Chapter 2. Structure and Properties

❒ What to master

- Recognizing Stable Bonding Arrangements
- Understanding Bond Strengths and Lengths
- Drawing Constitutional Isomers
- Using the Degree of Unsaturation
- Using Line/Condensed/Skeletal Structures
- Understanding How the Intermoleuclar Forces Affect Physical Properties
- Recognizing Functional Groups

Chapter 2. Structure and Properties

❒ Bonding arrangements

- ◆Hydrogen & Carbon: 📖 31 top, Figure 2.1
- ◆Nitrogen, Oxygen & Halogens: 📖 32 top, Figure 2.2
- ◆Phosphorus & Sulfur: 📖 32 bottom, Figure 2.3

❒ Bond strengths and bond lengths

- ◆Bond dissociation energy: a measure of the bond strength (E_{dis}), 📖 33 Table 2.1 & 2.2, 'the shorter, the stronger'
- ◆Bond strength: structure-dependent

  E_{dis} (kcal/mole): CH_3-H (104), C_2H_3-H (98), $(CH_3)_3$C-H (91)
- ◆Stronger H-C/N/O (100), C-C (81) & C-Y bonds

  O-O (34), Si-Si (54), N-O (39), Si-O (88)

❖ Structural (Constitutional) Isomers

- Definition

  two or more compounds having the same molecular formula differing in structure, i.e., connectivity (C_2H_6O, 📖 34 mid)

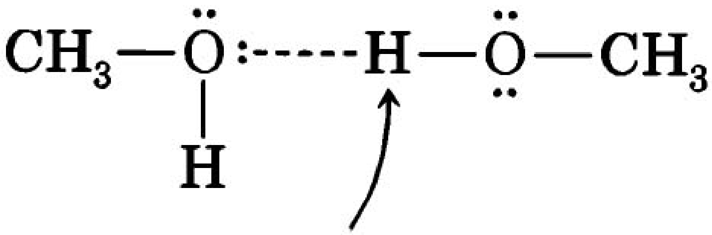
- Writing structural isomers from molecular formula
  - Calculate degree of unsaturation: (DU)=[(2C+2)-H]/2, 📖 39-40
    - counting heteroatoms: oxygen = 0, halogen = hydrogen, N = +1
  - Draw skeletal chain/structure from longer to shorter
    - bond line formula (structure): C_6H_{14}, 📖 36 Figure 2.4
  - Exercise problem: 'draw all the structural isomers of C_5H_{10}'
    - Line, condensed or skeletal structures: 📖 41 Figure 2.5

❖ Structure and Physical Properties (I)

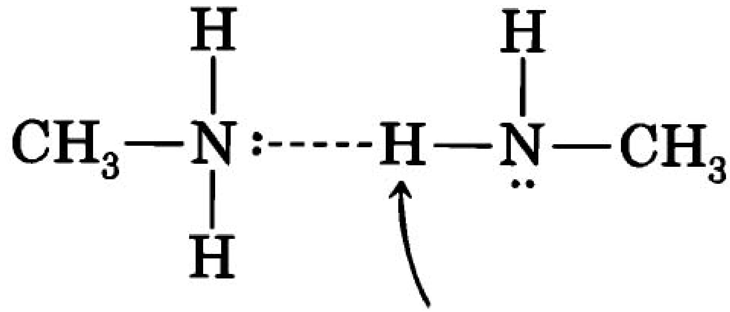
- Intermolecular forces: $\propto (q_1 \bullet q_2) / r^2$, 📖 44, Figure 2.7
  - ion-ion > ion-dipole > dipole-dipole > dipole-induced dipole > instantaneous dipole-induced dipole (London force): van der Waals forces (0.5~5 kcal/mol)
  - hydrogen bonding: 📖 45, Figure 2.8 (H-NR_2, H-OR, H-F)
    - a special type of dipole-dipole attraction: 3~8 kcal/mol

- Melting points: intermolecular forces, 📖 46 Table 2.4
  - larger molecules: more London forces, propane vs pentane
  - symmetric shape: more compact packing → closer intermolecular distance, pentane vs neo-pentane
    - cubane vs octane: 📖 47 Problem 2.13

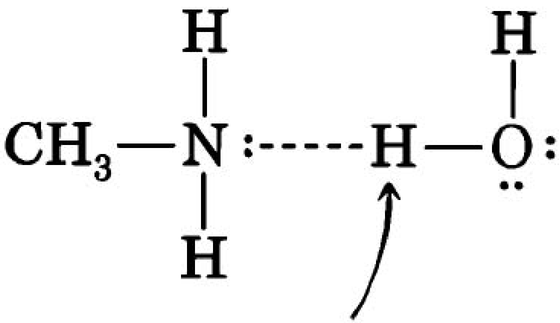
Strength of Hydrogen Bonding (I)



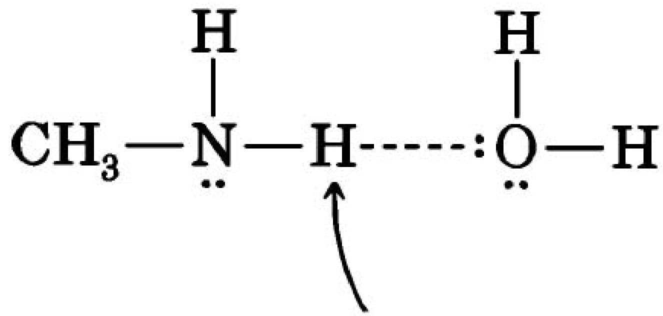
more positive H:
stronger hydrogen bond



less positive H:
weaker hydrogen bond

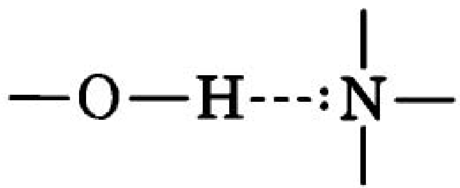
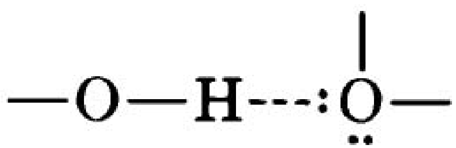
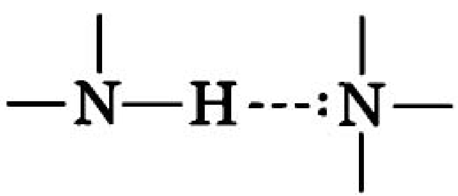
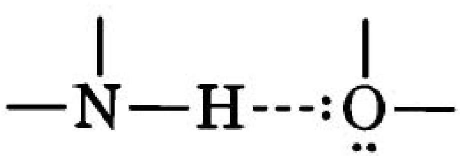


more positive H:
stronger hydrogen bond



less positive H:
weaker hydrogen bond

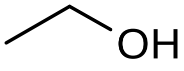
Strength of Hydrogen Bonding (II)

Type of Hydrogen Bond	Approximate Dissociation Energy (kcal/mol)
	7
	5
	3
	2

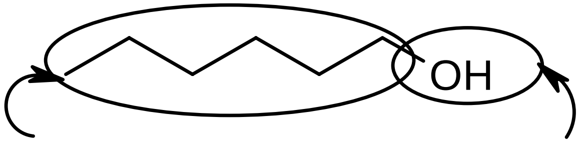
❖ Physical Properties and Structure (II)

- Boiling points: intermolecular forces, 48 Table 2.5
  - ◆larger molecules: more London forces, propane vs pentane
  - ◆bulky shape: steric hindrance of disordered molecules → longer intermolecular distance, pentane vs neo-pentane
    - ❍hydrogen bonding: more important than mp, butanol

- Solubilities: $\Delta G = \Delta H - T\bullet\Delta S$ ($\Delta G < 0$, soluble)
  - ◆$\Delta H = E_{\boldsymbol{solutes}} + E_{\boldsymbol{solvents}} - E_{\boldsymbol{(solute\text{-}solvent)}}$
    - ❍usually, $\Delta H>0$ (endothermic)
  - ◆dissolution: $\Delta S > 0$
  - ◆if $\Delta H \gg T\bullet\Delta S$, insoluble
    - ❍'like dissolves like'



ethanol
(miscible)



hydrophobic hydrophilic
(hexanol: 0.6 g/100 mL H_2O)

❖ Functional Groups

- Definition
  - a particular arrangement or group of atoms where the action takes place: e.g., alcohols; 📖 50 middle
    - R-OH: R=alkyl group, OH=functional group (alcohol)
  - organic compounds with the same functional group
    - similar properties and reactivity: alcohols
    - some contributions from alkyl (aryl) groups make differences
- Common functional groups: 📖 51 Table 2.6

Targets of *Organic Chemistry I & II*