

Structure and Properties of Organic Molecules

Reading: Wade chapter 2, sections 2-7- 2-14

Study Problems: 2-35, 2-37, 2-39, 2-40, 2-41, 2-42,

Key Concepts and Skills:

- Identify constitutional isomers and stereoisomers; identify polar and non-polar molecules and determine what type of substance can participate in hydrogen bonding
- Identify the general classes of hydrocarbons, oxygen containing compounds, and nitrogen containing compounds.
- Predict general trends in solubility and boiling points based on polarity, size, and hydrogen-bonding ability

Lecture Topics:

I. Isomerism

Isomers are different compounds with the same molecular formula

Constitutional isomers (structural isomers) are isomers that differ in their bonding sequence (example: pentane, isopentane, and neopentane)

Stereoisomers are isomers that differ only in how their atoms are oriented in space. Example: the cis/trans isomers of 2-butene (also called geometrical isomers)

The study of the structure and chemistry of stereoisomers is called **stereochemistry**

II. Bond polarities & Dipole moment

The polarity of a bond is measured by its dipole moment, μ , where $\mu = \delta \times d$

Units of dipole moment = Debye ; 1 debye = 3.3×10^{-30} coulomb-meter

Thus μ (in debyes) = $4.8 \times \delta$ (electron charge) $\times d$ (in angstroms)

Example: a C-Cl bond has a dipole moment of 1.56D and a bond length of 1.81 Å, calculate the extent of charge separation in this bond

Molecular Dipole Moment is the vector sum of the individual dipole moments within a molecule. Symmetry and geometrical factors **must** be taken into consideration.

Consider the following molecules: CCl_4 ($\mu = 0$); CH_3Cl ($\mu = 1.9\text{D}$); CO_2 ($\mu = 0$); CH_2CO ($\mu = 2.3\text{D}$); NH_3 ($\mu = 1.5\text{D}$); CH_3CN ($\mu = 3.9\text{D}$)

Note that lone pairs on atoms have a dipole moment as well, with the positive end of the dipole located at the atom.

III. Intermolecular forces

Melting points, boiling points, and solubilities of organic compounds reflect the strength of intermolecular forces (forces between molecules)

3 major kinds of IM forces will be studied: dipole-dipole forces, London forces, and Hydrogen bonding

Dipole-dipole forces are attractive forces resulting from the alignment of dipoles (polar molecules possessing a dipole moment) example: CH_3Cl . Properly aligned dipoles attract each other, providing a strong enough force to keep molecules in liquid phase at room temperature

London forces (van der Waals forces) are operative for non-polar molecules. They consist of temporary dipole moments induced in a molecule (due to a momentary shift of an electron cloud) by other nearby molecules. Induced dipole-induced-dipole interactions depend on close surface contact between two molecules and is correlated with surface area. The greater the surface area of a molecule, the greater the extent and strength of London forces. In general, London forces are weak attractive forces.

Compare the boiling points of n-pentane (36°C) vs. n-octane (127°C), and CCl_4 (77°C) vs. CHCl_3 (62°C).

Hydrogen Bonds are particularly strong dipole-dipole attractions due to a highly polarized O–H or N–H bond (only when H is bonded to an electronegative element). The partial positive charge on H in each of these bonds gives this atom a high affinity for non-bonded electrons (lone pairs). The strength of a typical H-bond is ~ 5 kcal/mol. Hydrogen bonds are the operative IM force holding together the following solvents: H_2O , $\text{CH}_3\text{CH}_2\text{OH}$, CH_3OH , NH_3 , etc. Compare boiling points of the following compounds with the same molecular formula: CH_3OCH_3 (-25°C) vs. $\text{CH}_3\text{CH}_2\text{OH}$ (78°C). Alcohols, containing the hydroxyl functional group (-OH) form stronger H-bonds than amines (because O is more electronegative than N, resulting in a more strongly polarized O–H bond)

IV. Solubility

Guiding principle: “like dissolves like”

Polar substances dissolve in polar solvents, non-polar substances dissolve in non-polar solvents

1. A polar solute (ionic compound) will dissolve in a polar solvent, such as water. For NaCl dissolving in water, solvation of the individual Na^+ and Cl^- ions by oriented water dipoles is known as hydration. For these solutes, the energy of hydration is greater than the lattice energy of the salt, and thus the salt dissolves and the ions separate in solution.
2. For a polar solute dissolving in a non-polar solvent, no dissolution is observed. Non-polar solvents, with no strong net dipole moment, cannot solvate ions and thus cannot overcome the lattice energy of an ionic solid.
3. Non-polar solutes dissolve in non-polar solvents: The van der Waals attractions to solvent are roughly as strong as the van der Waals attractions between the solute particles, thus dissolution is favorable. Ex. CCl_4 dissolves in pentane, C_5H_{12}

dissolution in this case is driven by entropy, since solution is a more disordered state than either solvent or solute alone.

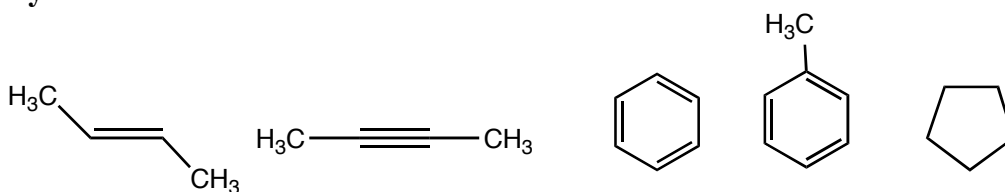
4. Non polar solutes do not dissolve in polar solvents, because non-polar molecules disrupt the stable H-bond network of water, resulting in an energetic penalty. Furthermore, there is no energy released from solvation of non-polar molecules. Thus, oil (non-polar molecules) and water (polar solvents) don't mix. Example: hexane (C_6H_{14}) and H_2O are immiscible.

V. Classes of organic compounds

A. Hydrocarbons: compounds consisting only of carbon and hydrogen.

- a. **Alkanes**: examples: CH_4 , $CH_3CH_2CH_2CH_3$, cyclopentane, cyclohexane. Alkyl groups are an alkane portion of a molecule: $-CH_3$ (methyl), $-CH_2CH_3$ (ethyl), $-CH_2CH_2CH_3$ (propyl). Alkanes are generally unreactive
- b. **Alkenes**: compounds containing a carbon-carbon double bond as a reactive functional group: $CH_2=CH_2$ (ethylene), $CH_2=CHCH_3$ (propylene), $CH_3CH=CHCH_3$ (cis and trans 2-butene), cyclopentene, cyclohexene. 6 atoms in a plane in an alkene.
- c. **Alkynes** contain the carbon-carbon triple-bond as a reactive functional group. Examples include acetylene, $HC\equiv CH$, butylene, $CH_3C\equiv CCH_3$, etc. In an alkyne, four atoms must be in a straight line.
- d. **Aromatic hydrocarbons** are derivatives of benzene, which is a particularly stable structure (cyclohexatriene) C_6H_6 ; methylbenzene, $CH_3C_6H_5$, and ethylbenzene ($CH_3CH_2C_6H_5$)

Identify:



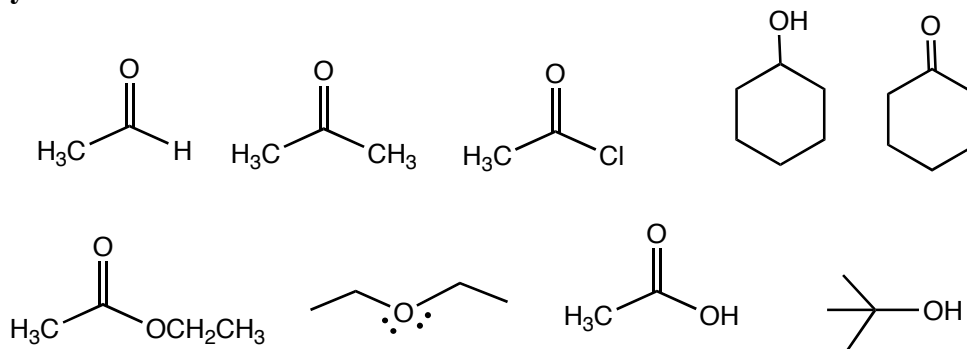
B. Oxygen Containing Functional Groups

- a. **Alcohols** possess the hydroxyl ($-OH$) functional group: $R-OH$, where R is any hydrocarbon group from above. Examples: CH_3CH_2OH (ethanol), $(CH_3)_3COH$ (2-methyl-2 propanol), cyclopentanol, etc.
- b. **Ethers** have the general form $R-O-R'$, with two alkyl groups bonded to oxygen. Examples: $(CH_3CH_2)_2O$, diethyl ether, $(CH_3)_2O$, dimethyl ether, etc.
- c. **Aldehydes and Ketones** possess the carbonyl functional group, $C=O$. Aldehydes have the form $RCHO$ or $RHC=O$; Ketones have the form $RR'C=O$. Examples of aldehydes include acetaldehyde,

CH_3CHO and propionaldehyde, $\text{CH}_3\text{CH}_2\text{CHO}$. Examples of ketones include acetone, $(\text{CH}_3)_2\text{CO}$, and cyclohexanone.

- d. **Carboxylic acids** contain the COOH functional group. An example is acetic acid, CH_3COOH , which acts as a Bronsted acid by donating H^+ to solvent.
- e. **Carboxylic acid derivatives.** These include esters $:\text{RCOOR}'$ (example: ethyl acetate, $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$), acid chlorides, RCOCl (example: acetyl chloride, CH_3COCl), and amides RCONH_2 (example: acetamide, CH_3CONH_2)

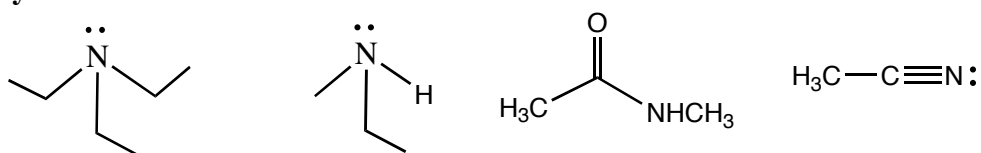
Identify:



C. Nitrogen-containing compounds

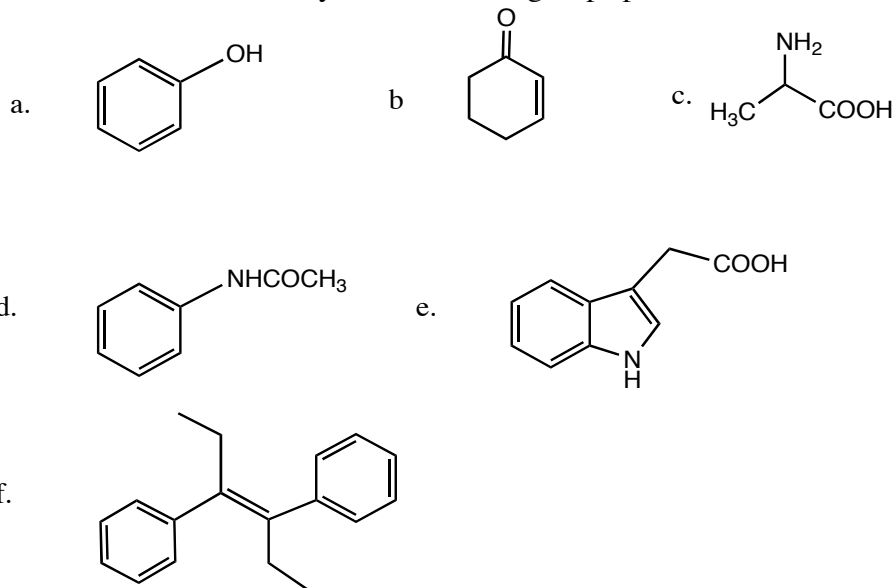
- a. **Amines:** basic nitrogen compounds containing a lone pair on nitrogen available for donation: RNH_2 (CH_3NH_2 , methylamine), RNHR' ($\text{CH}_3\text{NHCH}_2\text{CH}_3$, methyl ethylamine), and $\text{RR}'\text{R}''\text{N}$ ($(\text{CH}_3\text{CH}_2)_3\text{N}$, triethylamine)
- b. **Amides:** RCONH_2 ($\text{CH}_3\text{CONHCH}_3$, N-methylacetamide)
- c. **Nitriles:** contain the cyano functional group ($-\text{CN}$): CH_3CN , acetonitrile

Identify:



Additional Problems for practice:

1. Locate and identify the functional groups present in these molecules:



2. Which of the following molecules have polar bonds? Which compounds have a net dipole moment?

a. Cl_4 b. $\text{CH}_3\text{CH}_2\text{OH}$ c. H_3CCOCH_3 d. CH_3OCH_3 e. CH_3NH_2

3. Which solvent(s) would one use to dissolve each of the following compounds (choices: water, a polar organic solvent (CH_3Cl) or a non-polar organic solvent ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$))

- NaBr
- $(\text{CH}_3)_2\text{CHOH}$
- $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$
- $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$
- $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_3$

4. Order the following compounds according to their boiling points, from least to greatest:

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_3$, $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_3$

5. Draw a picture illustrating why each of the following pairs are miscible (soluble in each other)

- $\text{CH}_3\text{CH}_2\text{OH}$ and H_2O
- CH_3COCH_3 and H_2O
- NH_3 and CH_3OH
- CCl_4 and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$