L

TOPIC 2. ORGANIC COMPOUNDS (Chapter 2)

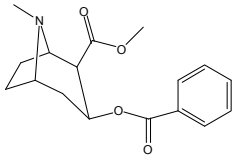
OBJECTIVES

1. Describe the structure of N, O and halogen containing functional groups: formal charges, hybridization, VSEPR theory, polarity, resonance.
2. Develop relationships between structure and physical properties (b.p., solubility).

A BRIEF INTRODUCTION TO ChemDraw, Chem3D and MOLECULAR MECHANICS

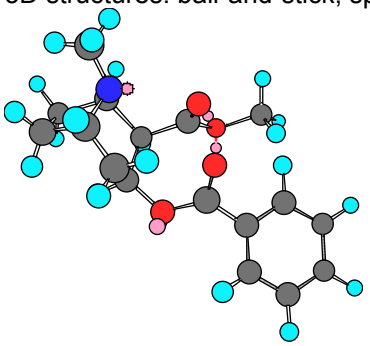
ChemDraw

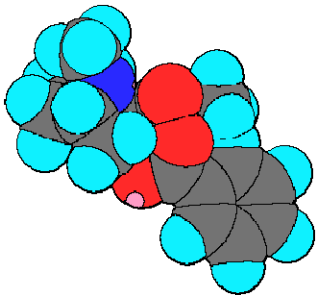
Bond-line structures



Chem3D

3D structures: ball-and-stick, space-filling

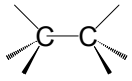
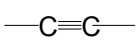
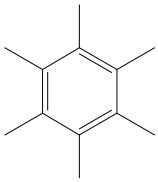




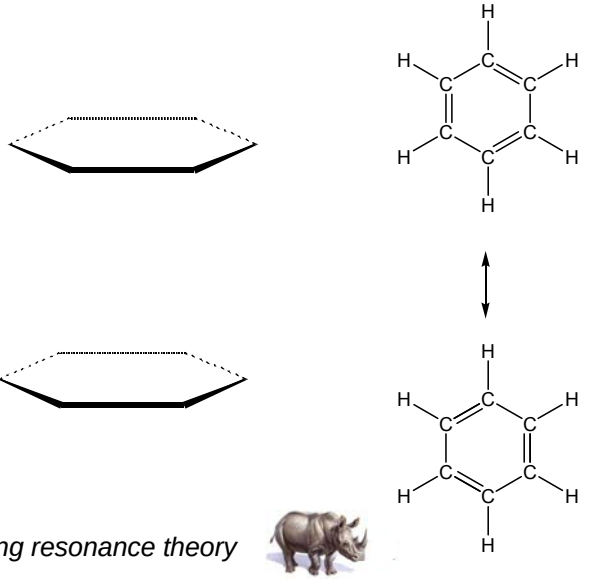
S:2.1-2.2

HYDROCARBONS

Molecules containing only C, H

		C-C bond length / Å	bond energy kcal/mol
alkanes		1.54	88
alkenes		1.34	152
alkynes		1.20	200
arenes		1.40	≈115

Molecular structure of benzene



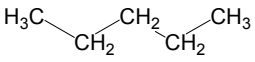
Validating resonance theory

BRANCHED ALKANES, CLASSIFICATION OF CARBON ATOMS, ALKYL GROUPS

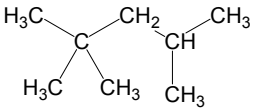
S:2.5

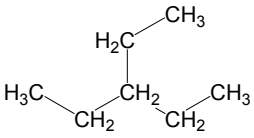
Prob: 2.20-27, 32,39,42

Linear alkane



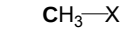
Branched alkanes

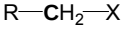


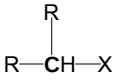


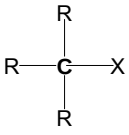
Classification of carbon atoms

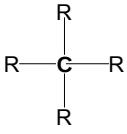
R = carbon, X ≠ C

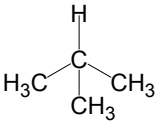
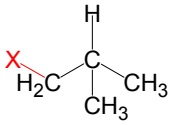
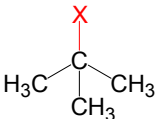










Alkane	Alkyl group	
CH_4 methane	X– CH_3	methyl, Me
CH_3CH_3 ethane	X– CH_2CH_3	ethyl, Et
$CH_3CH_2CH_3$ propane	X– $CH_2CH_2CH_3$	propyl, Pr, *n*-Pr, 1-propyl
	X– $CH(CH_3)_2$	isopropyl, *i*-Pr, 2-propyl
$CH_3CH_2CH_2CH_3$ butane	X– $CH_2CH_2CH_2CH_3$	butyl, Bu, 1-butyl
	$CH_3CH(X)CH_2CH_3$	*sec*-butyl, *s*-Bu, 2-butyl
 isobutane		isobutyl, i-Bu
		*tert*-butyl, t-Bu

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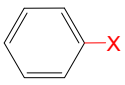
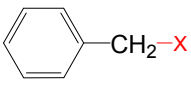
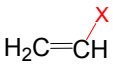


phenyl, Ph, Φ



benzyl, Bn



vinyl

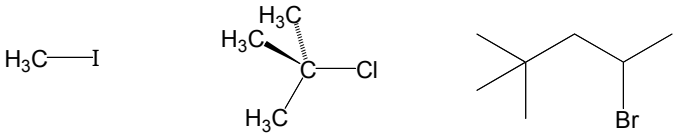
FUNCTIONAL GROUPS

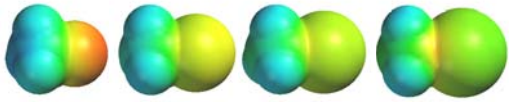
Alkyl Halides

ethylene dibromide
(banned pesticide)
chlorodane
(banned pesticide)
carbon tetrachloride
(banned dry cleaning agent)
methyl bromide
(banned fumigating agent)

R—Hal

Classes of alkyl halides





Carbon-Halogen Bonds

R—Hal

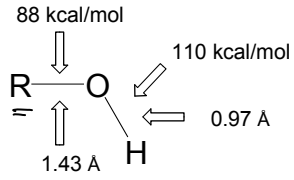
Halogen	C-Hal bond length / Å	C-Hal bond dipole / D	Bond energy kcal/mol
Fluorine	1.38	1.51	116
Chlorine	1.77	1.56	79
Bromine	1.94	1.48	66
Iodine	2.21	1.29	52

We will see later that in general the reactivity of alkyl halides increases in the order:

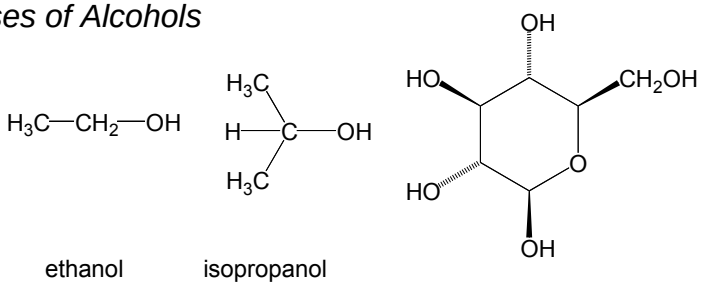
alkyl fluorides << alkyl chlorides < alkyl bromides < alkyl iodides

Why? A large part of the answer is bond strength

Alcohols



Classes of Alcohols

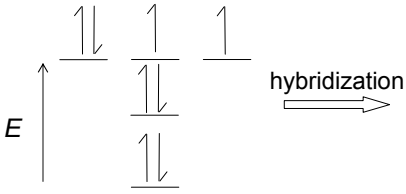


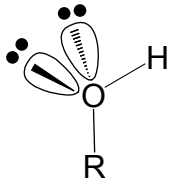
ethanol

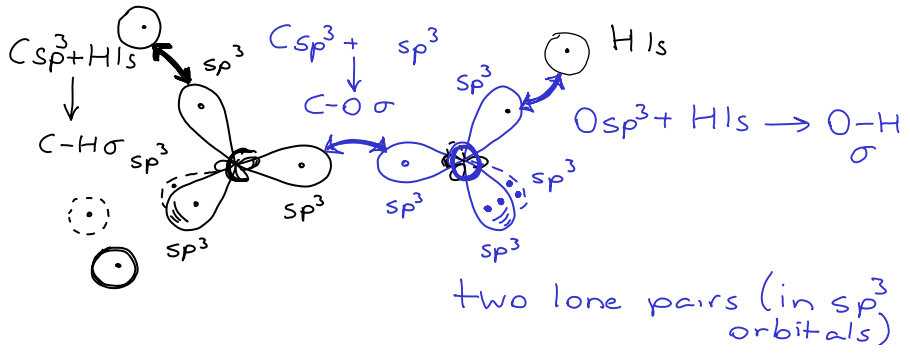
isopropanol
(rubbing alcohol)

glucose (5 OH groups)

Hybridization of Oxygen in Alcohols

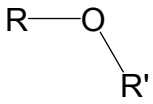


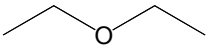




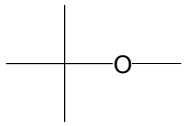
Ethers

S:2.8





diethyl ether
(old anesthetic)



methyl *tert*-butyl ether
(MTBE, *controversial fuel additive)*

ethylene oxide
(monomer for polymer in gel caps)

CNN.com
MTBE is not a carcinogen, California rules

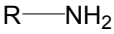
L

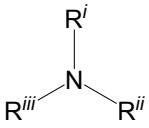
S:2.9

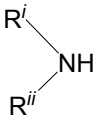
Amines

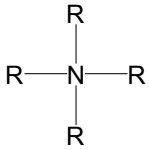
Classes of Amines: Classified by number of substituents *on the nitrogen atom* (*NOT* the attached carbon atom)

caffeine
nicotine









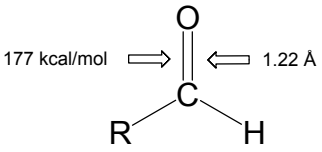
Problem: Using the concepts from topic 1….

- What is the geometry around the nitrogen of an amine

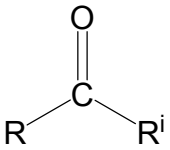
- What is the hybridization of the nitrogen of an amine

- What is the hybridization of the orbital containing the lone pairs of electrons on the nitrogen atom of amines?

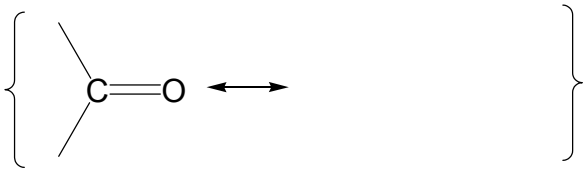
Aldehydes and Ketones



aldehyde



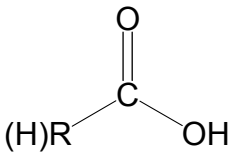
ketone



- Formaldehyde
  - *(biological preservative)*
- Benzaldehyde
  - *(almond flavoring)*
- Acetone
  - *(solvent)*
- Cortisone
  - *(antiinflammatory)*

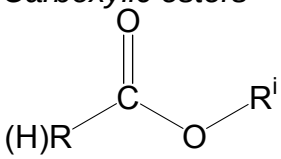
Carboxylic Acids and Derivatives

Carboxylic acids



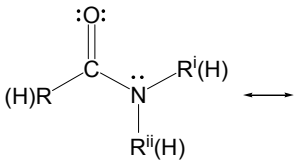
acetic acid
(vinegar)
acetylsalicylic acid
(aspirin)

Carboxylic esters



isoamyl acetate
(banana oil)
methyl salicylate
(wintergreen oil)

Amides



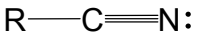
Validating resonance theory

The above resonance structures ***predict*** partial double bond character for the carbonyl–nitrogen bond.

Experimental studies ***show***

1. The four atoms attached to the carbonyl carbon and the nitrogen atoms are close to being planar
2. There is very slow rotation about the carbonyl carbon–nitrogen bond

Nitriles (cyanides)



S:2.12

laetrile - amygdalin
(cyanogen sugar in bitter almonds, peach and apricot seeds)
Methyl cyanoacrylate
(monomer in Superglue)

INTERMOLECULAR FORCES AND PHYSICAL PROPERTIES

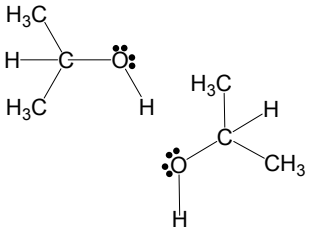
S:2.14-2.15
Prob:2.27, 29-32

Intermolecular Forces

Hydrogen Bonding

Electrostatic attraction between lone pairs (e.g., on N, O, S, F, Cl, …) and a hydrogen atom bonded to an electronegative atom (e.g., on N, O, S, F, Cl,…)

- Hydrogen is δ+ because of dipole
- Heteroatom has lone pair(s) of electrons



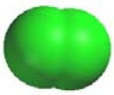
Dipole-Dipole Interactions

S:2.3-2.4
Prob: 2.37,41

Bond Dipoles

Dipoles occur when two atoms with different electronegativity are bonded to one another.

H—H



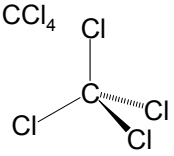
H—F

Dipole Moments

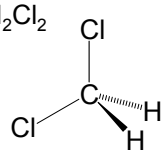
Add bond dipole vectors. C-H bonds are not polar (C and H have similar electronegativity), so they do not contribute much to polarity.

Chlorinated methanes

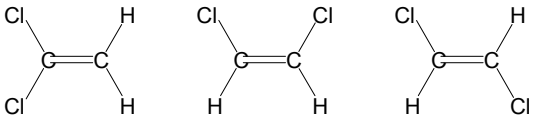
CCl_4



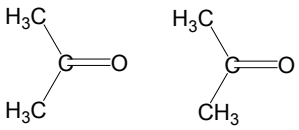
CH_2Cl_2



Dichloroethenes



Electrostatic attraction between permanent dipoles



Van der Waals (London) Forces

Electrostatic attraction between momentary dipoles and induced dipoles

Intermolecular forces determine a compound's physical properties.

Physical Properties

Boiling Points

$CH_3CH_2CH_2CH_3$
butane, mw = 58
bp = –1°C

$CH_3CH_2CH_2NH_2$
propylamine, mw = 59
bp = 48 °C

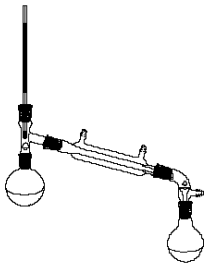
$CH_3CH_2CH_2OH$
1-propanol, mw = 60
bp = 97 °C

$CH_3CH_2CH_2F$
1-fluoropropane, mw = 62
bp = -3 °C

$(CH_3)_3N$
trimethylamine, mw = 59
bp = 3 °C

$CH_3CH_2OCH_3$
ethyl methyl ether, mw = 60
bp = 11 °C

CH_3CO_2H
acetic acid, mw = 62
bp = 118 °C



These differences in boiling point allow for the separation of compounds by distillation

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Solubility

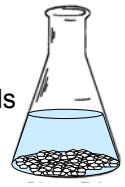
"Like dissolves like"

Polar solvents dissolve polar molecules and salts. Hydrogen bonding solvents dissolve hydrogen-bonding solutes.

- Soluble with water:
  - *Salts:* NaCl, NaOH
  - *Alcohols:* Methanol, CH_3OH, up to propanol, $CH_3CH_2CH_2OH$
  - *Acids:* Acetic acid, CH_3COOH, up to butanoic acid, $CH_3CH_2CH_2COOH$

- *Insoluble* in water
  - *Hydrocarbons:* Alkanes, alkenes
  - *Relatively non-polar functional molecules:* Alkyl halides, ethers, etc

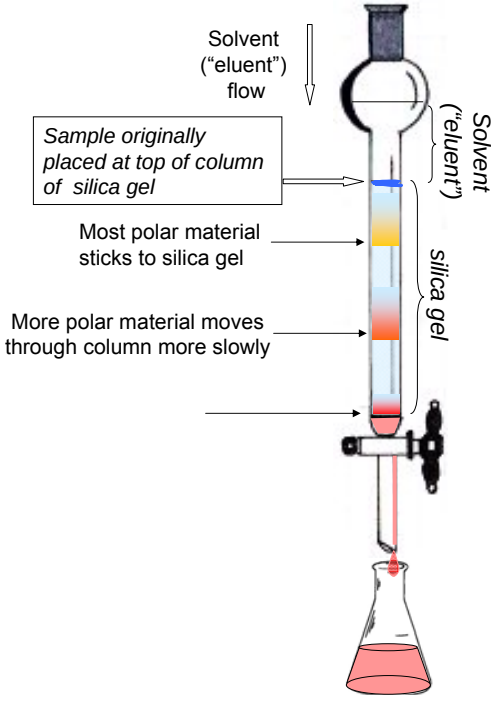
Differences in solubility allows for the separation of organic compounds by recrystallization and extraction (see later – Acids and Bases)



Polarity

Differences in polarity allows for the separation of organic compounds by *chromatography*.

Polar compounds stick to polar solids, non-polar compounds are eluted more rapidly



TOPIC 2 ON EXAM 1

Types of Questions

- Identify functional groups, geometry (bond lengths, angles), hybridization of atoms.
- *The problems in the book are good examples of the types of problems on the exam.*

Preparing for Exam 1

- Work as many problems as possible.
- Work in groups.
- Do the "Learning Group Problem" at the end of the chapter.
- Work through the practice exam