. Figure 2
3. Figure 3
4. **Both Figures 1 and 3. Figure 2 makes no sense because it involves removal of an H atom so is therefore not a contributing structure. Both 1 and 3 are reasonable contributing structures for an amide bond.**

D) The following structure is called imidazolium. Which of the following statements about imidazolium are true?



Imidazolium

a. Both nitrogens are sp^2 hybridized, and the lone pair of electrons is in $2p$ orbitals.
b. The nitrogen on the right is sp^3 hybridized while the nitrogen on the left is sp^2 hybridized, and the lone pair of electrons shown is in an sp^3 hybrid orbital.
c. The molecule has an identical contributing structure not shown.
d. The molecule has no reasonable contributing structures.

1. **Statements a. and c. are true. Both N atoms in imidazolium are sp^2 hybridized and there is a symmetric contributing structure that moves the upper double bond and interconverts the locations of the plus charge and lone pair as shown above.**
2. Statements a. and d. are true.
3. Statements b. and c. are true.
4. Statements b. and d. are true.

Electronic Structures of Atoms

Problem 1.20 Write ground-state electron configuration for each atom. After each atom is its atomic number in parentheses.

(a) Sodium (11) **Na (11 electrons) $1s^2 2s^2 2p^6 3s^1$**

(b) Magnesium (12) **Mg (12 electrons) $1s^2 2s^2 2p^6 3s^2$**

(c) Oxygen (8) **O (8 electrons) $1s^2 2s^2 2p^4$**

(d) Nitrogen (7) **N (7 electrons) $1s^2 2s^2 2p^3$**

Problem 1.21 Identify the atom that has each ground-state electron configuration.

(a) $1s^2 2s^2 2p^6 3s^2 3p^4$

Sulfur (16) has this ground-state electron configuration

(b) $1s^2 2s^2 2p^4$

Oxygen (8) has this ground-state electron configuration

Problem 1.22 Define valence shell and valence electron.

The valence shell is the outermost occupied shell of an atom. A valence electron is an electron in the valence shell.

Problem 1.23 How many electrons are in the valence shell of each atom?

(a) Carbon

With a ground-state electron configuration of $1s^2 2s^2 2p^2$, there are four electrons in the valence shell of carbon.

(b) Nitrogen

With a ground-state electron configuration of $1s^2 2s^2 2p^3$, there are five electrons in the valence shell of nitrogen.

(c) Chlorine

With a ground-state electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^5$, there are seven electrons in the valence shell of chlorine.

(d) Aluminum

With a ground-state electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^1$, there are three electrons in the valence shell of aluminum.

Lewis Structures and Formal Charge

Problem 1.24 Judging from their relative positions in the Periodic Table, which atom in each set is more electronegative?
(a) Carbon or nitrogen

In general, electronegativity increases from left to right across a row (period) and from bottom to top of a column in the Periodic Table. This is because electronegativity increases with increasing positive charge on the nucleus and with decreasing distance of the valence electrons from the nucleus. Nitrogen is farther to the right than carbon in Period 2 of the Periodic Table. Thus, nitrogen is more electronegative than carbon.

(b) Chlorine or bromine

Chlorine is higher up than bromine in column 7A of the Periodic Table. Thus, chlorine is more electronegative than bromine.

(c) Oxygen or sulfur

Oxygen is higher up than sulfur in column 6A of the Periodic Table. Thus, oxygen is more electronegative than sulfur.

Problem 1.25 Which compounds have nonpolar covalent bonds, which have polar covalent bonds, and which have ions?
(a) LiF (b) CH_3F (c) $MgCl_2$ (d) HCl

Using the rule that ions are formed between atoms with an electronegativity difference of 1.9 or greater, the following table can be constructed:

Bond	Difference in electronegativity	Type of bond
Li-F	**4.0 - 1.0 = 3.0**	**Ions**
C-H	**2.5 - 2.1 = 0.4**	**Nonpolar covalent**
C-F	**4.0 - 2.5 = 1.5**	**Polar covalent**
Mg-Cl	**3.0 - 1.2 = 1.8**	**Polar covalent**
H-Cl	**3.0 - 2.1 = 0.9**	**Polar covalent**

Based on these values, only LiF has ions. The other compounds have nonpolar covalent (C-H) or polar covalent (C-F, Mg-Cl, H-Cl) bonds.

Problem 1.26 Using the symbols δ- and δ+, indicate the direction of polarity, if any, in each covalent bond.

(a) C-Cl $\overset{\delta+\ \delta-}{\textbf{C-Cl}}$ **Chlorine is more electronegative than carbon.**

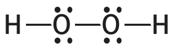
(b) S-H $\overset{\delta-\ \delta+}{\textbf{S-H}}$ **Sulfur is more electronegative than hydrogen.**

(c) C-S **Carbon and sulfur have the same electronegativity so there is no polarity in a C-S bond.**

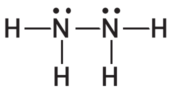
(d) P-H **Phosphorus and hydrogen have the same electronegativity, so there is no polarity in a P-H bond.**

Problem 1.27 Write Lewis structures for these compounds. Show all valence electrons. None of them contains a ring of atoms.

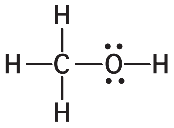
(a) H_2O_2
Hydrogen peroxide



(b) N_2H_4
Hydrazine

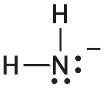


(c) CH_3OH
Methanol

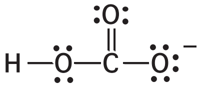


Problem 1.28 Write Lewis structures for these ions. Show all valence electrons and all formal charges.

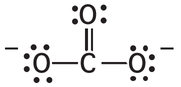
(a) NH_2^-
Amide ion



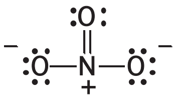
(b) HCO_3^-
Bicarbonate ion



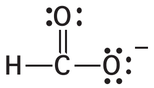
(c) CO_3^{2-}
Carbonate ion



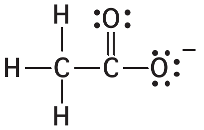
(d) NO_3^-
Nitrate ion



(e) $HCOO^-$
Formate ion



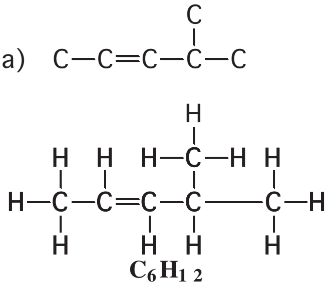
(f) CH_3COO^-
Acetate ion



Problem 1.29 Complete these structural formulas by adding enough hydrogens to complete the tetravalence of each carbon. Then write the molecular formula of each compound.

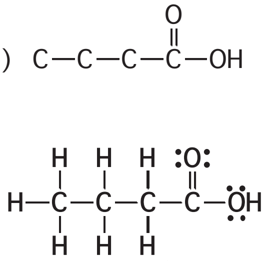
Lone pairs were added to the following structural formulas for clarity.

(a)



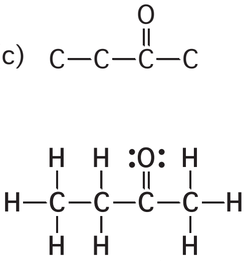
C_6H_{12}

(b)



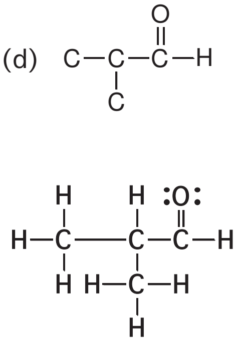
$C_4H_8O_2$

(c)



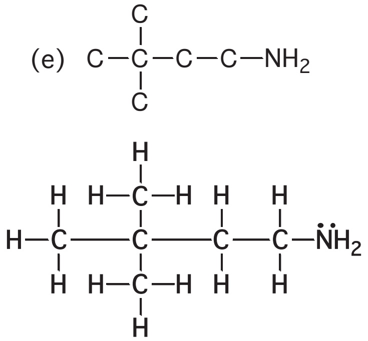
C_4H_8O

(d)



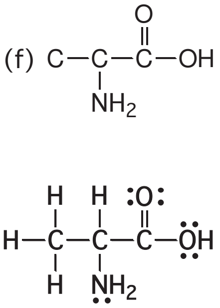
C_4H_8O

(e)



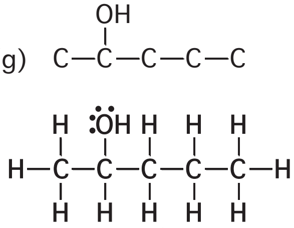
$C_6H_{15}N$

(f)



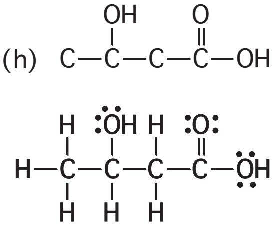
$C_3H_7NO_2$

(g)



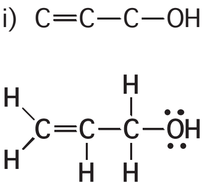
$C_5H_{12}O$

(h)



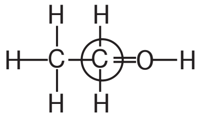
$C_4H_8O_3$

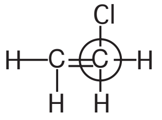
(i)



C_3H_6O

Problem 1.30 Some of these structural formulas are incorrect (i.e. they do not represent a real compound) because they have atoms with an incorrect number of bonds. Which structural formulas are incorrect? Which atoms in them have an incorrect number of bonds?

(a)


(b)


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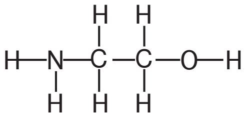
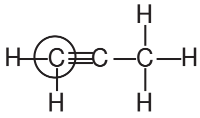
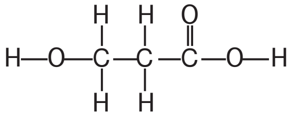
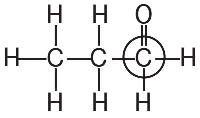
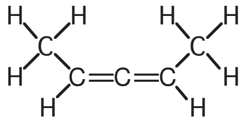
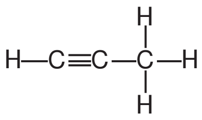


(d)


(e)


(f)


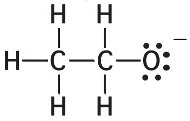
(g)


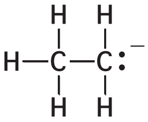
(h)


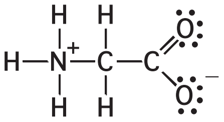
The molecules in (a), (b), (d), and (f) are incorrect, because there are five bonds to the circled carbon atom, not four.

Problem 1.31 Following the rule that each atom of carbon, oxygen, and nitrogen reacts to achieve a complete outer shell of eight valence electrons, add unshared pairs of electrons as necessary to complete the valence shell of each atom in these ions. Then assign formal charges as appropriate.

The following structural formulas show all valence electrons and all formal charges for clarity.

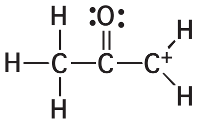
(a)


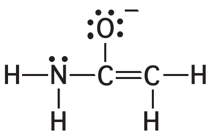
(b)


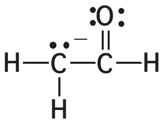
(c)


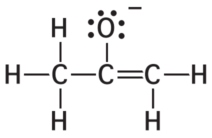
Problem 1.32 Following are several Lewis structures showing all valence electrons. Assign formal charges in each structure as appropriate.

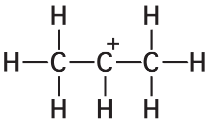
There is a positive formal charge in parts (a), (e), and (f). There is a negative formal charge in parts (b), (c), and (d).

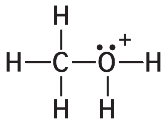
(a)


(b)


(c)


(d)


(e)


(f)


Polarity of Covalent Bonds

Problem 1.33 Which statements are true about electronegativity?
(a) Electronegativity increases from left to right in a period of the Periodic Table.
(b) Electronegativity increases from top to bottom in a column of the Periodic Table.
(c) Hydrogen, the element with the lowest atomic number, has the smallest electronegativity.
(d) The higher the atomic number of an element, the greater its electronegativity.

Electronegativity *increases* from left to right across a period and from bottom to top of a column in the Periodic Table. Thus, statement (a) is true, but (b), (c), and (d) are false.

Problem 1.34 Why does fluorine, the element in the upper right corner of the Periodic Table, have the largest electronegativity of any element?

Electronegativity increases with increasing positive charge on the nucleus and with decreasing distance of the valence electrons from the nucleus. Fluorine is that element for which these two parameters lead to maximum electronegativity.

Problem 1.35 Arrange the single covalent bonds within each set in order of increasing polarity.

(a) C-H, O-H, N-H	(b) C-H, B-H, O-H	(c) C-H, C-Cl, C-I
C-H < N-H < O-H	**B-H < C-H < O-H**	**C-I < C-H < C-Cl**
(d) C-S, C-O, C-N	(e) C-Li, C-B, C-Mg	
C-S < C-N < C-O	**C-B < C-Mg < C-Li**	

Problem 1.36 Using the values of electronegativity given in Table 1.5, predict which indicated bond in each set is the more polar and, using the symbols δ+ and δ-, show the direction of its polarity

(a) CH_3-OH or CH_3O-H	(b) CH_3-NH_2 or CH_3-PH_2
$CH_3\overset{\delta-}{O}\text{-}\overset{\delta+}{H}$	$H_3\overset{\delta+}{C}\text{-}\overset{\delta-}{NH_2}$
(c) CH_3-SH or CH_3S-H	(d) CH_3-F or H-F
$CH_3\overset{\delta-}{S}\text{-}\overset{\delta+}{H}$	$\overset{\delta+}{H}\text{-}\overset{\delta-}{F}$

Problem 1.37 Identify the most polar bond in each molecule.

(a) $HSCH_2CH_2OH$	(b) $CHCl_2F$	(c) $HOCH_2CH_2NH_2$
The O-H bond **(1.4)**	**The C-F bond** **(1.5)**	**The O-H bond** **(1.4)**

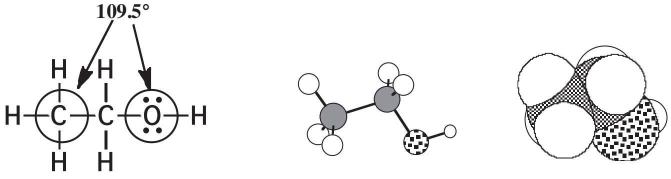
The difference in electronegativities is given in parentheses underneath each answer.

Bond Angles and Shapes of Molecules

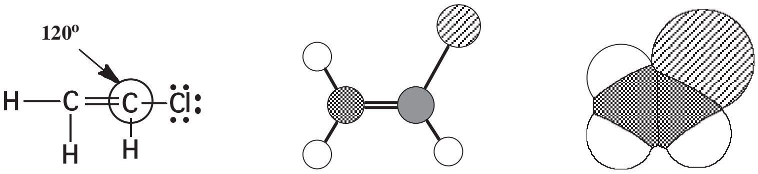
Problem 1.38 Use VSEPR to predict bond angles about each highlighted atom

Approximate bond angles as predicted by valence-shell electron-pair repulsion are as shown.

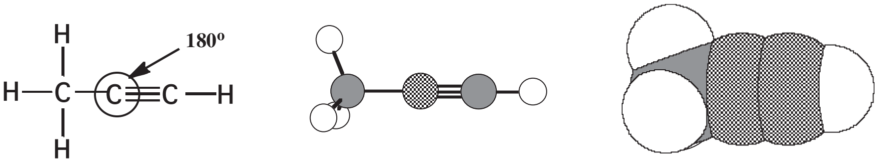
(a)



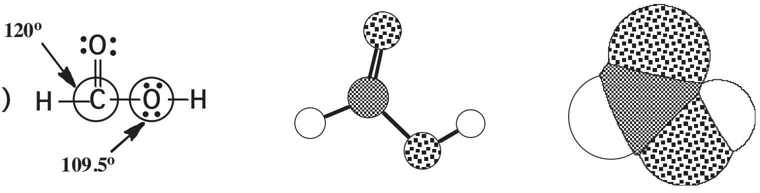
(b)



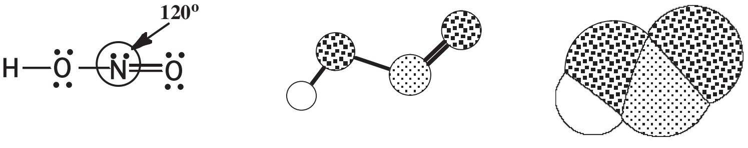
(c)



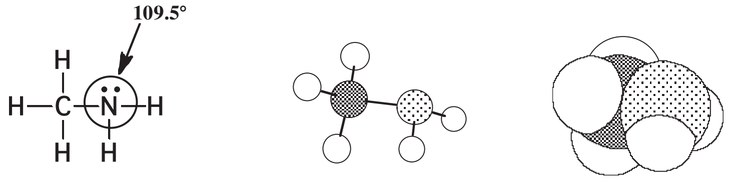
(d)



(e)

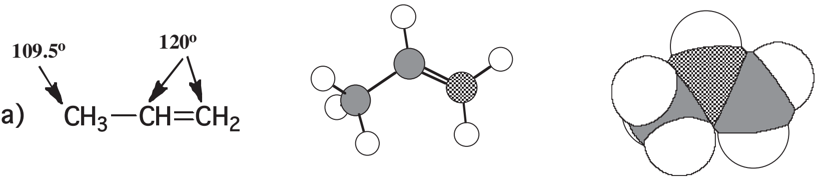


(f)

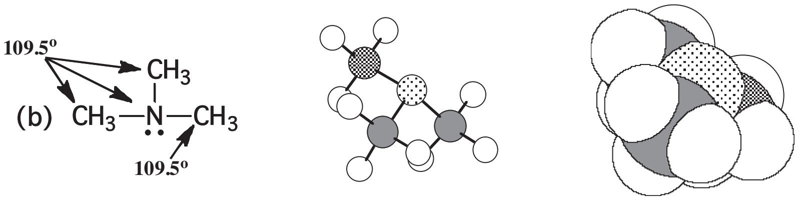


Problem 1.39 Use VSEPR to predict bond angles about each atom of carbon, nitrogen, and oxygen in these molecules.

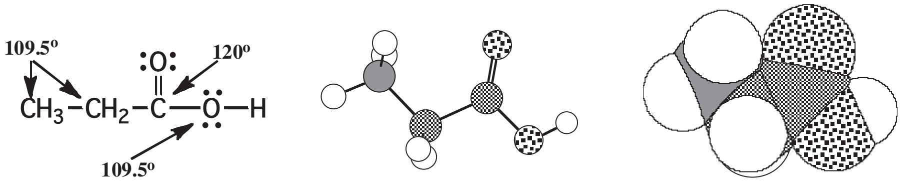
(a)



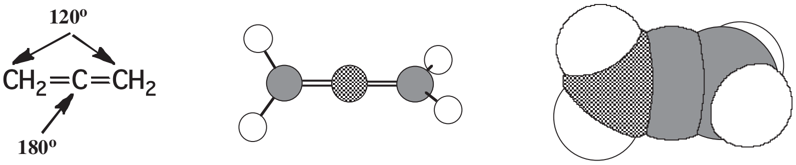
(b)



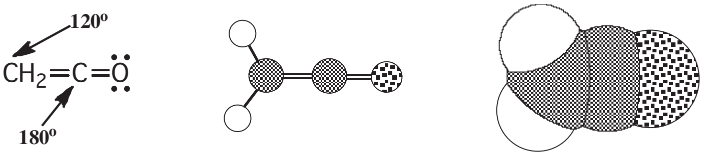
(c)



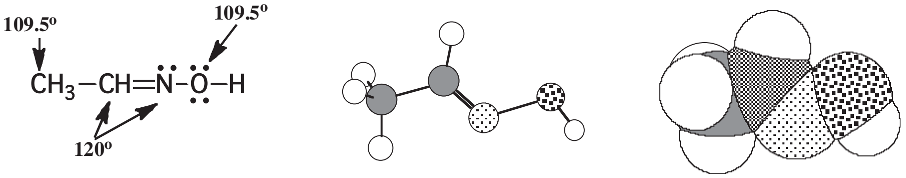
(d)



(e)

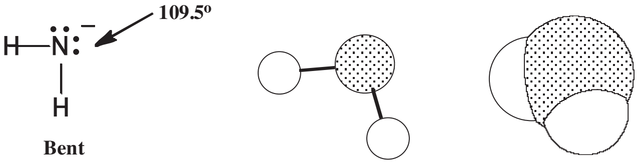


(f)

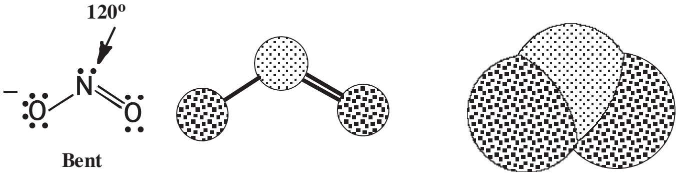


Problem 1.40 Use VSEPR to predict the geometry of these ions.

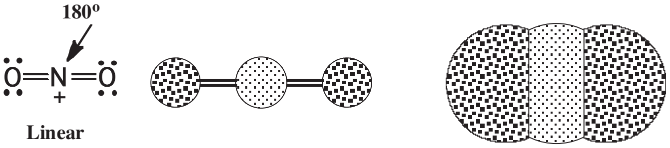
(a) NH_2^-



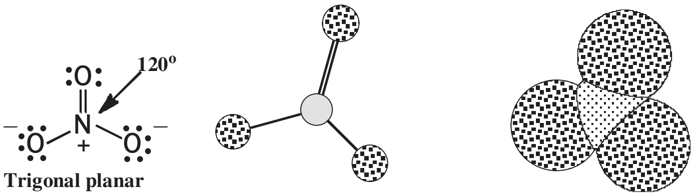
(b) NO_2^-



(c) NO_2^+



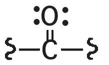
(d) NO_3^-



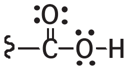
Functional Groups

Problem 1.41 Draw Lewis structures for these functional groups. Be certain to show all valence electrons on each.

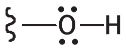
(a) Carbonyl group



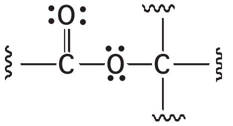
(b) Carboxyl group



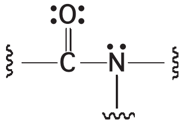
(c) Hydroxyl group



(d) Ester group



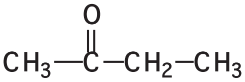
(e) Amide group



Problem 1.42 Draw condensed structural formulas for all compounds with the molecular formula C_4H_8O that contain

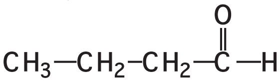
(a) A carbonyl group (there are two aldehydes and one ketone).

Ketone

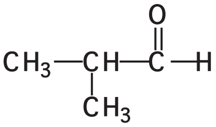


$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$ **also written as** $CH_3COCH_2CH_3$

Aldehydes



$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-H$ **also written as** $CH_3CH_2CH_2CHO$

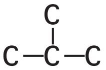


$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-H$ **also written as** $(CH_3)_2CHCHO$

(b) A carbon-carbon double bond and a hydroxyl group (there are eight)

There are three separate but related things to build into this answer; the carbon skeleton (the order of attachment of carbon atoms), the location of the double bond, and the location of the -OH group. Here, as in other problems of this type, it is important to have a system and to follow it. As one way to proceed, first decide the number of different carbon skeletons that are possible. A little doodling with paper and pencil should convince you that there are only two.

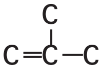
C-C-C-C **and**



$C-\overset{C}{C}-C$

Next locate the double bond on these carbon skeletons. There are three possible locations for it.

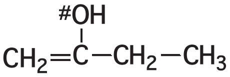
$C{=}C-C-C$ **and** $C-C{=}C-C$ **and**



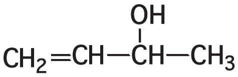
$C{=}\overset{C}{C}-C$

Finally, locate the -OH group and then add the remaining seven hydrogens to complete each structural formula. For the first carbon skeleton, there are four possible locations of the -OH group; for the second carbon skeleton there are two possible locations; and for the third, there are also two possible locations. Four of these compounds (marked by a # symbol) are not stable and are in equilibrium with a more stable aldehyde or ketone. You need not be concerned, however, with this now. Just concentrate on drawing the required eight condensed structural formulas.

$\overset{\#}{HO}-CH{=}CH-CH_2-CH_3$



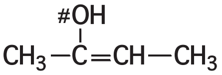
$CH_2{=}\overset{\#OH}{C}-CH_2-CH_3$



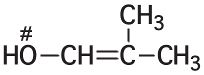
$CH_2{=}CH-\overset{OH}{CH}-CH_3$

$CH_2{=}CH-CH_2-CH_2-OH$

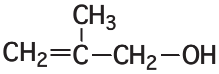
$HO-CH_2-CH{=}CH-CH_3$



$CH_3-\overset{\#OH}{C}{=}CH-CH_3$



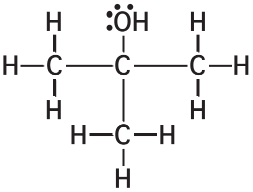
$\overset{\#}{HO}-CH{=}\overset{CH_3}{C}-CH_3$



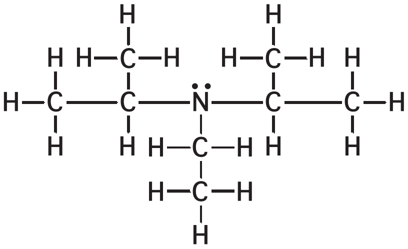
$CH_2{=}\overset{CH_3}{C}-CH_2-OH$

Problem 1.43 What is the meaning of the term tertiary (3°) when it is used to classify alcohols? Draw a structural formula for the one tertiary (3°) alcohol with the molecular formula $C_4H_{10}O$.

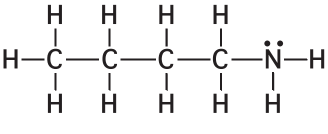
A tertiary alcohol is one in which the -OH group is on a tertiary carbon atom. A tertiary carbon atom is one that is bonded to three other carbon atoms.

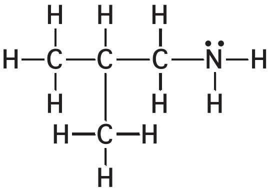


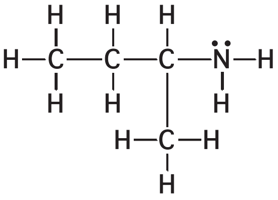
Problem 1.44 What is the meaning of the term tertiary (3°) when it is used to classify amines? Draw a structural formula for the one tertiary (3°) amine known as Hunig's base (*N,N*-diisopropylethylamine).

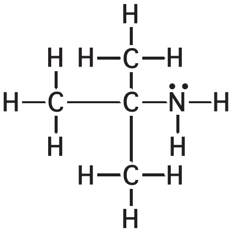


Problem 1.45 Draw structural formulas for
(a) The four primary (1°) amines with the molecular formula $C_4H_{11}N$.

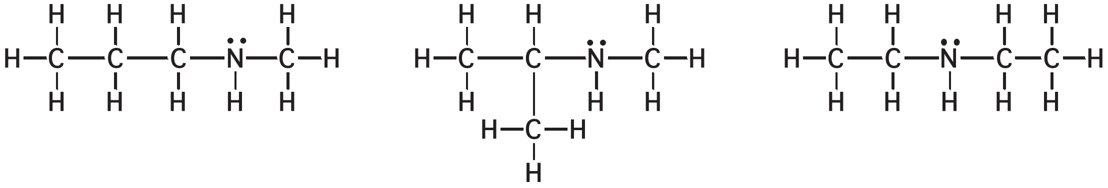




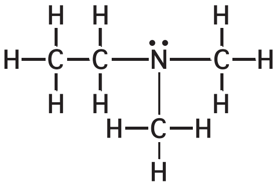




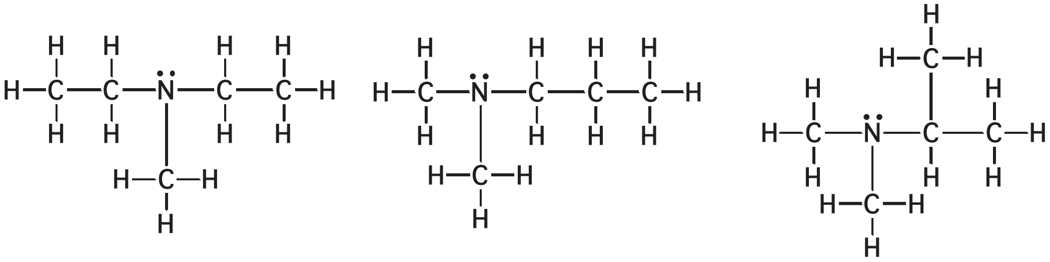
(b) The three secondary (2°) amines with the molecular formula $C_4H_{11}N$.



(c) The one tertiary (3°) amine with the molecular formula $C_4H_{11}N$.



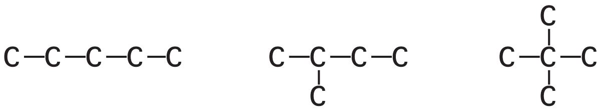
Problem 1.46 Draw structural formulas for the three tertiary (3°) amines with the molecular formula $C_5H_{13}N$.



Problem 1.47 Draw structural formulas for
(a) The eight alcohols with the molecular formula $C_5H_{12}O$.

To make it easier for you to see the patterns of carbon skeletons and functional groups, only carbon atoms and hydroxyl groups are shown in the following solutions. To complete these structural formulas, you need to supply enough hydrogen atoms to complete the tetravalence of each carbon.

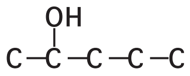
There are three different carbon skeletons on which the -OH group can be placed:



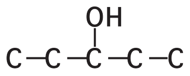
Three alcohols are possible from the first carbon skeleton, four from the second carbon skeleton, and one from the third carbon skeleton.

HO—C—C—C—C—C

(1)



(2)



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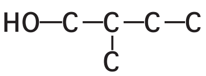

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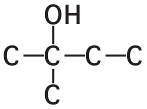

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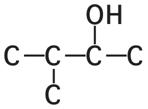

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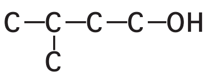

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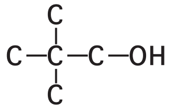
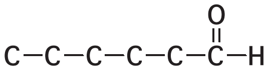


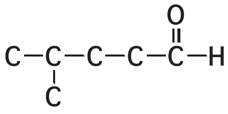
(8)

(b) The eight aldehydes with the molecular formula $C_6H_{12}O$.

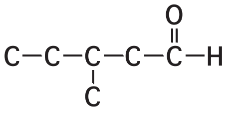
Following are structural formulas for the eight aldehydes with the molecular formula $C_6H_{12}O$. They are drawn starting with the aldehyde group and then attaching the remaining five carbons in a chain (structure 1), then four carbons in a chain and one carbon as a branch on the chain (structures 2, 3, and 4) and finally three carbons in a chain and two carbons as branches (structures 5, 6, 7, and 8).


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

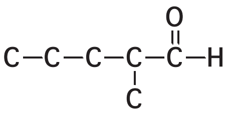
(1)


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

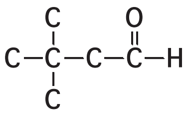
(2)


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

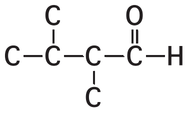
(3)


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

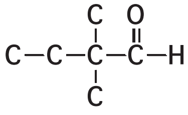
(4)


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

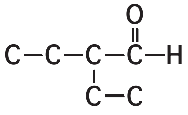
(5)


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

(6)


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

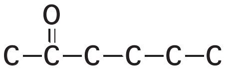
(7)


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

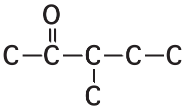
(8)

(c) The six ketones with the molecular formula $C_6H_{12}O$.

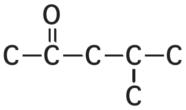
Following are structural formulas for the six ketones with the molecular formula $C_6H_{12}O$. They are drawn first with all combinations of one carbon to the left of the carbonyl group and four carbons to the right (structures 1, 2, 3, and 4) and then with two carbons to the left and three carbons to the right (structures 5 and 6).


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

(1)


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

(2)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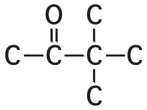
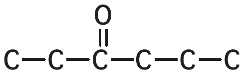
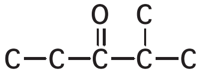
(3)


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

(4)


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

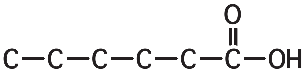
(5)


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

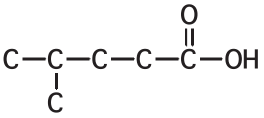
(6)

(d) The eight carboxylic acids with the molecular formula $C_6H_{12}O_2$.

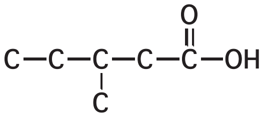
There are eight carboxylic acids of molecular formula $C_6H_{12}O_2$. They have the same carbon skeletons as the eight aldehydes of molecular formula $C_6H_{12}O$ shown in part (b) of this problem. In place of the aldehyde group, substitute a carboxyl group.


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

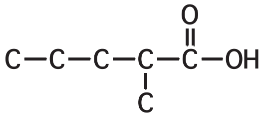
(1)


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

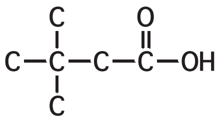
(2)


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

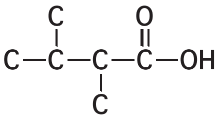
(3)


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

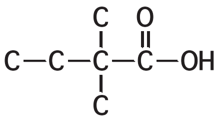
(4)


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

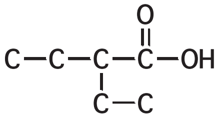
(5)


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

(6)


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

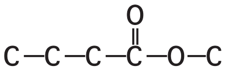
(7)


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

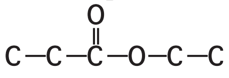
(8)

(e) The nine carboxylic esters with the molecular formula $C_5H_{10}O_2$.

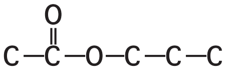
Start with unbranched carbon chains of all possible lengths, then add branching to complete the set.


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

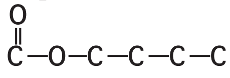
(1)


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

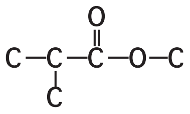
(2)


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

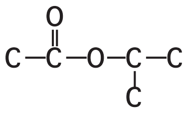
(3)


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

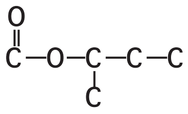
(4)


$\mathrm{C{-}\underset{\underset{C}{|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}O{-}C}$

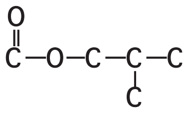
(5)


$\mathrm{C{-}\overset{\overset{O}{\|}}{C}{-}O{-}\underset{\underset{C}{|}}{C}{-}C}$

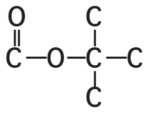
(6)


$\mathrm{\overset{\overset{O}{\|}}{C}{-}O{-}\underset{\underset{C}{|}}{C}{-}C{-}C}$

(7)

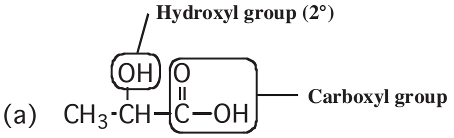

$\mathrm{\overset{\overset{O}{\|}}{C}{-}O{-}C{-}\underset{\underset{C}{|}}{C}{-}C}$

(8)

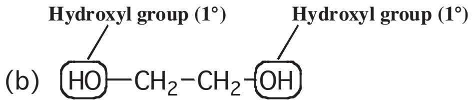

$\mathrm{\overset{\overset{O}{\|}}{C}{-}O{-}\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}{-}C}$

(9)

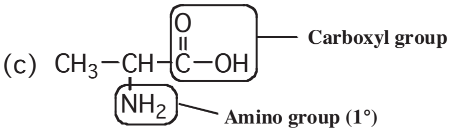
Problem 1.48 Identify the functional groups in each compound.



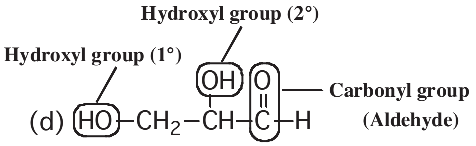
Lactic acid



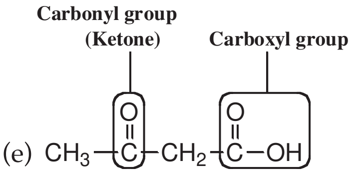
Ethylene glycol



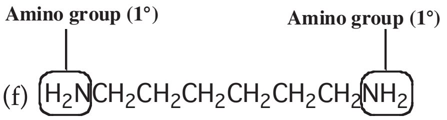
Alanine



Glyceraldehyde



Acetoacetic acid



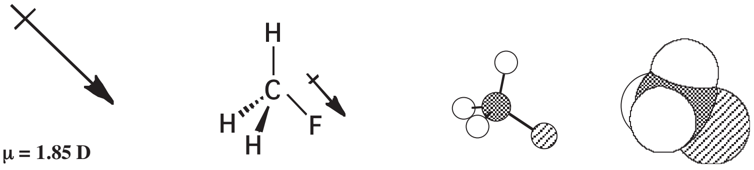
1,6-Hexanediamine

Polar and Nonpolar Molecules

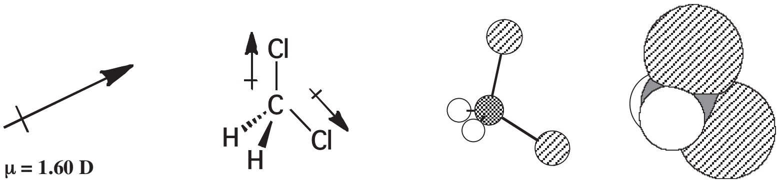
Problem 1.49 Draw a three-dimensional representation for each molecule. Indicate which ones have a dipole moment and in what direction it is pointing.

In the following diagrams, the C-H bond dipole moment has been left out because it is a nonpolar covalent bond. The listed dipole moments were looked up in the chemical literature and are only added for reference. You will not be expected to calculate these.

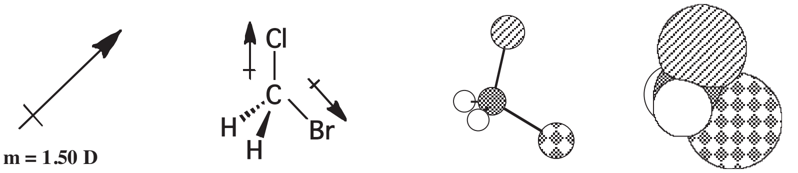
(a) CH_3F



(b) CH_2Cl_2

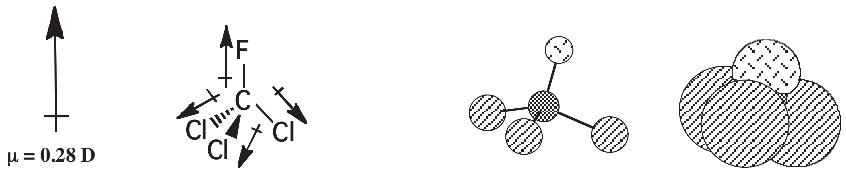


(c) CH_2ClBr



The bond dipole moment of the C-Cl bond dominates because chlorine is more electronegative than bromine.

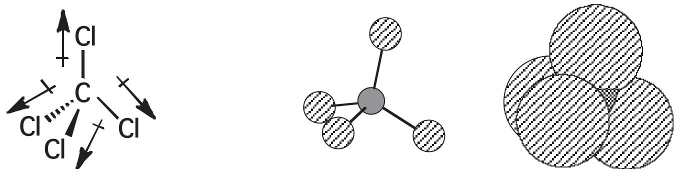
(d) $CFCl_3$



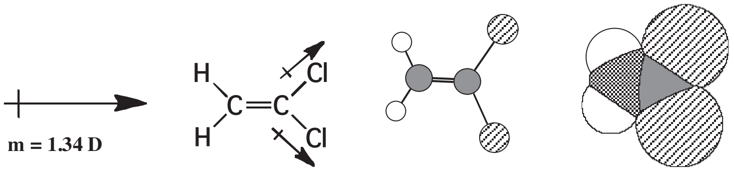
The bond dipole moment of the C-F bond dominates because of the higher electronegativity of fluorine.

(e) CCl_4

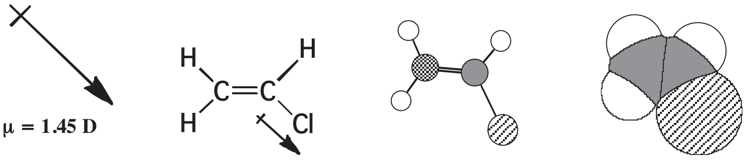
No molecular dipole moment



(f) $CH_2=CCl_2$

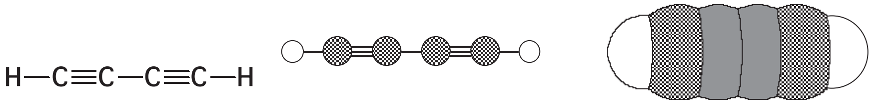


(g) $CH_2=CHCl$

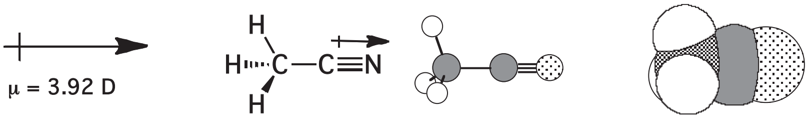


(h) HC≡C-C≡CH

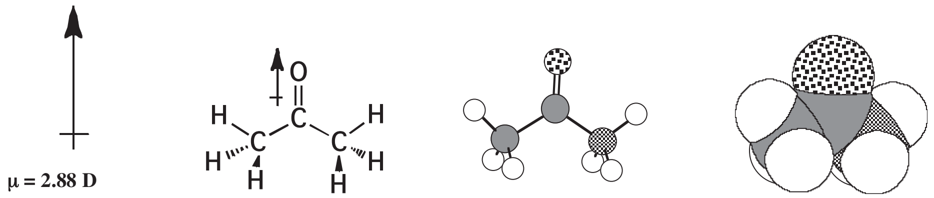
No molecular dipole moment



(i) $CH_3C≡N$



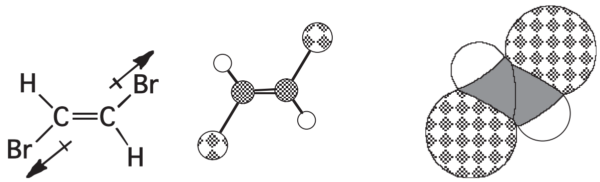
(j) $(CH_3)_2C{=}O$

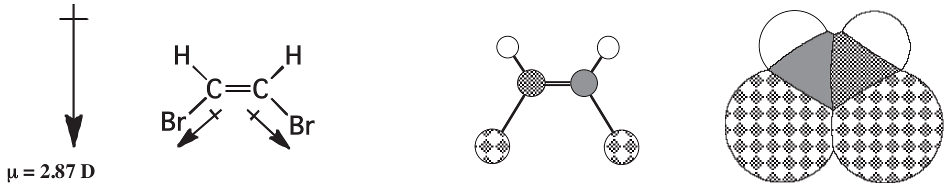


(k) BrCH=CHBr (two answers)

The two bromine atoms can either be on opposite sides or on the same side of the double bond. Recall that double bonds do not rotate.

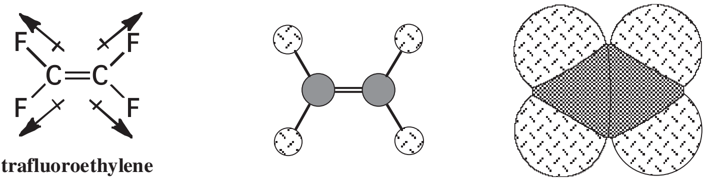
No molecular dipole moment





Problem 1.50 Tetrafluoroethylene, C_2F_4, is the starting material for the synthesis of the polymer polytetrafluoroethylene (PTFE), one form of which is known as Teflon. Tetrafluoroethylene has a dipole moment of zero. Propose a structural formula for this molecule.

No molecular dipole moment



Tetrafluoroethylene

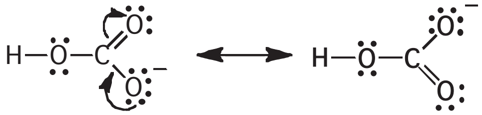
Resonance and Contributing Structures

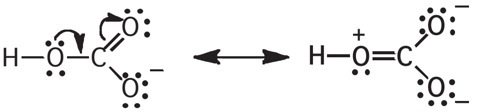
Problem 1.51 Which statements are true about resonance contributing structures?
(a) All contributing structures must have the same number of valence electrons.
(b) All contributing structures must have the same arrangement of atoms.
(c) All atoms in a contributing structure must have complete valence shells.
(d) All bond angles in sets of contributing structures must be the same.

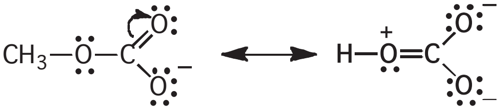
For sets of contributing structures, electrons (usually π electrons or lone pair electrons) move, but the atomic nuclei maintain the same arrangement in space. The atoms are arranged the same with the same bond angles among them, so statements (b) and (d) are true. In addition, the total number of electrons, valence and inner shell electrons, in each contributing structure must be the same, so statement (a) is also true. However, the movement of electrons often leaves one or more atoms without a filled valence shell in a given contributing structure, so statement (c) is false.

Problem 1.52 Draw the contributing structure indicated by the curved arrow(s). Assign formal charges as appropriate.

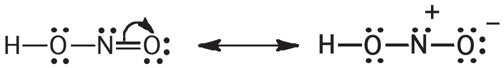
(a)

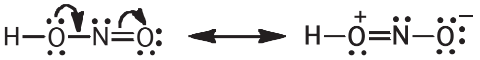


(b)


(c)


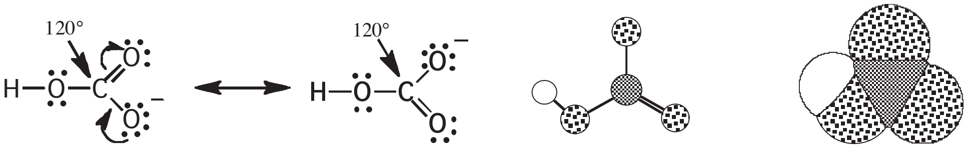
(d)

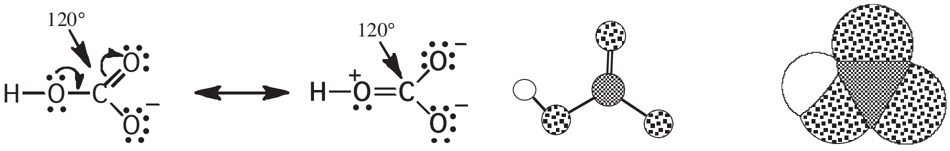

(e)


(f)


Problem 1.53 Using VSEPR, predict the bond angles about the carbon and nitrogen atoms in each pair of contributing structures in problem 1.52. In what way do these bond angles change from one contributing structure to the other?

As stated in the answer to Problem 1.51, bond angles do not change from one contributing structure to another.

(a)


(b)


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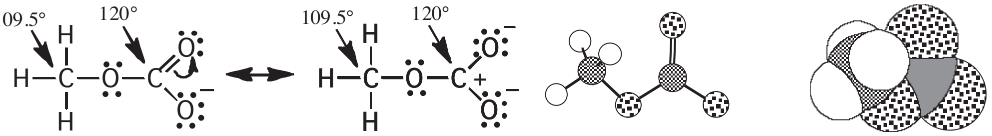

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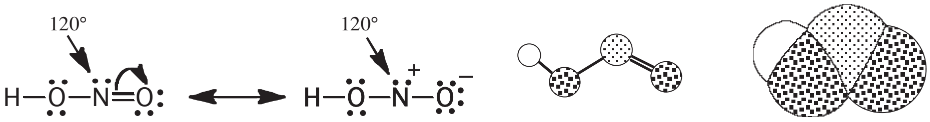

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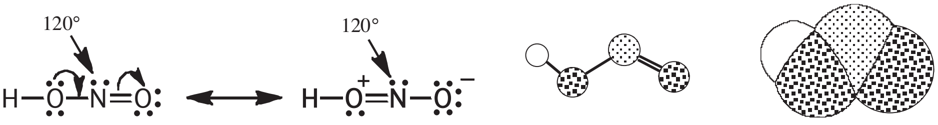
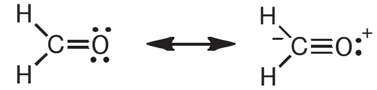


Problem 1.54 In the Problem 1.52 you were given one contributing structure and asked to draw another. Label pairs of contributing structures that are equivalent. For those sets in which the contributing structures are not equivalent, label the more important contributing structure.

(a) The two structures are equivalent because each involves a similar separation of charge.
(b, c, d, e, f) The first structure is more important, because the second involves creation and separation of unlike charges.

Problem 1.55 Are the structures in each set valid contributing structures?

(a)

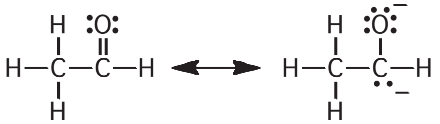


The structure on the right is not a valid contributing structure because there are 10 electrons in the valence shell of the carbon atom.

(b)

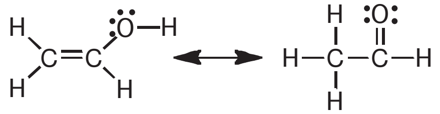
Both of these are valid contributing structures.

(c)



The structure on the right is not a valid contributing structure because there are two extra electrons and thus it is a completely different species.

(d)



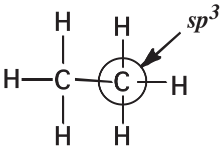
Although each is a valid Lewis structure, they are not valid contributing structures for the same resonance hybrid. An atomic nucleus, namely a hydrogen, has changed position. Later you will learn that these two molecules are related to each other and are called tautomers.

Valence Bond Theory

Problem 1.56 State the orbital hybridization of each highlighted atom.

Each circled atom is either sp, sp^2, or sp^3 hybridized.

(a)



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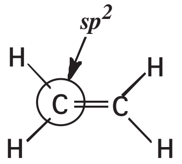

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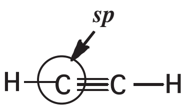

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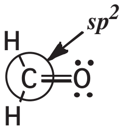

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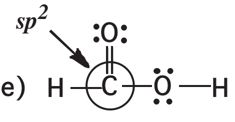

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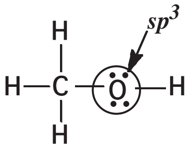
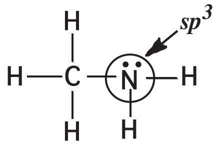


(g)



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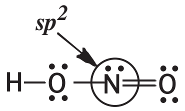
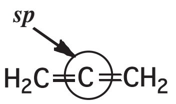
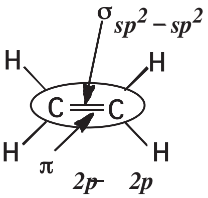


(i)



Problem 1.57 Describe each highlighted bond in terms of the overlap of atomic orbitals.

Shown is whether the bond is σ or π, as well as the orbitals used to form it.

(a)


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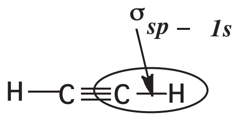

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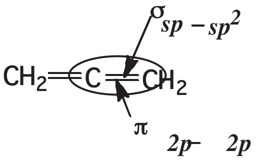

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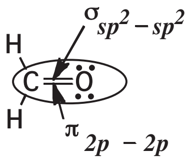

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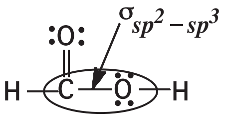

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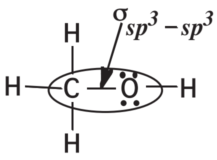

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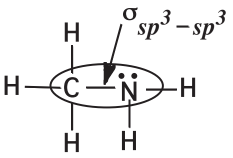

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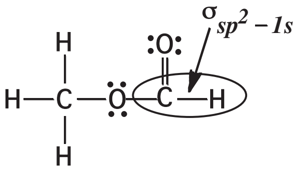
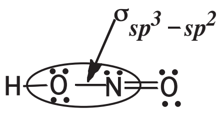
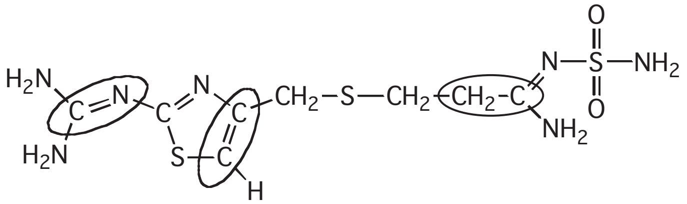
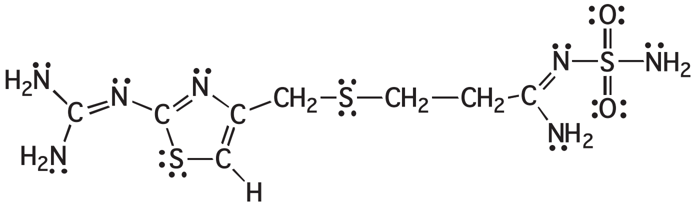


(i)


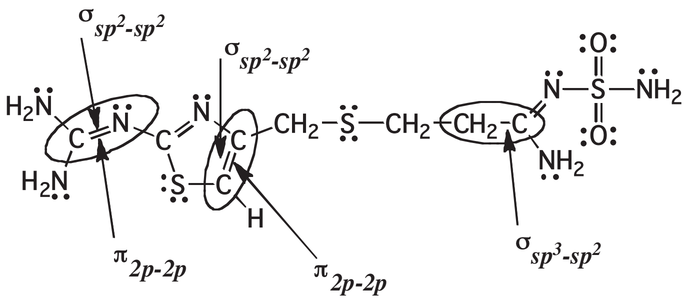
Problem 1.58 Following is a structural formula of the prescription drug famotidine marketed by by McNeil Consumer Pharmaceuticals Co. under the name Pepcid. The primary clinical use of Pepcid is for the treatment of active duodenal ulcers and benign gastric ulcers. Pepcid is a competitive inhibitor of histamine H_2 receptors and reduces both gastric acid concentration and the volume of gastric secretions.



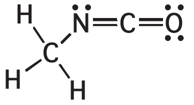
(a) Complete the Lewis structure of famotidine showing all valence electrons and any positive or negative charges.

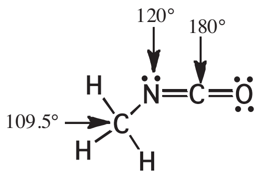


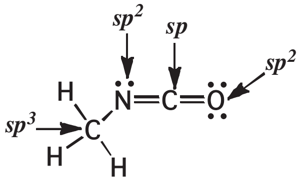
(b) Describe each circled bond in terms of the overlap of atomic orbitals.

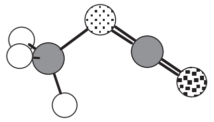


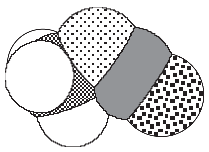
Problem 1.59 Draw a Lewis structure for methyl isocyanate, CH_3NCO, showing all valence electrons. Predict all bond angles in this molecule and the hybridization of each atom C, N, and O.





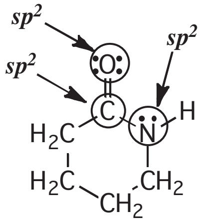


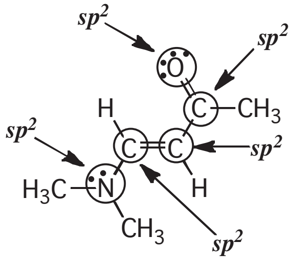


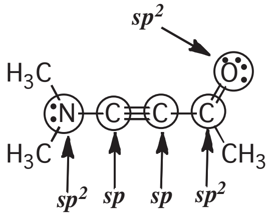


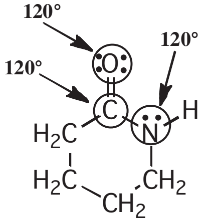
Combined MO/VB Theory

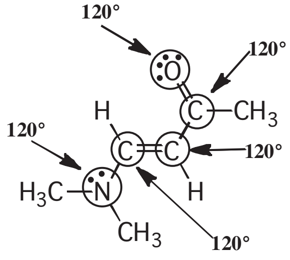
Problem 1.60 What is the hybridization of the highlighted atoms in the following structures? What are your estimates for the bond angles around these highlighted atoms? In each case, in what kind of orbital does the lone pair of electrons on the nitrogen reside?

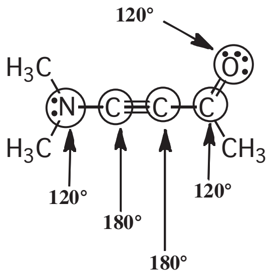




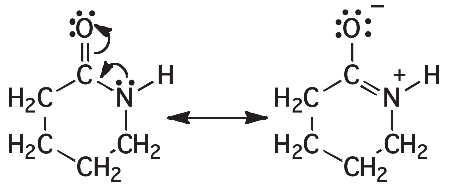


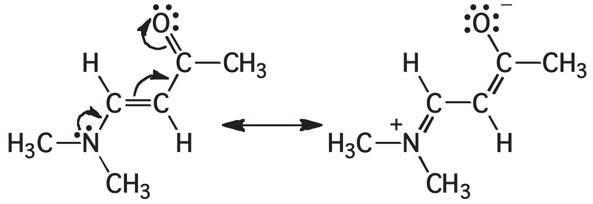


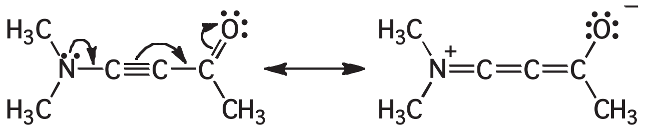




In each case there are significant contributing structures that have a π bond involving nitrogen.

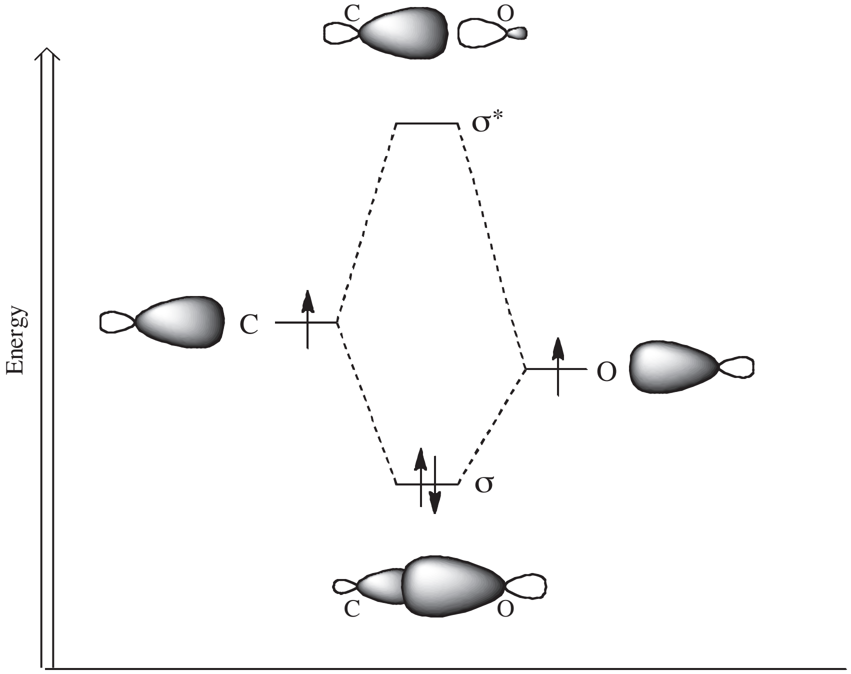






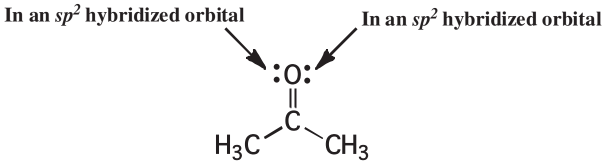
These are examples of nitrogen lone pairs delocalizing into adjacent π bonds, a common feature of many organic molecules you will come across. For this to happen, the nitrogen atoms must be *sp*^{2} hydridized, so the lone pairs on nitrogen are best thought of as being in *2p* orbitals. Such delocalization of electron density in π orbitals is stabilizing and therefore favorable, a phenomenon that is best explained using quantum mechanical arguments (beyond the scope of this text).

Problem 1.61 Using cartoon representations, draw a molecular orbital mixing diagram for a C-O σ-bond. In your picture, consider the relative energies of C and O, and how this changes the resulting bonding and antibonding molecular orbitals relative to a C-C σ-bond.



The O atom, being more electronegative, is of lower energy than the C atom. This means the O orbital makes a larger contribution to the σ-bonding orbital, while the C atom makes a larger contribution to the σ*-antibonding orbital. For a σ-bonding orbital formed from two C atoms of the same hybridization, both C orbitals make equal contributions.

Problem 1.62 In what kind of orbitals do the lone-pair electrons on the oxygen of acetone reside? Are they in the same plane as the methyl -CH_3 groups or are they perpendicular to the methyl -CH_3 groups?



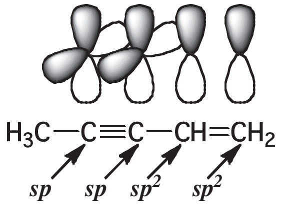
Acetone

In acetone, both lone pairs reside in *sp*^{2} hybridized orbitals, so they are in the same plane as the two methyl groups.

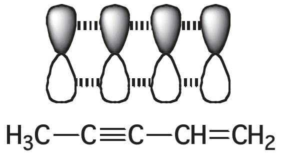
Problem 1.63 Draw the delocalized molecular orbitals for the following molecule. Are both π-bonds of the triple bond involved in the delocalized orbitals?

$$H_3C—C\equiv C—CH=CH_2$$

Shown below are the *2p* orbitals involved with delocalized π-bonding.



The delocalized molecular orbital involves only the four parallel *2p* orbitals as shown below. The perpendicular *2p* orbitals of the two *sp* hybridized carbons only overlap with each other, so they are not involved with delocalized bonding.



Additional Problems

Problem 1.64 Why are the following molecular formulas impossible?

(a) CH_5

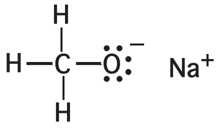
Carbon atoms can only accommodate 8 electrons in their valence shell, and each hydrogen atom can only accommodate one bond. Thus, there is no way for a stable bonding arrangement to be created that utilizes one carbon atom and all five hydrogen atoms.

(b) C_2H_7

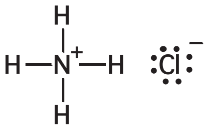
Because hydrogen atoms can only accommodate one bond each, no single hydrogen atom can make stable bonds to both carbon atoms. Thus, the two carbon atoms must be bonded to each other. This means that each of the bonded carbon atoms can accommodate only three more bonds. Therefore, only six hydrogen atoms can be bonded to the carbon atoms, not seven hydrogen atoms.

Problem 1.65 Each compound contains both ions and covalent bonds. Draw the Lewis structure for each compound. Show by dashes which are covalent bonds and show with charges which are ions.

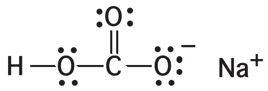
(a) CH_3ONa
Sodium methoxide



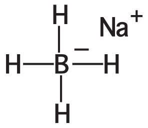
(b) NH_4Cl
Ammonium chloride



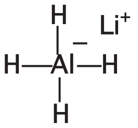
(c) $NaHCO_3$
Sodium bicarbonate



(d) $NaBH_4$
Sodium borohydride

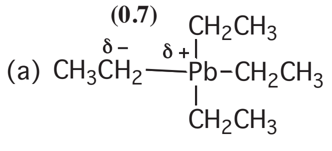


(e) $LiAlH_4$
Lithium aluminum hydride

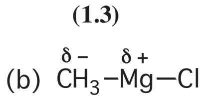


In naming these compounds, the cation is named first followed by the name of the anion.

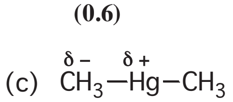
Problem 1.66 Predict whether the carbon-metal bond in these organometallic compounds is nonpolar covalent, polar covalent, or ionic. For each polar covalent bond, show the direction of its polarity by the symbols **δ+** and **δ-**.



Tetraethyllead



Methylmagnesium chloride

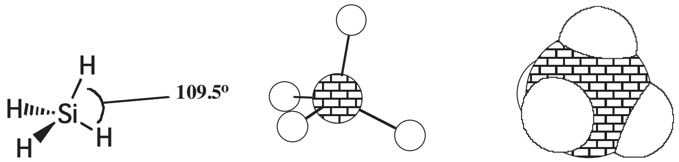


Dimethylmercury

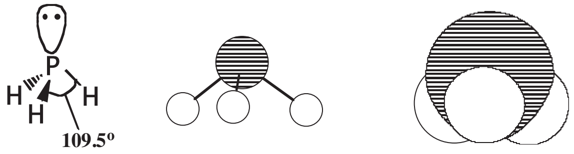
All of these carbon-metal bonds are polar covalent because the difference in electronegativities is between 0.5 and 1.9. In each case, carbon is the more electronegative element so it has the partial negative charge. The difference in electronegativities is given above the carbon-metal bond in each answer.

Problem 1.67 Silicon is immediately under carbon in the Periodic Table. Predict the geometry of silane, SiH_4.

Silicon is in Group 4 of the Periodic Table, and like carbon, has four valence electrons. In silane, SiH_4, silicon is surrounded by four regions of electron density. Therefore, you should predict all H-Si-H bond angles to be 109.5°, so the molecule is tetrahedral around Si.



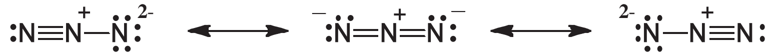
Problem 1.68 Phosphorus is immediately under nitrogen in the Periodic Table. Predict the molecular formula for phosphine, the compound formed by phosphorus and hydrogen. Predict the H-P-H bond angle in phosphine.



Like nitrogen, phosphorus has five valence electrons, so you should predict that phosphine has the molecular formula of PH_3 in analogy to ammonia, NH_3. In phosphine, the phosphorus atom is surrounded by four regions of electron density; one lone pair of electrons and single bonds to three hydrogen. Therefore, predict all H-P-H bond angles to be roughly 109.5°, meaning the molecule is pyramidal.

Problem 1.69 Draw a Lewis structure for the azide ion, N_3^-. (The order of attachment is N-N-N and they do not form a ring). How does the resonance model account for the fact that the lengths of the N-N bonds in this ion are identical.

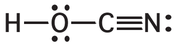
It is not possible to draw a single Lewis structure that adequately describes the azide ion. Rather, it can be drawn as the hybrid of three contributing structures.



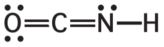
Taken together, the three contributing structures present a symmetric picture of azide ion bonding, thus explaining why both N-N bonds are identical.

Problem 1.70 Cyanic acid, HOCN, and isocyanic acid, HNCO, dissolve in water to yield the same anion on loss of H^+.

(a) Write a Lewis structure for cyanic acid.

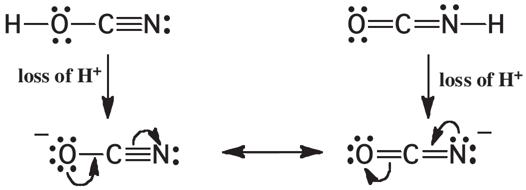


(b) Write a Lewis structure for isocyanic acid.



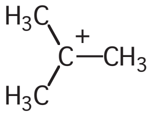
(c) Account for the fact that each acid gives the same anion on loss of H^+.

Loss of an H^+ from the two different acids gives the same anion that can best be described by drawing the following two contributing structures.



Looking Ahead

Problem 1.71 In Chapter 6, we study a group of organic cations called carbocations. Following is the structure of one such carbocation, the *tert*-butyl cation.



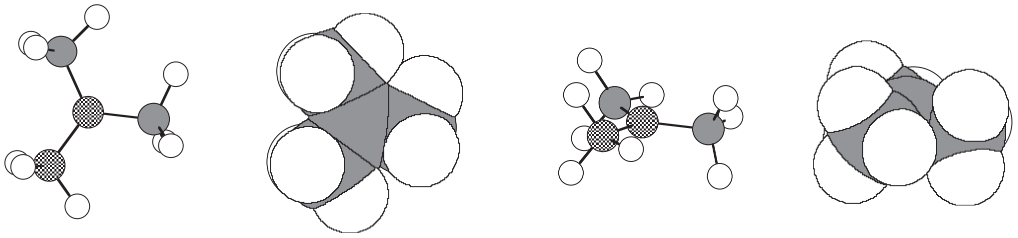
tert-Butyl cation

(a) How many electrons are in the valence shell of the carbon bearing the positive charge?

There are six valence shell electrons on the carbon atom bearing the positive charge, two contained in each of the three single bonds.

(b) Using VSEPR predict the bond angles about this carbon.

According to VSEPR, there are three regions of electron density around the central carbon atom, so you should predict a trigonal planar geometry and C-C-C bond angles of 120°.



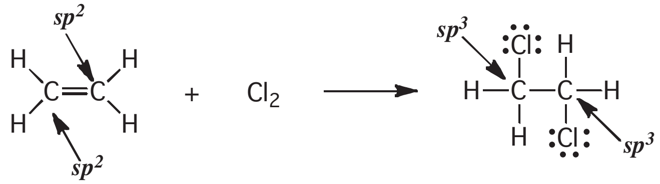
Top view **Side view**

(c) Given the bond angle you predicted in (b), what hybridization do you predict for this carbon?

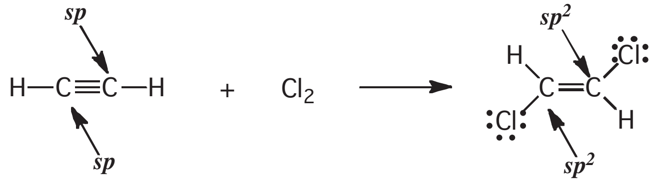
Given the trigonal planar geometry predicted in (b), so you should predict *sp*^{2} hybridization of this carbon atom.

Problem 1.72 Many reactions involve a change in hybridization of one or more atoms in the starting material. In each reaction, identify the atoms in the organic starting material that change hybridization and indicate the change. We examine these reactions in more detail later in the course.

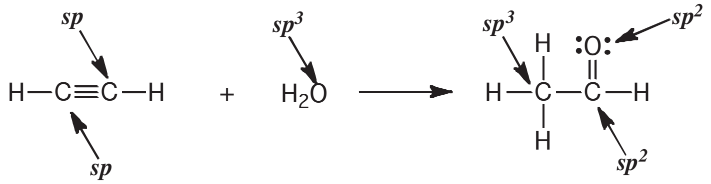
(a)



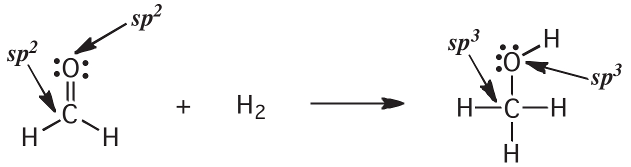
(b)



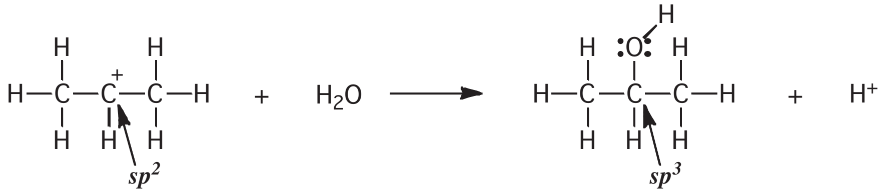
(c)



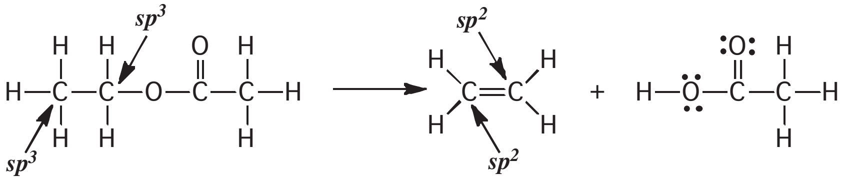
(d)



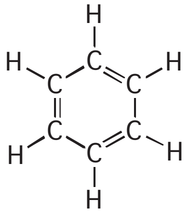
(e)



(f)



Problem 1.73 Following is a structural formula of benzene, C_6H_6, which we study in Chapter 21



(a) Using VSEPR, predict each H-C-C and C-C-C bond angle in benzene.

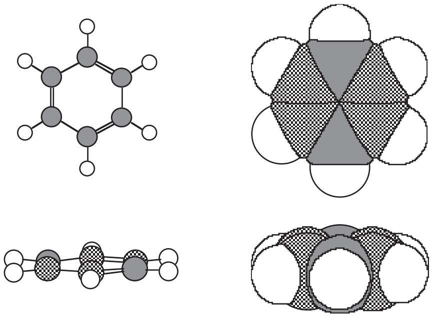
Each carbon atom in benzene has three regions of electron density around it, so according to VSEPR, the carbon atoms are trigonal planar. You should predict each H-C-C bond angle to be 120° and each C-C-C bond angle to be 120°.

(b) State the hybridization of each carbon atom in benzene.

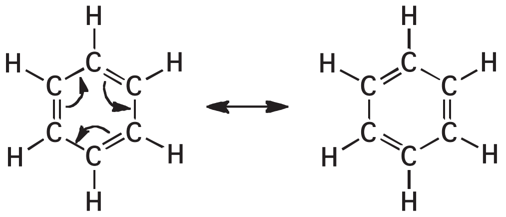
Each carbon atom is *sp*^{2} hybridized because each one makes three σ bonds and one π bond.

(c) Predict the shape of a benzene molecule.

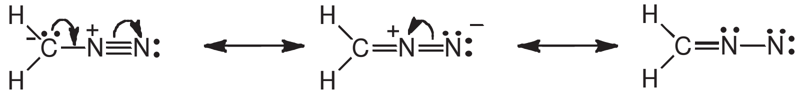
Because all of the carbon atoms in the ring are *sp*^{2} hybridized and thus trigonal planar, predict carbon atoms in benzene to form a flat hexagon in shape, with the hydrogen atoms in the same plane as the carbon atoms.



(d) Draw important resonance contributing structures.



Problem 1.74 Following are three contributing structures for diazomethane, CH_2N_2. This molecule is used to make methyl esters from carboxylic acids (Section 17.7C).



(a) Using curved arrows, show how each contributing structure is converted to the one on its right.

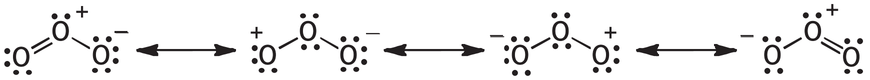
The arrows are indicated on the above structures.

(b) Which contributing structure makes the largest contribution to the hybrid?

The middle and left structures have filled valence shells, so these will make a larger contribution to the hybrid than the structure on the right, in which the terminal nitrogen atom has an unfilled valence shell. The structure in the middle has the negative charge on the more electronegative atom, N, compared with the structure on the left (negative charge on C), so the structure in the middle will make the largest contribution to the resonance hybrid.

Problem 1.75 Draw a Lewis structure for the ozone molecule, O_3. (The order of atom attachment is O-O-O and they do not form a ring). How does the resonance model account for the fact that the length of each O-O bond in ozone (128 pm) is shorter than the O-O single bond in hydrogen peroxide (HOOH 147 pm), but longer than the O-O double bond in the oxygen molecule (123 pm).

It is not possible to draw a single Lewis structure that adequately describes the ozone molecule. Rather, it is better to draw ozone as a hybrid of four contributing structures, each with a separation of charges.



Taken together, the four contributing structures present a symmetric picture of the bonding in which each O-O bond is intermediate between a single bond and a double bond. Recall that bonds become shorter as bond order increases. As a result, the bonds in ozone are shorter than the single O-O bond in HOOH, but longer than the O=O double bond in the oxygen molecule.

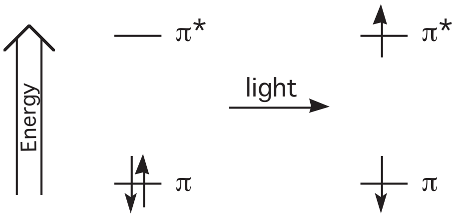
Molecular Orbitals

Problem 1.76 The following two compounds are isomers; that is, they are different compounds with the same molecular formula. We discuss this type of isomerism in Chapter 5.

(a) Why are these different molecules that do not interconvert?

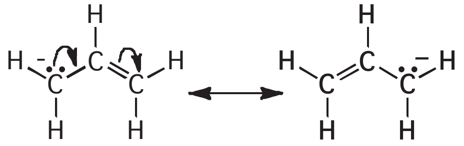
Interconversion of the two isomers involves rotation about the carbon-carbon double bond. This cannot occur without breaking the π bond. The π bond is strong enough so that this does not happen spontaneously at room temperature and the isomers do not interconvert.

(b) Absorption of light by a double bond in a molecule excites one electron from a π molecular orbital to a π* molecular orbital. Explain how this absorption can lead to interconversion of the two isomers.



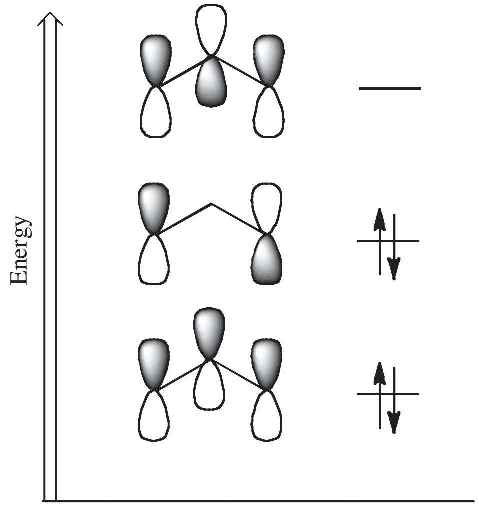
Putting electron density into an antibonding (*) orbital of a bond weakens that bond. Excitation of the electron from the π bond to the π* orbital upon absorption of light weakens the π bond, allowing the molecule to rotate about the carbon-carbon bond. This rotation interconverts the two isomers. A similar alkene rotation reaction is responsible for the mammalian photoreceptor molecules that allow us to see visible light.

Problem 1.77 In future chapters we will encounter carbanions-ions in which a carbon atom has three bonds and a lone pair of electrons and bears a negative charge. Draw another contributing structure for the allyl anion. Now using cartoon representations, draw the three orbitals that represent the delocalized π system (look at Figure 1.26 for a hint). Which of the three orbitals are populated with electrons?



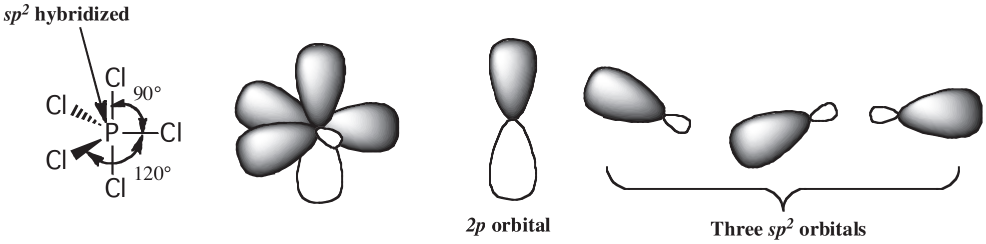
Allyl anion

Below is drawn a cartoon representation of the allyl anion π molecular orbitals.



The lowest two molecular orbitals are filled with a pair of electrons each. Notice that filling of the middle orbital, with lobes on only the two terminal carbon atoms, indicates the negative charge will be found on these two atoms consistent with the contributing structures.

Problem 1.78 Describe the bonding in PCl_5 without using *d* orbitals. As a hint, the geometry of PCl_5 is as shown:



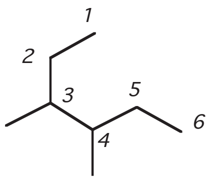
Based on the bond angles, the bonding in PCl_5 can be explained if the P atom is *sp*^{2} hybridized. The three *sp*^{2} hybridized orbitals would overlap with Cl orbitals to form the three "equatorial" σ bonds spaced at 120°, while the unhybridized *2p* orbital would overlap with Cl orbitals to form the two "axial" σ bonds.

Gray reef shark *Carcharhinus ambylrhynchos*
Rangiroa, French Polynesia

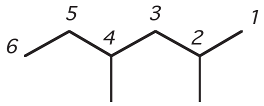
CHAPTER 2
Solutions to the Problems

Problem 2.1 Do the line-angle formulas in each pair represent the same compound or constitutional isomers.

(a)

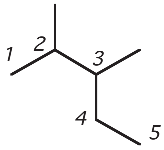


and

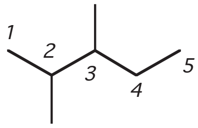


These molecules are constitutional isomers. Each has six carbons in the longest chain. The first has one-carbon branches on carbons 3 and 4 of the chain; the second has one-carbon branches on carbons 2 and 4 of the chain.

(b)

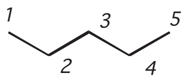


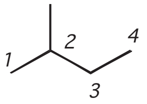
and

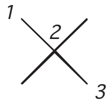


These molecules are identical. Each has five carbons in the longest chain, and one-carbon branches on carbons 2 and 3 of the chain.

Problem 2.2 Draw line-angle formulas for the three constitutional isomers with the molecular formula C_5H_{12}.

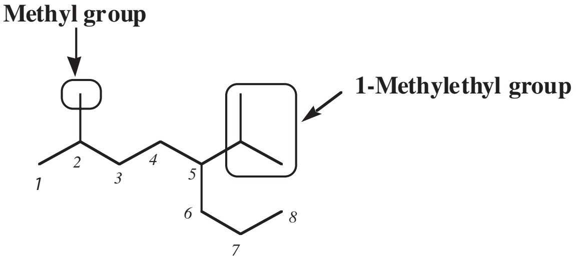


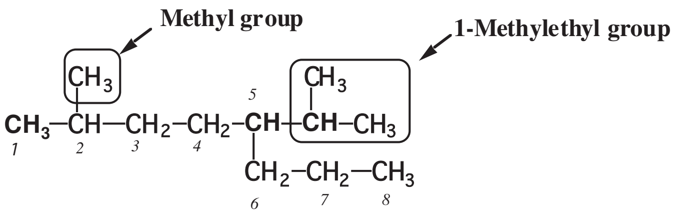




Problem 2.3 Write IUPAC names for these alkanes.

(a)

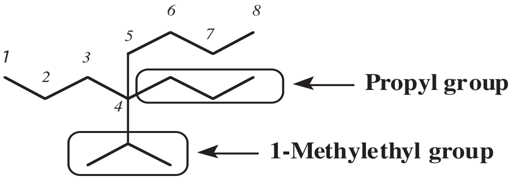


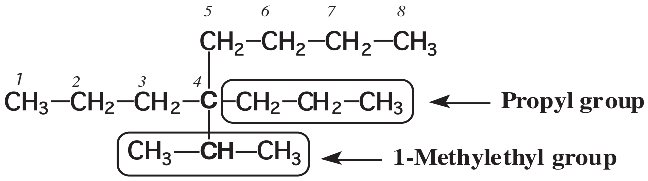


$$CH_3-\overset{\boxed{CH_3}}{\overset{|}{CH}}-CH_2-CH_2-\underset{\underset{CH_2-CH_2-CH_3}{|}}{\overset{}{CH}}-\boxed{\overset{CH_3}{\overset{|}{CH}}-CH_3}$$

2-Methyl-5-(1-methylethyl)octane

(b)

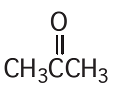




4-(1-Methylethyl)-4-propyloctane

Problem 2.4 Combine the proper prefix, infix, and suffix and write the IUPAC name for each compound.

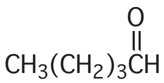
(a)



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

Propanone

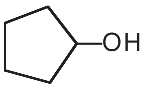
(b)



$CH_3(CH_2)_3\overset{\overset{O}{\|}}{C}H$

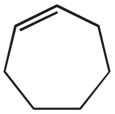
Pentanal

(c)



Cyclopentanol

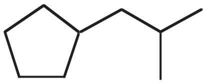
(d)



Cycloheptene

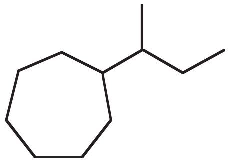
Problem 2.5 Write the molecular formula, IUPAC name, and common name for each cycloalkane.

(a)



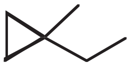
Molecular Formula C_9H_{18}
(2-Methylpropyl)cyclopentane (IUPAC)
Isobutylcyclopentane (Common)

(b)



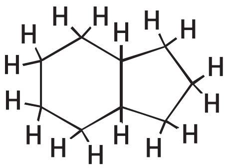
Molecular Formula $C_{11}H_{22}$
(1-Methylpropyl)cycloheptane (IUPAC)
***sec*-Butylcycloheptane (Common)**

(c)

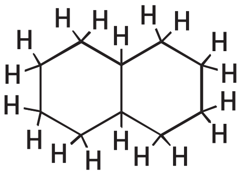


Molecular Formula C_6H_{12}
1-Ethyl-1-methylcyclopropane (IUPAC and Common)

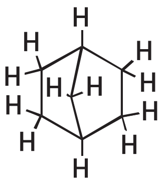
Problem 2.6 Write molecular formulas for each bicycloalkane, given its number of carbon atoms.
(a) Hydrindane (9 carbons) (b) Decalin (10 carbons) (c) Norbornane (7 carbons)



Hydrindane
Molecular Formula C_9H_{16}



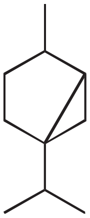
Decalin
Molecular Formula $C_{10}H_{18}$



Norbornane
Molecular Formula C_7H_{12}

Problem 2.7 Following are the structural formulas and names of four bicycloalkanes. Write the molecular formula of each compound. Which of these compounds are constitutional isomers?

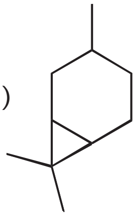
(a)



Thujane

Molecular formula $C_{10}H_{18}$

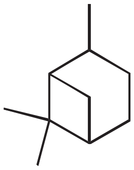
(b)



Carane

Molecular formula $C_{10}H_{18}$

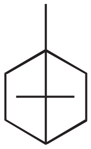
(c)



Pinane

Molecular formula $C_{10}H_{18}$

(d)

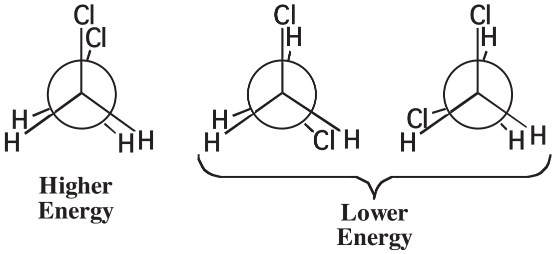


Bornane

Molecular formula $C_{10}H_{18}$

As shown by comparing molecular formulas, the first three bicycloalkanes are constitutional isomers.

Problem 2.8 For 1,2-dichloroethane,
(a) Draw Newman projections for all eclipsed conformations formed by rotation from 0° to 360° about the carbon-carbon single bond.



(b) Which eclipsed conformation(s) has (have) the lowest energy? Which has (have) the highest energy?

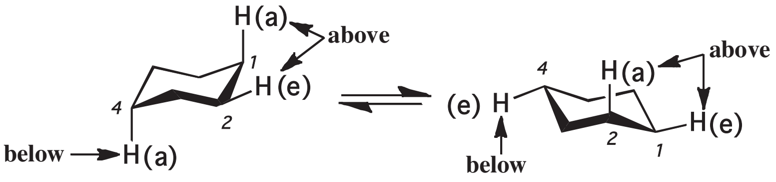
The chlorine atoms are the largest by far. As a result, when the chlorine atoms are eclipsed with each other (structure on the left), their steric interaction causes the higher overall energy.

(c) Which, if any, of these eclipsed conformations are related by reflection?

The two lower energy conformations (structures on the right) are related by reflection as they represent "mirror images" of each other.

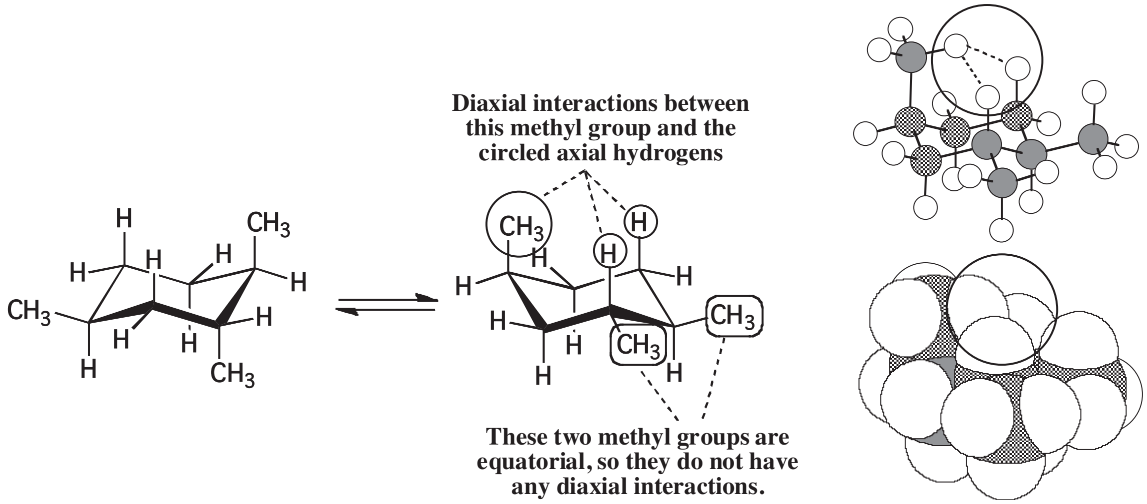
Problem 2.9 Following is a chair conformation of cyclohexane with the carbon atoms numbered 1 through 6.

(a) Draw hydrogen atoms that are above the plane of the ring on carbons 1, 2 and below the plane of the ring on carbon 4.
(b) Which of these hydrogens are equatorial? Which are axial?
(c) Draw the alternative chair conformation. Which hydrogens are equatorial? Which are axial? Which are above the plane of the ring? Which are below it?



In the above figure (a) = axial and (e) = equatorial.

Problem 2.10 Draw the alternative chair conformation for the trisubstituted cyclohexane given in Example 2.10. Label all CH_3/H 1,3-diaxial interactions in this chair conformation.

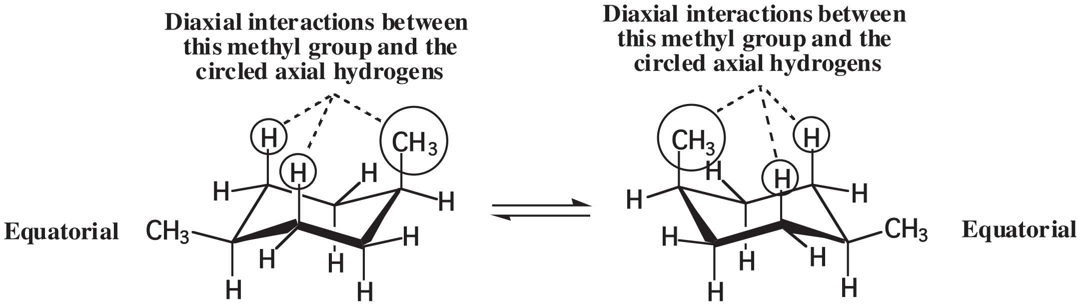


Diaxial interactions between this methyl group and the circled axial hydrogens

These two methyl groups are equatorial, so they do not have any diaxial interactions.

Note how in the above equilibrium, the new chair conformation (on the right) is the more stable due to having fewer diaxial interactions (See Problem 2.13)

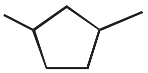
Problem 2.11 Draw a chair conformation of 1,4-dimethylcyclohexane in which one methyl group is equatorial and the other is axial. Draw the alternative chair conformation and calculate the ratio of the two conformations at 25° C.

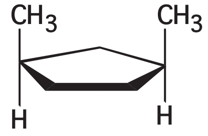


Each chair conformation has diaxial interactions between the circled axial methyl group and circled axial hydrogen atoms. Because each chair has the same number of diaxial interactions, they are of the same energy. The ratio of these two conformations must therefore be 1:1.

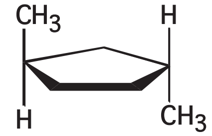
Problem 2.12 Which cycloalkanes show *cis, trans* isomerism? For each that does, draw both isomers.

(a)





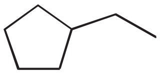
***cis*-1,3-Dimethyl-cyclopentane**



***trans*-1,3-Dimethyl-cyclopentane**

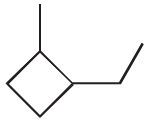
1,3-Dimethylcyclopentane shows *cis, trans* isomerism. Here, the ring is drawn as a planar pentagon with substituents above and below the plane of the pentagon.

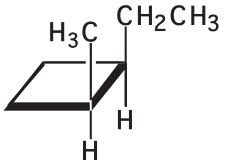
(b)



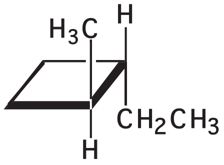
Ethylcyclopentane does not show *cis, trans* isomerism.

(c)





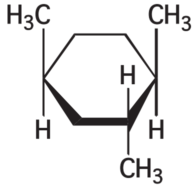
***cis*-1-Ethyl-2-methyl-cyclobutane**



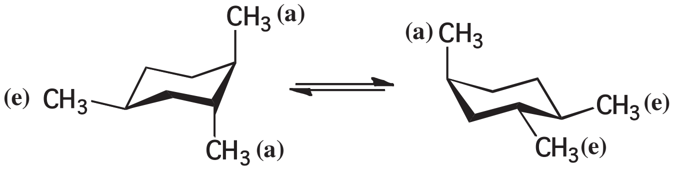
***trans*-1-Ethyl-2-methyl-cyclobutane**

1-Ethyl-2-methylcyclobutane shows *cis, trans* isomerism.

Problem 2.13 Following is a planar hexagon representation for one isomer of 1,2,4-trimethylcyclohexane. Draw the alternative chair conformations of this compound, and state which of the two is the more stable.



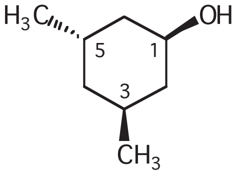
Following are alternative chair conformations for this isomer of 1,2,4-trimethylcyclohexane. The alternative chair conformation on the right is the more stable because it has only one axial methyl group.

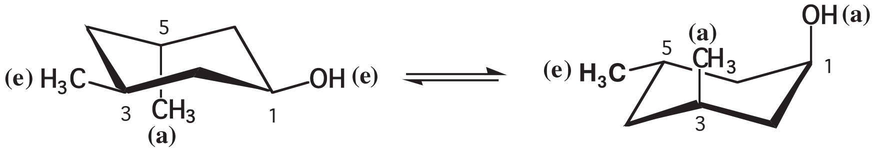


less stable chair
(two methyl groups axial)

more stable chair
(one methyl group axial,
one gauche interaction)

Problem 2.14 Here is one *cis, trans* isomer of 3,5-dimethylcyclohexanol. Complete the alternative chair conformations.





More stable

Problem 2.15 Arrange the alkanes in each set in order of increasing boiling point.

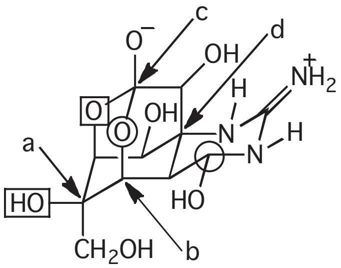
(a) 2-Methylbutane, 2,2-dimethylpropane, and pentane

2,2-Dimethylpropane	**2-Methylbutane**	**Pentane**
(bp 9.5°C)	**(bp 29°C)**	**(bp 36°C)**

(b) 3,3-Dimethylheptane, 2,2,4-trimethylhexane, and nonane

2,2,4-Trimethylhexane	**3,3-Dimethylheptane**	**Nonane**
(bp 130°C)	**(bp 138°C)**	**(bp 151°C)**

MCAT Practice: Questions
Tetrodotoxin



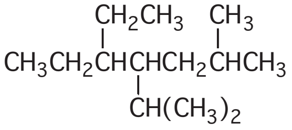
Tetrodotoxin

A) What are the relationships of the boxed atoms and the circled atoms?
   1. The boxed atoms are *trans* and the circled atoms are *cis*.
   2. The boxed atoms are *cis* and the circled atoms are *trans*.
   3. Both sets of atoms are *cis*.
   4. Both sets of atoms are *trans*.

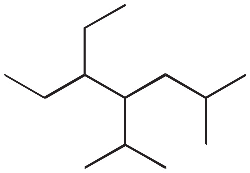
B) To what kinds of carbons, 1°, 2°, 3°, or 4°, do the arrows a, b, c and d, point?
   1. They are all tertiary.
   2. Carbons a and c are tertiary, while b and d are secondary.
   3. Carbon b is secondary, while carbons a, b and c are tertiary.
   4. Carbon c is primary, carbon b is secondary, and carbons a and d are tertiary. This is based on the number of bonds to other carbons. Bonds to atoms like O and N do not count.

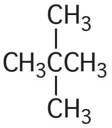
C) What is the hybridization of the nitrogens within the ring on the right and the nitrogen protruding from the ring?
   1. The nitrogens within the ring are sp^3 while the other nitrogen is sp^2.
   2. They are all sp^3.
   3. They are all sp^2. This is a delocalized pi system and there are contributing structures that explain the sp^2 hybridization.

Problem 2.16 Write a line-angle formula for each condensed structural formula.

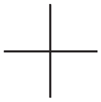
(a) 

$CH_3CH_2\overset{CH_2CH_3}{CH}\underset{CH(CH_3)_2}{CH}CH_2\overset{CH_3}{CH}CH_3$

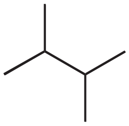


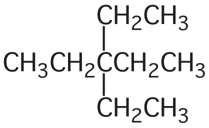
(b) 

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

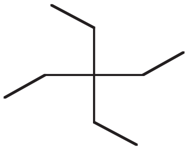


(c) $(CH_3)_2CHCH(CH_3)_2$

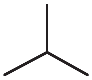


(d) 

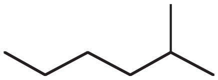
$CH_3CH_2\overset{CH_2CH_3}{\underset{CH_2CH_3}{C}}CH_2CH_3$



(e) $(CH_3)_3CH$

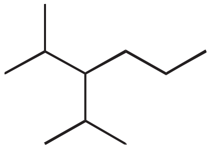


(f) $CH_3(CH_2)_3CH(CH_3)_2$



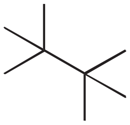
Problem 2.17 Write the molecular formula of each alkane.

(a)



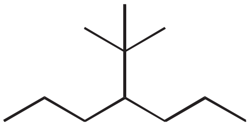
$C_{10}H_{22}$

(b)



C_8H_{18}

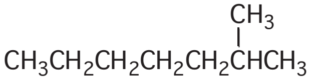
(c)



$C_{11}H_{24}$

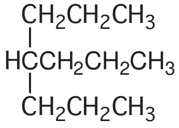
Problem 2.18 Using parentheses and subscripts, provide an even more abbreviated formula for each structural formula.

(a)



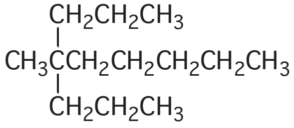
$$CH_3CH_2CH_2CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_3$$

(b)



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

(c)



$$CH_3\overset{CH_2CH_2CH_3}{\underset{CH_2CH_2CH_3}{\overset{|}{\underset{|}{C}}}}CH_2CH_2CH_2CH_2CH_3$$

$CH_3(CH_2)_4CH(CH_3)_2$ $HC(CH_2CH_2CH_3)_3$ $CH_3C(CH_2CH_2CH_3)_2(CH_2)_4CH_3$

Constitutional Isomerism

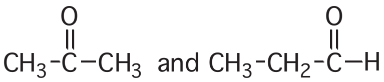
Problem 2.19 Which statements are true about constitutional isomers?
(a) They have the same molecular formula.
(b) They have the same molecular weight.
(c) They have the same order of attachment of atoms.
(d) They have the same physical properties.

Statements (a) and (b) are true, statements (c) and (d) are false.

Problem 2.20 Indicate whether the compounds in each set are constitutional isomers.

(a) $CH_3\text{-}CH_2\text{-}OH$ and $CH_3\text{-}O\text{-}CH_3$

(b)

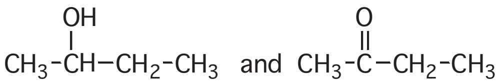


$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \text{ and } CH_3\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}H$$

(c)

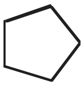
$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_3 \text{ and } CH_3\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH$$

(d)



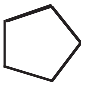
$$CH_3\text{-}\overset{OH}{\overset{|}{C}}H\text{-}CH_2\text{-}CH_3 \text{ and } CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}CH_3$$

(e)



and $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$

(f)

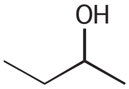


and $CH_2\text{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH_3$

Sets (a), (b), (c), and (f) are constitutional isomers; sets (d) and (e) are not.

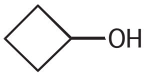
Problem 2.21 Each member of the following set of compounds is an alcohol; that is, each contains an -OH (hydroxyl group, Section 1.3A). Which line angle formulas represent the same compound? Which represent constitutional isomers?

(a)



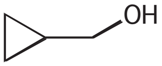
$C_4H_{10}O$

(b)



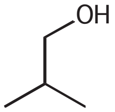
C_4H_8O

(c)



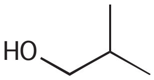
C_4H_8O

(d)



$C_4H_{10}O$

(e)

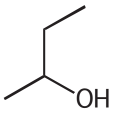


$C_4H_{10}O$

(f)

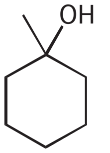
$C_4H_{10}O$

(g)



$C_4H_{10}O$

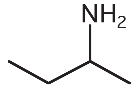
(h)

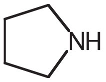


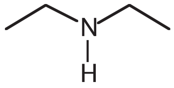
$C_7H_{14}O$

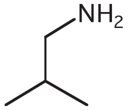
Structural formulas (d) and (e) are the same structural formula, and structural formulas (a) and (g) are also the same structural formula. Constitutional isomers have the same molecular formula but different connectivities between atoms. Structural formulas (a)/(g), (d)/(e) and (f) are constitutional isomers. Structural formulas (b) and (c) represent another set of constitutional isomers.

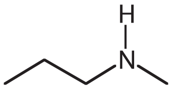
Problem 2.22 Each of the following compounds is an amine (Section 1.3B). Which structural formulas represent the same compound? Which represent constitutional isomers?

(a)

$C_4H_{11}N$

(b)

C_4H_9N

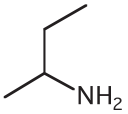
(c)

$C_4H_{11}N$

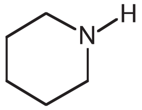
(d)

$C_4H_{11}N$

(e)

$C_4H_{11}N$

(f)

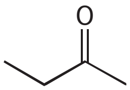
$C_4H_{11}N$

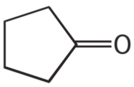
(g)

$C_4H_{11}N$

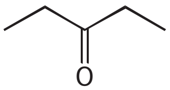
(h)

$C_5H_{11}N$

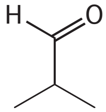
Structural formulas (a) and (g) represent the same structural formula. Constitutional isomers have the same molecular formula but different connectivities between atoms. Structural formulas (a)/(g), (c), (d), (e), and (f) are constitutional isomers.

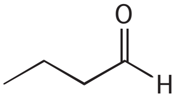
Problem 2.23 Each of the following compounds is either an aldehyde or a ketone (Section 1.3C). Which line-angle formulas represent the same compound? Which represent constitutional isomers?

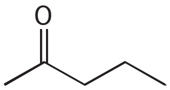
(a)

C_4H_8O

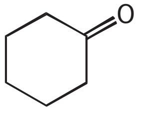
(b)

C_5H_8O

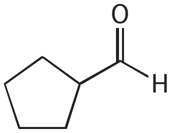
(c)

$C_5H_{10}O$

(d)

C_4H_8O

(e)

C_4H_8O

(f)

$C_5H_{10}O$

(g)

$C_6H_{10}O$

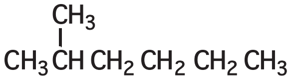
(h)

$C_6H_{10}O$

All of these molecules are different. Constitutional isomers have the same molecular formula but different connectivities between atoms. Compounds (a), (d), and (e) are constitutional isomers. Compounds (c) and (f) represent another set of constitutional isomers. A third set of constitutional isomers is composed of (g) and (h).

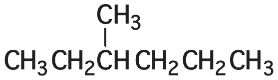
Problem 2.24 Draw structural formulas, and write IUPAC names for the nine constitutional isomers with the molecular formula C_7H_{16}.

$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$

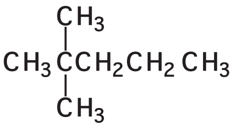
Heptane
(bp 94.8°C)


$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_2CH_3$

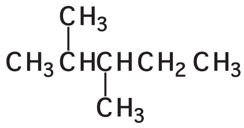
2-Methylhexane
(bp 90.0°C)


$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_3$

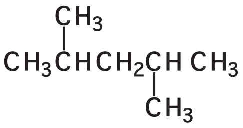
3-Methylhexane
(bp 92.0°C)


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

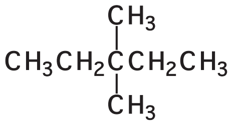
2,2-Dimethylpentane
(bp 79.2°C)


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

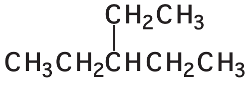
2,3-Dimethylpentane
(bp 89.8°C)


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

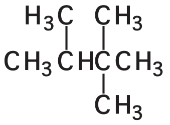
2,4-Dimethylpentane
(bp 80.5°C)


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

3,3-Dimethylpentane
(bp 86.1°C)


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

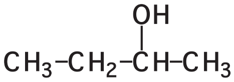
3-Ethylpentane
(bp 93.5°C)

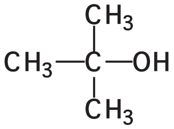

$CH_3\overset{\overset{H_3C}{|}}{C}H\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_3$

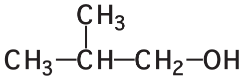
2,2,3-Trimethylbutane
(bp 80.9°C)

Problem 2.25 Draw structural formulas for all of the following.
(a) Alcohols with the molecular formula $C_4H_{10}O$.

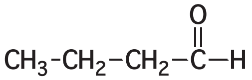
$CH_3-CH_2-CH_2-CH_2-OH$

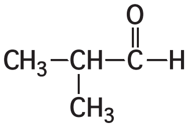

$CH_3-CH_2-\overset{OH}{\overset{|}{C}}H-CH_3$


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

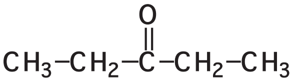

$CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-OH$

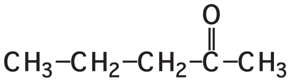
(b) Aldehydes with the molecular formula C_4H_8O.

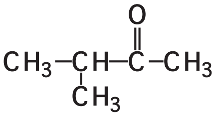

$CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}-H$


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

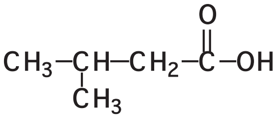
(c) Ketones with the molecular formula $C_5H_{10}O$.

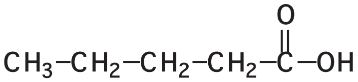

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

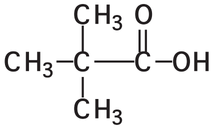

$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

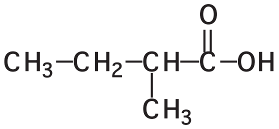

$CH_3-\underset{CH_3}{\underset{|}{C}}H-\overset{O}{\overset{\|}{C}}-CH_3$

(d) Carboxylic acids with the molecular formula $C_5H_{10}O_2$.


$CH_3-\underset{CH_3}{\underset{|}{C}}H-CH_2-\overset{O}{\overset{\|}{C}}-OH$


$CH_3-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$

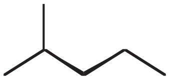

$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-OH$


$CH_3-CH_2-\underset{CH_3}{\underset{|}{C}}H-\overset{O}{\overset{\|}{C}}-OH$

Nomenclature of Alkanes and Cycloalkanes

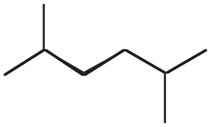
Problem 2.26 Write IUPAC names for these alkanes and cycloalkanes.

(a)



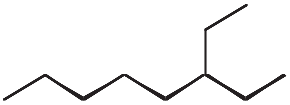
2-Methylpentane

(b)



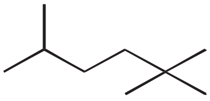
2,5-Dimethylhexane

(c)



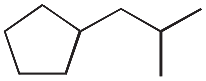
3-Ethyloctane

(d)



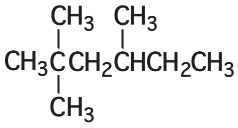
2,2,5-Trimethylhexane

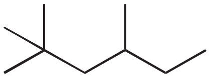
(e)



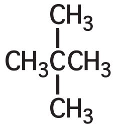
(2-Methylpropyl)cyclopentane

Problem 2.27 Write structural formulas and line-angle formulas for the following alkanes and cycloalkanes.
(a) 2,2,4-Trimethylhexane

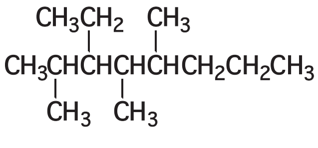

$CH_3\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$

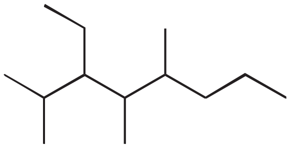


(b) 2,2-Dimethylpropane

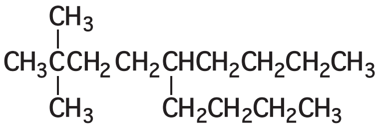

$CH_3\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_3$

(c) 3-Ethyl-2,4,5-trimethyloctane

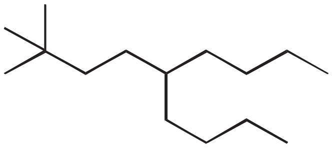

$CH_3\underset{CH_3}{\underset{|}{C}}H\overset{CH_3CH_2}{\overset{|}{C}}H\underset{CH_3}{\underset{|}{C}}H\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_3$



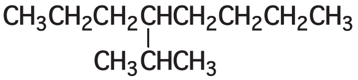
(d) 5-Butyl-2,2-dimethylnonane



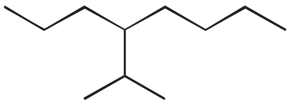
$$\mathrm{CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_2CH_2\underset{\displaystyle CH_2CH_2CH_2CH_3}{CH}CH_2CH_2CH_2CH_3}$$



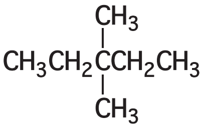
(e) 4-(1-Methylethyl)octane



$$\mathrm{CH_3CH_2CH_2\underset{\displaystyle CH_3CHCH_3}{CH}CH_2CH_2CH_2CH_3}$$

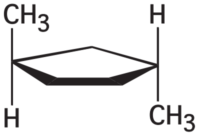


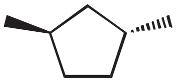
(f) 3,3-Dimethylpentane



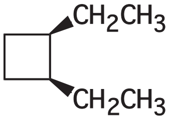
$$\mathrm{CH_3CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_2CH_3}$$

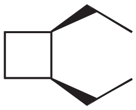
(g) *trans*-1,3-Dimethylcyclopentane





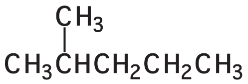
(h) *cis*-1,2-Diethylcyclobutane





Problem 2.28 Explain why each is an incorrect IUPAC name, and write the correct IUPAC name for the intended compound.

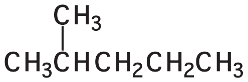
(a) 1,3-Dimethylbutane



$$\mathrm{CH_3\overset{\displaystyle CH_3}{C}HCH_2CH_2CH_3}$$

The longest chain is pentane.
Its IUPAC name is 2-methylpentane.

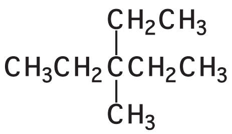
(b) 4-Methylpentane



$$\mathrm{CH_3\overset{\displaystyle CH_3}{C}HCH_2CH_2CH_3}$$

The pentane is numbered incorrectly.
Its IUPAC name is 2-methylpentane.

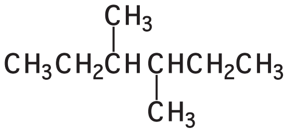
(c) 2,2-Diethylbutane



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

The longest chain is pentane.
Its IUPAC name is 3-ethyl-3-methylpentane.

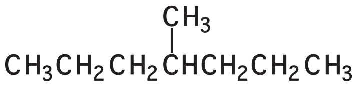
(d) 2-Ethyl-3-methylpentane



$$\mathrm{CH_3CH_2\overset{\displaystyle CH_3}{C}H\,\underset{\displaystyle CH_3}{C}HCH_2CH_3}$$

The longest chain is hexane.
Its IUPAC name is 3,4-dimethylhexane.

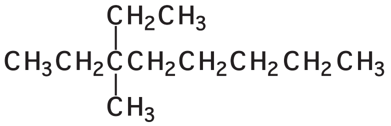
(e) 2-Propylpentane



$$\mathrm{CH_3CH_2CH_2\overset{\displaystyle CH_3}{C}HCH_2CH_2CH_3}$$

The longest chain is heptane.
Its IUPAC name is 4-methylheptane.

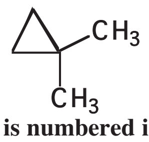
(f) 2,2-Diethylheptane



$$\mathrm{CH_3CH_2\overset{\displaystyle CH_2CH_3}{\underset{\displaystyle CH_3}{C}}CH_2CH_2CH_2CH_2CH_3}$$

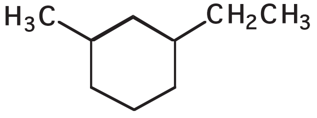
The longest chain is octane.
Its IUPAC name is 3-ethyl-3-methyloctane.

(g) 2,2-Dimethylcyclopropane



The ring is numbered incorrectly.
Its IUPAC name is 1,1-dimethylcyclopropane.

(h) 1-Ethyl-5-methylcyclohexane

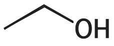


The ring is numbered incorrectly.
Its IUPAC name is 1-ethyl-3-methylcyclohexane.

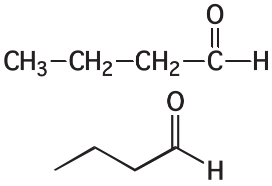
Problem 2.29 For each IUPAC name, draw the corresponding structural formula and line-angle formula.

(a) Ethanol

CH_3-CH_2-OH

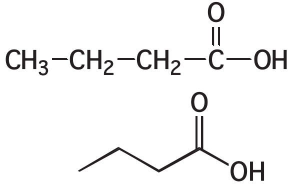


(b) Butanal



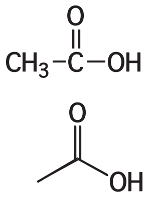
$$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$$

(c) Butanoic acid



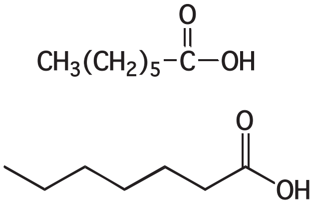
$$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

(d) Ethanoic acid



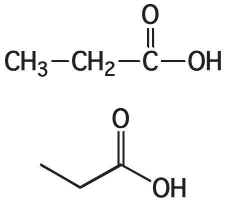
$$CH_3-\overset{O}{\overset{\|}{C}}-OH$$

(e) Heptanoic acid



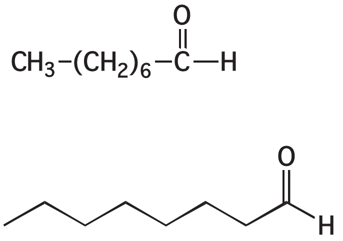
$$CH_3(CH_2)_5-\overset{O}{\overset{\|}{C}}-OH$$

(f) Propanoic acid



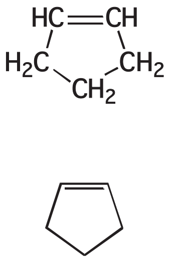
$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

(g) Octanal

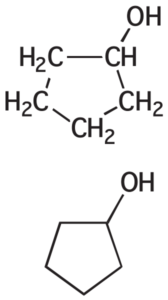


$$CH_3-(CH_2)_6-\overset{O}{\overset{\|}{C}}-H$$

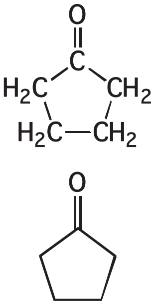
(h) Cyclopentene



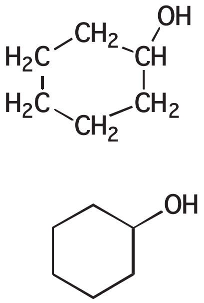
(i) Cyclopentanol



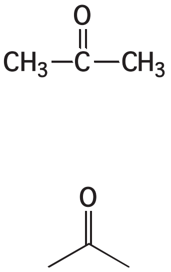
(j) Cyclopentanone



(k) Cyclohexanol

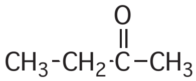


(l) Propanone



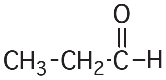
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

Problem 2.30 Write the IUPAC name for each compound.

(a) 

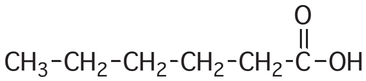
$$CH_3\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}-CH_3$$

Butanone

(b) 

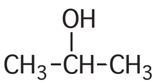
$$CH_3\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}-H$$

Propanal

(c) 

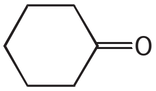
$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH$$

Hexanoic acid

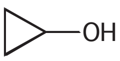
(d) 

$$CH_3\text{-}\overset{OH}{\overset{|}{C}H}\text{-}CH_3$$

2-Propanol

(e) 

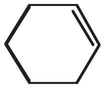
Cyclohexanone

(f) 

Cyclopropanol

(g) $CH_3-CH=CH_2$

Propene

(h) 

Cyclohexene

Problem 2.31 Assume for the purposes of this problem that, to be an alcohol (-ol) or an amine (-amine), the hydroxyl or amino group must be bonded to a tetrahedral (*sp*^{3} hybridized) carbon atom. Write the structural formula of a compound with an unbranched chain of four carbon atoms that is an:

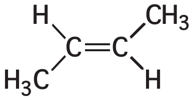
The IUPAC names are only provided for your reference. You do not yet know how to name all of these.

(a) Alkane

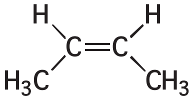
$CH_3-CH_2-CH_2-CH_3$

Butane

(b) Alkene



***trans*-2-Butene**



***cis*-2-Butene**

$CH_3-CH_2-CH=CH_2$

1-Butene

(c) Alkyne

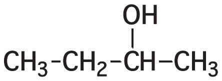
$CH_3-C\equiv C-CH_3$

2-Butyne

$CH_3-CH_2-C\equiv CH$

1-Butyne

(d) Alkanol



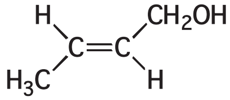
$CH_3-CH_2-CH(OH)-CH_3$

2-Butanol

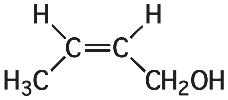
$CH_3-CH_2-CH_2-CH_2OH$

1-Butanol

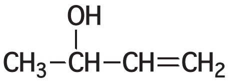
(e) Alkenol



***trans*-2-Buten-1-ol**



***cis*-2-Buten-1-ol**



$CH_3-CH(OH)-CH=CH_2$

3-Buten-2-ol

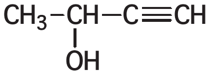
$HOCH_2-CH_2-CH=CH_2$

3-Buten-1-ol

(f) Alkynol

$CH_3-C\equiv C-CH_2OH$

2-Butyn-1-ol



$CH_3-CH(OH)-C\equiv CH$

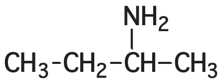
3-Butyn-2-ol

$HOCH_2-CH_2-C\equiv CH$

3-Butyn-1-ol

Note: you will learn later why the OH group cannot be bonded directly to a double bond or a triple bond.

(g) Alkanamine



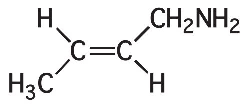
$CH_3-CH_2-\overset{NH_2}{\overset{|}{C}}H-CH_3$

2-Butanamine

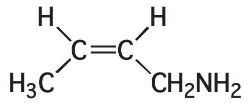
$CH_3-CH_2-CH_2-CH_2NH_2$

1-Butanamine

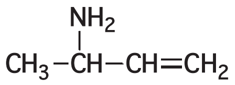
(h) Alkenamine



***trans*-2-Buten-1-amine**



***cis*-2-Buten-1-amine**



$CH_3-\overset{NH_2}{\overset{|}{C}}H-CH=CH_2$

3-Buten-2-amine

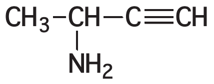
$H_2NCH_2-CH_2-CH=CH_2$

3-Buten-1-amine

(i) Alkynamine

$CH_3-C\equiv C-CH_2NH_2$

2-Butyn-1-amine



$CH_3-\underset{NH_2}{\underset{|}{C}}H-C\equiv CH$

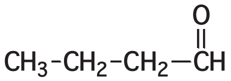
3-Butyn-2-amine

$H_2NCH_2-CH_2-C\equiv CH$

3-Butyn-1-amine

Note: you will learn later why the NH_2 group cannot be attached directly to a double bond or a triple bond.

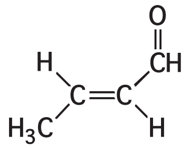
(j) Alkanal



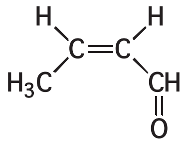
$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}H$

Butanal

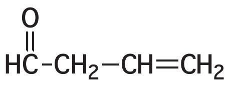
(k) Alkenal



***trans*-2-Butenal**



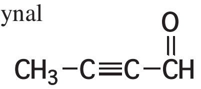
***cis*-2-Butenal**



$H\overset{O}{\overset{\|}{C}}-CH_2-CH=CH_2$

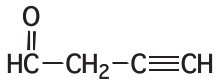
3-Butenal

(l) Alkynal



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

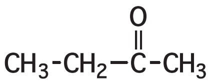
2-Butynal



$H\overset{O}{\overset{\|}{C}}-CH_2-C\equiv CH$

3-Butynal

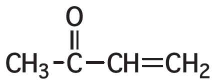
(m) Alkanone



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

Butanone

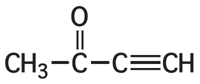
(n) Alkenone



$CH_3-\overset{O}{\overset{\|}{C}}-CH=CH_2$

3-Butenone

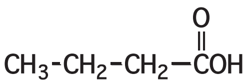
(o) Alkynone



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

3-Butynone

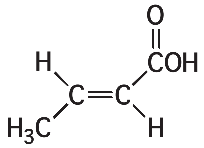
(p) Alkanoic acid



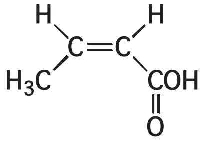
$CH_3{-}CH_2{-}CH_2{-}\overset{O}{\overset{\|}{C}}OH$

Butanoic acid

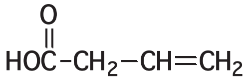
(q) Alkenoic acid



***trans*-2-Butenoic acid**



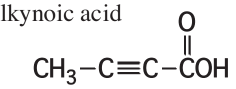
***cis*-2-Butenoic acid**



$HO\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH{=}CH_2$

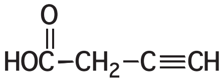
3-Butenoic acid

(r) Alkynoic acid



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

2-Butynoic acid



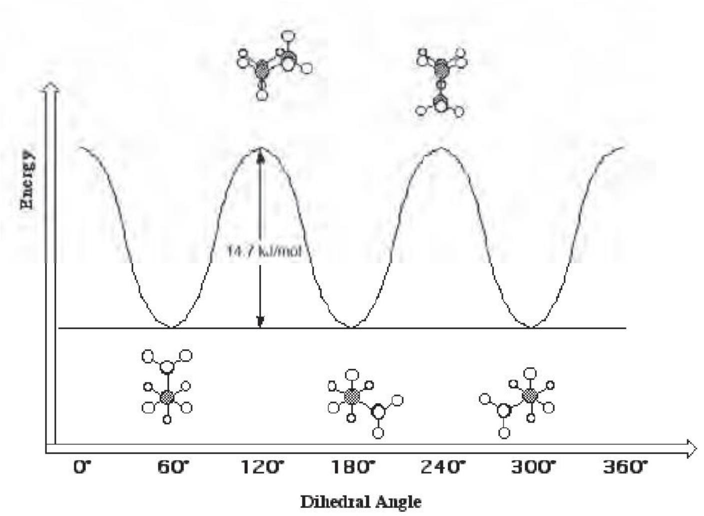
$HO\overset{O}{\overset{\|}{C}}{-}CH_2{-}C{\equiv}CH$

3-Butynoic acid

(*Note*: Only one structural formula is possible for some parts of this problem. For other parts, two or more structural formulas are possible. Where two are more are possible, we will deal with how the IUPAC system distinguishes between them when we come to the chapters on those particular functional groups.)

Conformations of Alkanes and Cycloalkanes

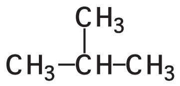
Problem 2.32 Torsional strain resulting from eclipsed C-H bonds is approximately 4.2 kJ (1.0 kcal)/mol, and that for eclipsed C-H and C-CH_3 bonds is approximately 6.3 kJ (1.5 kcal)/mol. Given this information, sketch a graph of energy versus dihedral angle for propane.



Notice that the energy of the eclipsed conformations is 14.7 kJ/mol higher in energy than the staggered conformations. This is because each eclipsed conformation has two C-H bonds eclipsed with other C-H bonds (worth 4.2 kJ/mol each) and one C-H bond eclipsed to a C-CH_3 bond (worth 6.3 kJ/mol).

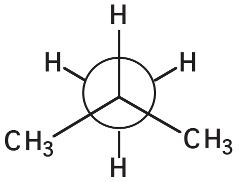
Problem 2.33 How many different staggered conformations are there for 2-methylpropane? How many different eclipsed conformations are there?

Looking down any of the carbon-carbon bonds, there is one staggered and one eclipsed conformation of 2-methylpropane.

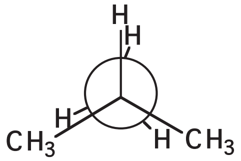


$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}H-CH_3$$

2-Methylpropane



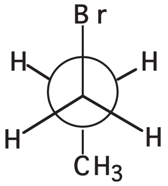
Staggered



Eclipsed

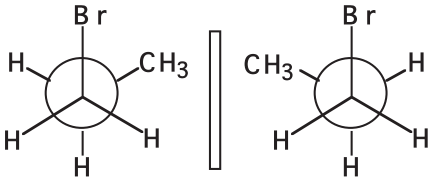
Problem 2.34 Consider 1-bromopropane, $CH_3CH_2CH_2Br$.

(a) Draw a Newman projection for the conformation in which -CH_3 and -Br are anti (dihedral angle 180°).



lowest in energy

(b) Draw Newman projections for the conformations in which -CH_3 and -Br are gauche (dihedral angles 60° and 300°).



related by reflection

(c) Which of these is the lowest energy conformation.

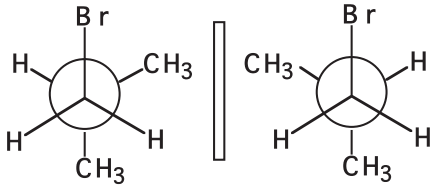
The anti (dihedral angle 180°) is the lowest energy conformation.

(d) Which of these conformations, if any, are related by reflection?

The two gauche conformations are of equal energy and are related by reflection.

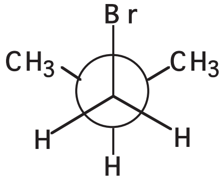
Problem 2.35 Consider 1-bromo-2-methylpropane and draw the following.

(a) The staggered conformation(s) of lowest energy.



lowest in energy
(related by reflection)

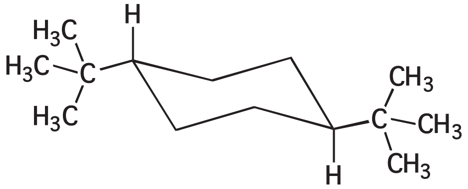
(b) The staggered conformation(s) of highest energy.



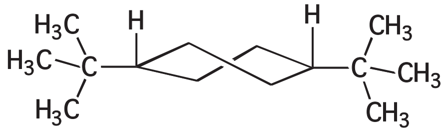
highest in energy

The lower energy staggered conformations have one methyl group anti (dihedral angle 180°) to the bromine and are related by reflection. The staggered conformation with methyl groups at dihedral angles of both 60° and 300° to the bromine have more nonbonded interaction strain and are thus higher in energy.

Problem 2.36 *Trans*-1,4-di-*tert*-butylcyclohexane exists in a normal chair conformation. *Cis*-1,4-di-*tert*-butylcyclohexane, however, adopts a twist-boat conformation. Draw both isomers and explain why the *cis* isomer is more stable in the twist-boat conformation.



The *trans* isomer in the chair form



The *cis* isomer in the twist-boat form

The *cis* isomer adopts a twist-boat conformation because each of the bulky *tert*-butyl groups can be in an pseudo-equatorial position. If the *cis* isomer existed in a normal chair conformation, then one *tert*-butyl group would be equatorial, while the other would be forced axial resulting in a large nonbonded interaction strain.

Problem 2.37 From studies of the dipole moment of 1,2-dichloroethane in the gas phase at room temperature (25°C), it is estimated that the ratio of molecules in the anti conformation to gauche conformation is 7.6 to 1. Calculate the difference in Gibbs free energy between these two conformations.

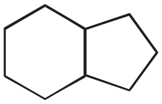
$$\Delta G^\circ = -RT\ln K_{eq}$$

$$K_{eq} = \frac{7.6}{1} = 7.6 \qquad \text{so } \ln K_{eq} = 2.0$$

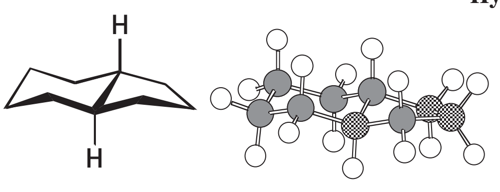
Plugging in the gas constant ($R = 8.314\ \mathrm{J{\bullet}K^{-1}{\bullet}mol^{-1}}$) and temperature ($T = 298\ \mathrm{K}$)

$$\Delta G^\circ = -\ (8.314\ \mathrm{J{\bullet}K^{-1}{\bullet}mol^{-1}})(298\ \mathrm{K})(2.0) = 5.0 \times 10^3\ \mathrm{J/mol} = \boxed{5.0\ \mathrm{kJ/mol}}$$

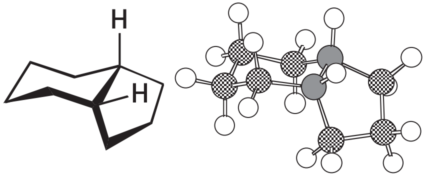
Problem 2.38 Draw structural formulas for the *cis* and *trans* isomers of hydrindane. Show each ring in its most stable conformation. Which of these isomers is the more stable?



Hydrindane



***trans*-Hydridane**



***cis*-Hydridane**

Shown above are the *trans* and *cis* isomers of hydrindane. Note that the *cis*-hydrindane displays some distortion from the ideal cyclohexane ring structure. The result is that the *trans*-hydrindane is the more stable.

Problem 2.39 Following are the alternative chair conformations for *trans*-1,2-dimethylcylohexane.

***trans*-1,2-Dimethylcyclohexane**

(a) Estimate the difference in free energy between these two conformations.

As described in Example 2.11, the difference in energy between a diaxial and diequatorial dimethyl cyclohexane conformation is 14.56 kJ (3.5 kcal)/mol. In the case of *trans*-1,2-dimethylcyclohexane, in the diequatorial conformation, there is also a gauche interaction between the two methyl groups that must be considered. Estimate the gauche interaction to be 3.8 kJ (0.91 kcal)/mol based on the gauche interaction in butane (Figure 2.9). This gauche interaction introduces a small amount of steric strain into the more stable diequatorial conformation reducing the absolute value of the total ΔG° as follows:

$$\Delta G^\circ = -14.56 \text{ kJ } (3.5 \text{ kcal})/\text{mol} + 3.8 \text{ kJ } (0.91 \text{ kcal})/\text{mol} = \boxed{-10.76 \text{ kJ } (2.59 \text{ kcal})/\text{mol}}$$

(b) Given your value in (a), calculate the percent of each chair present in an equilibrium mixture of the two at 25°C.

$$\Delta G^\circ = -RT\ln K_{eq}$$

Plugging in the gas constant ($R = 8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), temperature ($T = 298$ K) and value of ΔG° for the equilibrium (-10.76 kJ (2.59 kcal)/mol) gives the following

$$\ln K_{eq} = \frac{-(-10{,}760 \text{ J/mol})}{8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \times 298 \text{ K}} = 4.343$$

$$K_{eq} = \frac{76.9}{1} = \frac{\text{diequatorial}}{\text{diaxial}}$$

Based on this calculation, at equilibrium, there is 1.3% in the diaxial chair conformation, and 98.7% in the diequatorial chair conformation.

***Cis, trans* Isomerism in Cycloalkanes**

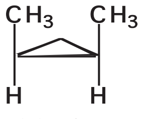
Problem 2.40 What structural feature of cycloalkanes makes *cis, trans* isomerism possible?

Because the atoms are connected in a ring, the C-C bonds cannot rotate around all 360°. As a result, groups on the ring have a fixed relationship with respect to each other, either *cis* or *trans*.

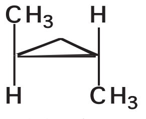
Problem 2.41 Is *cis, trans* isomerism possible in alkanes?

The C-C bonds in alkanes can rotate 360°, so *cis, trans* isomerism in not possible.

Problem 2.42 Draw structural formulas for the *cis* and *trans* isomers of 1,2-dimethylcyclopropane.



***cis*-1,2-Dimethyl-
cyclopropane**



***trans*-1,2-Dimethyl-
cyclopropane**