**CHEM 221 section 01**

**LECTURE #09a** Tues., Oct. 04, 2005

## ASSIGNED READINGS:

**TODAY'S CLASS:** *structure-property relationships*
*start conformations…*

**NEXT CLASS:** finish Ch.2

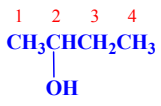
http://artsandscience.concordia.ca/facstaff/P-R/rogers



## 2.6 Nomenclature of Alcohols

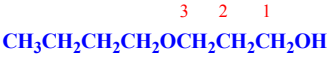
IUPAC naming: the OH functional group is "important enough" to name the compound after it…
→ use suffix "-ol"

1. Determine the parent hydrocarbon that <u>contains the highest-priority functional group</u> *(here: the hydroxyl)*




2-butanol
or
butan-2-ol

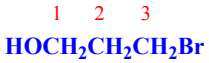

2-ethyl-1-pentanol
or
2-ethylpentan-1-ol



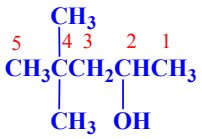

3-butoxy-1-propanol
or
3-butoxypropan-1-ol

Note: the position # for the –OH group can appear in 1 of 2 places:
(i) immediately before the "-ol" suffix
*or* (ii) before the parent chain's name

2. The highest-priority functional group suffix gets the lowest position number possible




3-bromo-1-propanol




4,4-dimethyl-2-pentanol

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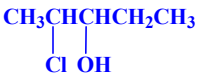
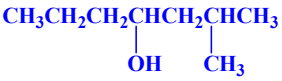
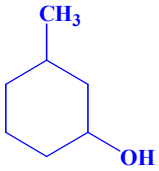
3. And…then give the lowest possible #s to the other substituents




2-chloro-3-pentanol
not
4-chloro-3-pentanol



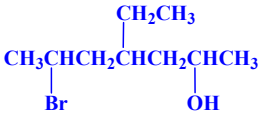

2-methyl-4-heptanol
not
6-methyl-4-heptanol



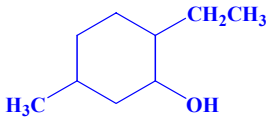

3-methylcyclohexanol
not
5-methylcyclohexanol

(3)

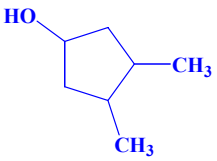
4. If there is more than one substituent, the substituents are cited in alphabetical order *(as always!)*
*& the rest of the rules are followed too*




6-bromo-4-ethyl-2-heptanol




2-ethyl-5-methylcyclohexanol

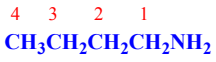



3,4-dimethylcyclopentanol

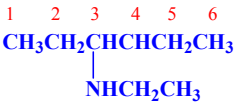
(4)

# 2.7 Nomenclature of Amines

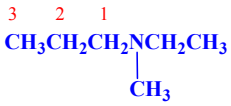
IUPAC naming: based on functional group, suffix "-amine"



1-butanamine
or
butan-1-amine

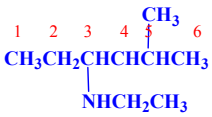


N-ethyl-3-hexanamine
or
N-ethylhexan-3-amine

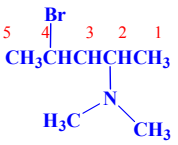


N-ethyl-N-methyl-1-propanamine
or
N-ethyl-N-methylpropan-1-amine

- The substituents are listed in alphabetical order and a number or an "*N*" is assigned to each one



N-ethyl-5-methyl-3-hexanamine



4-bromo-N,N-dimethyl-2-pentanamine

2-ethyl-N-propylcyclohexanamine



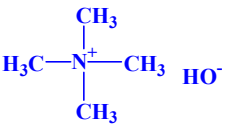
## Naming Quaternary Ammonium Salts

*Ionic compounds: name cation first, then name anion*

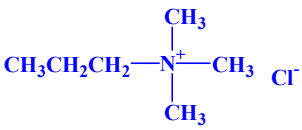
*Common names:*

1. Name all substituents on the nitrogen
2. Use suffix "-ammonium"
3. Name the counterion

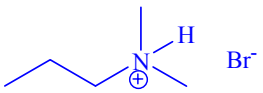
*Don't worry about their IUPAC names*



tetramethylammonium hydroxide



ethyltrimethylammonium chloride



dimethylpropylammonium bromide

*We'll see how alkylammonium salts can form later…*
*but we DO know that amines can be protonated (act as base!)*

## 2.8–2.9 Understanding relationships between chemical structure & properties…

**Physical properties include:**
- boiling point
- melting point
- solubility

**Chemical properties:**
- types of rxns that occur
- we're getting to those soon!

**What determines the physical properties of a compound ?**

→ ***Strength of interaction between the particles***
- what type(s) of interaction are occurring?
- how strong are those interactions?
- & how large are the regions of the molecules over which these interactions are operating?

→ *To predict:* ***consider shape, polarity & size of the molecules***



**1st task: analyze the molecule's polarity**

- Must consider: bond dipoles, lone pairs, + geometry
  *& realize also that organic molecules can be large…*
- Helpful to know typical hybridization of atoms in molecules
  *(but recall it might be different if have option of resonance delocalization…)*

| | | | |
|---|---|---|---|
| alkanes: | all C atoms are… | $sp^3$ | → Td geometry |
| halides: | C & X in C-X are… | $sp^3$ | → both have Td geometry |
| alcohols: | O in –OH group is… | $sp^3$ | → Td geometry about O |
| ethers: | O in –O- group is… | $sp^3$ | → Td geometry about O |
| amines: | N in $-NR_2$ group is… | $sp^3$ | → Td geometry about N |

**Draw, add polarities, & identify polar *vs.* nonpolar regions**

$(CH_3)_3CH$ $CH_3NH_2$ $CH_3(CH_2)_5OH$

## 2nd task: identify nature of intermolecular interactions

- Type(s) of interaction:

Review Chem206 Kotz&Treichel Ch.13

strongest

- ion-ion — Electrostatic attraction between fully charged species. Similar strength to covalent bonds (100's of kJ/mol) but no geometric requirements (~ no orbital overlap)
- hydrogen bonding — 1/10th strength of covalent bond (10-50 kJ/mol). Part electrostatic, part covalent character. Between: $\delta^+$ H on N,O,F *and* lone pair on N,O,F
- ion-dipole
- dipole-dipole

} Electrostatic attraction between *permanently* charged (& partially charged) entities (strength varies with magnitude of charge,dipole)

- dipole-induced dipole
- induced dipole – induced dipole
  also called: London dispersion forces, van der Waals forces

} Electrostatic attraction involving small, short-lived (transient) dipoles. *Polarizability increases with: size of atom, number of atoms*

weakest



## 2nd task: identify nature of intermolecular interactions

- Type(s) of interaction:

Review Chem206 Kotz&Treichel Ch.13

strongest

- ion-ion — Between ions. *e.g.,* tetramethylammonium chloride
- hydrogen bonding — Between: $\delta^+$ H on N,O,F *and* lone pair on N,O,F. *e.g.,* water, alcohols, amines
- ion-dipole
- dipole-dipole

} Between ions & polar molecules: $(CH_3)_4NCl$ & $H_2O$; polar molecules & other polar molecules

- dipole-induced dipole
- induced dipole – induced dipole
  also called: London dispersion forces, van der Waals forces

} Between ALL molecules BUT.. most important for NONPOLAR molecules (only force acting!)

weakest

## 3rd task: identify extent of interacting regions

- How large are the regions of the molecules that can participate in the various types of interaction?
  - identify polar regions *vs.* nonpolar regions

Stronger forces — But: often only small fraction of molecule is polar

Weaker forces — But: often large proportion of molecule is nonpolar…

**Physical properties are determined by the SUM of all interactions**

- Strong forces (H-bonding, d-d…) usually limited to 1 or 2 interactions per pair of molecules

*BUT…*

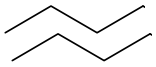
- Weak forces (van der Waals) can really add up!
  - if have larger nonpolar regions:
    - ⇨ more points of contact between molecules
      - ⇨ many individual induced dipoles present at any moment
        - ⇨ stronger force of attraction

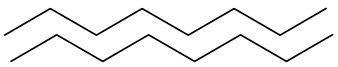


## Always consider the net effect of all interactions

- Nonpolar molecules: melting & boiling points increase with chain length

Butane
bp -0.5°C





Octane
bp 125°C

- Branched chains: *weaker interactions*
  - ⇨ disrupt packing between molecules (poorer contact between chains)
  - ⇨ weaker vdw forces ⇨ mp & bp lower than expected

Pentane (bp 36.1°C) *vs.* Neopentane (bp 9.5°C)

- Higher polarizabilty: *stronger interactions*
  - larger atoms ⇨ more polarizable ⇨ easier to induce dipoles ⇨ stronger interactions

**Table 2.6 Comparative Boiling Points of Alkanes and Alkyl Halides (°C)**

| | Y | | | | |
|---|---|---|---|---|---|
| | H | F | Cl | Br | I |
| $CH_3—Y$ | −161.7 | −78.4 | −24.2 | 3.6 | 42.4 |
| $CH_3CH_2—Y$ | −88.6 | −37.7 | 12.3 | 38.4 | 72.3 |
| $CH_3CH_2CH_2—Y$ | −42.1 | −2.5 | 46.6 | 71.0 | 102.5 |
| $CH_3CH_2CH_2CH_2—Y$ | −0.5 | 32.5 | 78.4 | 101.6 | 130.5 |
| $CH_3CH_2CH_2CH_2CH_2—Y$ | 36.1 | 62.8 | 107.8 | 129.6 | 157.0 |

## Always consider the net effect of all interactions

- Polar molecules: melting & boiling points also increase with # carbons but most dramatic effects due to hydrogen bonding

*Example: 3 isomeric amines with very different bp's*

| 2-methylbutanamine | *N*-methyl-2-butanamine | *N*-ethyl-*N*-methylethanamine (diethyl methyl amine) |
|---|---|---|
| bp 97°C | bp 84°C | bp 65°C |
| 1° amine | 2° amine | 3° amine |
| can donate 2 H-bonds & accept 1 H-bond | can donate 1 H-bond & accept 1 H-bond | can only accept 1 H-bond |



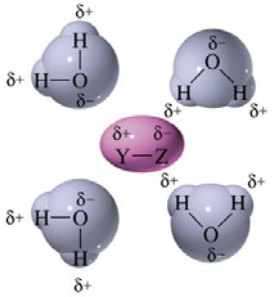
## Physical properties are determined by intermolecular interactions

- Melting
- Boiling

} Thermal energy must be sufficient to overcome (break) the intermolecular interactions
• stronger interactions ⇨higher temperature required

- Solubility: *like dissolves like*

When dissolving:
interactions between solute molecules
are replaced by
interactions between solute & solvent molecules
• *Does solute interact more strongly*
*with itself? (low solubility)*
*or with the solvent? (high solubility)*
*or are both interactions similar?*

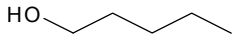


solvation of a polar compound (Y—Z) by water

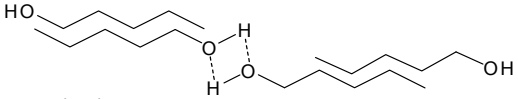
## Solubility guidelines…

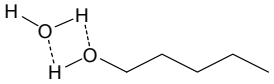
- Molecules with polar groups do not always ACT as if they are polar…

*Observation:* Alcohols with > 4 C in chain do not dissolve in water




vdw forces between chains adds up to be stronger than H-bonding to $H_2O$




*Similarly:*

1. Ethers with > 3 C do not dissolve in water
   - Ethers can only act as H-bond acceptors (no $\delta^+$ hydrogens)
   - H-bonding only occurs between ether's O & water's H
   - Strong enough only to pull 3 C (nonpolar!) into water
2. Short chain amines are more water-soluble than ethers
   - 1° & 2° amines: both H-bond donors & acceptors
   - 3° less soluble: only H-bond acceptors (no $\delta^+$-H)
3. Branching of hydrocarbon chains increases solubility
   - Disrupts efficiency of vdw forces,
   - & makes smaller surface to be solvated by water molecules



## ASSIGNED READINGS

**BEFORE NEXT LECTURE:**

**Read:** rest of Ch.2

**Practice:** nomenclature & structural drawings