CHEM 22000 (Organic Chemistry I) Problem Sets

Steven Labalme

November 1, 2021

Contents

1	Bonding and Molecular Structure	1
2	Acidity and Conformers	6

1 Bonding and Molecular Structure

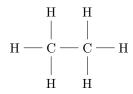
- 10/14: 1. Write a Lewis structure for each of the following compounds and indicate whether the bonding is nonpolar covalent, polar covalent, or ionic. Assume that a difference in electronegativity greater than 1.7 corresponds to a bond that is considered predominantly ionic.
 - (a) HCl.

Answer.

Polar covalent.

(b) C_2H_6 .

Answer.



Nonpolar covalent.

(c) NaBr.

Answer.

Ionic. \Box

(d) CH_3I .

Answer.



Nonpolar covalent. \Box

(e) H_2S .

Answer.

н —
$$\ddot{\mathbf{s}}$$
 — н

Nonpolar covalent.

(f) N_2H_4 .

Answer.

$$\mathbf{H} \longrightarrow \ddot{\mathbf{N}} \longrightarrow \ddot{\mathbf{N}} \longrightarrow \mathbf{H}$$

$$\begin{vmatrix} & & & \\ & & \\ & & \\ & & \\ & & \\ & & & \\ & & & \\ & & & \\ & & & \\$$

Polar covalent.

(g) CsF.

Answer.

Ionic. \Box

- 2. For the following covalent bonds...
 - (a) Use the symbols δ^+ and δ^- to indicate the direction of polarity (if any).
 - (i) C-F.

Answer.

$$^{\delta^+}\!\!\mathrm{C} -\!\!\!-\!\!\!-\!\!\!\!- \mathrm{F}^{\,\delta^-}$$

(ii) N-Br.

Answer. Nonpolar.

(iii) B-C.

Answer.

$$\delta^+$$
B — C^{δ^-}

(iv) Si-H.

Answer. Nonpolar.

- (b) Rank the following covalent bonds in order of *increasing* polarity.
 - (i) C-H, O-H, N-H.

Answer.

$$C-H < N-H < O-H$$

(ii) C-N, C-O, B-O.

Answer.

$$C-N < C-O < B-O$$

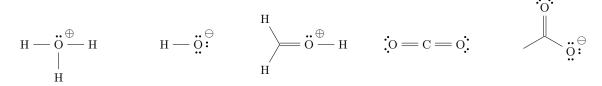
(iii) C-P, C-S, C-N.

Answer.

$$C-S < C-P < C-N$$

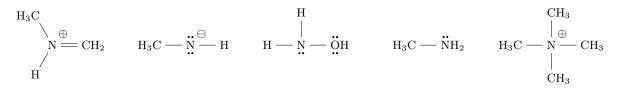
- 3. Formal charge.
 - (a) Consider the oxygen atom in the structures below and determine if it has a formal charge. If so, label it on the molecule.

Answer.



(b) Consider the nitrogen atom in the structures below and determine if it has a formal charge. If so, label it on the molecule.

Answer



4. Draw Lewis structures and resonance structures (if any) that satisfy the octet rule for each of the following ions with all valence electrons and formal charges clearly noted.

(a) NH_2^- .

Answer.

$$[H - \ddot{\ddot{\mathbf{n}}} - H]^{-}$$

(b) NO_2^- .

Answer.

$$[\dot{\ddot{0}} = \ddot{\ddot{N}} - \ddot{\ddot{0}}\dot{\ddot{0}}]^{-} \longleftrightarrow [\dot{\ddot{0}}\dot{\ddot{0}} - \ddot{\ddot{N}} = 0\dot{\ddot{0}}]^{-}$$

(c) ClO⁻.

Answer.

$$[:\ddot{\mathbf{C}}\mathbf{l}-\ddot{\mathbf{O}}:]^{-}$$

(d) HCOO⁻.

Answer.

$$\begin{bmatrix} H - C \\ \vdots \\ \vdots \\ \vdots \end{bmatrix}^{-} \longleftrightarrow \begin{bmatrix} H - C \\ \vdots \\ \vdots \\ \vdots \end{bmatrix}^{-}$$

(e) BH_4^- .

Answer.

$$\begin{bmatrix} H & \\ |_{\Theta} \\ H - B - H \end{bmatrix}^{-}$$

(f) $CH_3CH_2CO_2H$.

Answer.

 $(g) O_3.$

Answer.

$$\vdots \circ = \overset{\circ}{\circ} - \overset{\circ}{\circ} \vdots \longleftrightarrow \vdots \overset{\circ}{\circ} - \overset{\circ}{\circ} = \overset{\circ}{\circ} \vdots$$

(h) CH_2N_2 .

Answer.

$$\begin{array}{c} H \\ C = N = \stackrel{.}{N} \stackrel{\ominus}{=} \\ \vdots \\ \end{array}$$

5. For the following chemical species, draw a resonance structure that satisfies the octet rule. Indicate whether you expect it to be a major or minor contributor to the actual structure of the species and briefly state your reasoning. Use curved arrows to clearly show how the structure converts to another structure (if any).

$$(a) \qquad \longleftrightarrow \qquad$$

Answer.

The right structure will be a minor contributor because it has formal charges while the original one doesn't. $\hfill\Box$

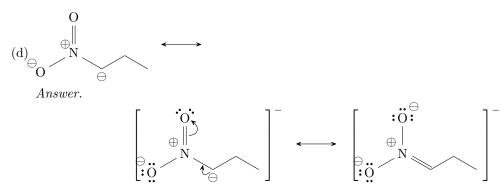
Answer.

The right structure will be a major contributor because the negative formal charge is on the more electronegative atom. \Box

Labalme 4

(c)
$$\bigcap_{N} \longleftrightarrow$$
 $Answer$.

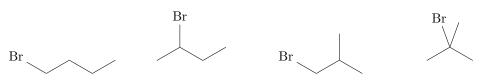
The right structure will be a major contributor because the negtive formal charge is on the more electronegative atom. \Box



The right structure will be a major contributor because the negative formal charges are on the more electronegative atoms. \Box

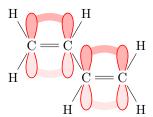
6. Draw all four constitutional isomers of C₄H₉Br using bond-line formulas.

Answer. \Box



- 7. For each of the following condensed structures: (i) draw the corresponding Lewis structures, (ii) provide the hybridization to all carbon atoms, and (iii) draw individual p orbitals for all the π bonds with directions clearly indicated.
 - (a) $CH_2CHCHCH_2$.

Answer. (i) / (iii):



- (ii): Every carbon atom is sp^2 .
- (b) CH₃CCCH₃.

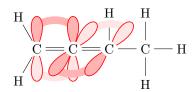
Answer. (i) / (iii):

$$\begin{array}{c|c} H & H \\ \hline | & C \\ \hline | & C \\ \hline | & H \end{array}$$

(ii): The outer two carbon atoms are sp^3 . The inner two carbon atoms are sp.

(c) CH₂CCHCH₃.

Answer. (i) / (iii):



(ii): The first and third carbon atoms from the left are sp^2 . The second carbon atom from the left is sp. The right carbon atom is sp^3 .

2 Acidity and Conformers

1. For the following compounds, write the conjugate bases that would result if the labeled protons were removed. Include resonance structures if there are any. Indicate which of the two labeled protons you expect to be more acidic and why.

$$\begin{array}{c|c} (b) & & H_a \\ \hline \\ O & & \\ \end{array}$$

(c)
$$\stackrel{\text{H}_a}{\swarrow} \stackrel{\text{H}}{\searrow} N$$
 $\stackrel{\text{H}_b}{\searrow} \stackrel{\text{H}}{\searrow} H$

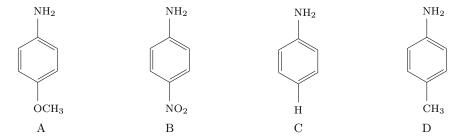
$$(d) \begin{picture}(100,0) \put(0,0){\line(1,0){100}} \put(0,0){\line(1,0$$

2. Rank the labeled H's in the following molecule in order of increasing acidity (1 = least acidic, 5 = most acidic). Provide a brief explanation for your ordering.

Labalme 6

$$\begin{array}{c} \mathbf{c} \\ \mathrm{OH} \\ \mathrm{O} \\ \mathrm{O} \\ \mathrm{HO} \\ \end{array}$$

3. Rank the following primary amines (anilines in this case) in order of increasing basicity (1 = least basic, 4 = most basic). Write the conjugate acid and provide a brief explanation for your ordering.



4. Using curved arrows, draw a reaction mechanism and predict the products.

(a) Lewis Acid-Base Reaction:
$$+$$
 \dot{N}

(b) Brønsted Acid-Base Reaction:
$$\nearrow$$
 + AlCl₃ \longrightarrow

5. Perform a conformational analysis of 3-bromo-2-methylpentane using Newman projections viewed through the C3-C4 bond (C3 in the front, C4 in the back). Write the relevant conformations in 60° increments, indicate whether they are eclipsed or staggered, gauche, anti, or syn, and plot their relative potential energy. As you plot their relative potential energy, consider the isopropyl group on carbon 3 to be bulkier than the bromo group on carbon 3.

6. For each compound below, draw two chair conformations. Indicate whether the substituents are axial or equatorial. Indicate which chair conformation is more stable.

