

Unit 2: Structures & Properties

IMPORTANT STRUCTURES:

Functional groups..

Name	Structure	Name	Structure
Alkene		Aromatic	
Alkyne		Ether	
Alcohol		Ketone	
Aldehyde		Ester	
Carboxylic Acid		Amide	
Amine			

Hybridization...

MOLECULAR TYPE	n_{σ}	n_{hyb}	ELECTRON REGION GEOMETRY	MOLECULAR GEOMETRY	IDEAL BOND ANGLES	HYBRIDIZATION OF THE CENTRAL ATOM
AX_4	4	4	Tetrahedral	Tetrahedral	109.5°	sp^3
AX_3E_1	3	4	Tetrahedral	Triangular pyramidal	109.5°	sp^3
AX_2E_2	2	3	Trigonal planar	Bent	120°	sp^2
AX_3	3	3	Trigonal planar	Trigonal Planar	120°	sp^2
AX_2E_1	2	3	Trigonal planar	Bent	120°	sp^2
AX_2	2	2	Linear	Linear	180°	sp

MORE COMPLEX MOLECULAR STRUCTURES

<i>Line structures</i>	<u>only the C – C bonds are shown; element symbols and C – H are omitted</u>
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→ Must include the formal charge on any atom that has a nonzero formal charge

<i>Isomers</i>	<u>when more than one molecular structure corresponds to the same molecular formula, the two or more structures</u>
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- When two molecular formulas are different, the formulas must correspond to substances with different properties
- Occurs because the formula conveys how many atoms of each type are in a molecule, and chemical bonds would have to be broken to change the number of atoms or type of atoms
 - Breaking covalent bonds require energy, and at room temp, very few molecules have enough energy for bond breaking to occur

<i>Constitutional isomers</i>	<u>compounds with the same molecular formula but different atomic connectivity</u>
<i>Functional group</i>	<u>specific structure that has similar chemical properties whenever it is present in a molecule</u>

→ Alkane parts of a molecule don't usually participate in reactions and are *not* defined as functional groups

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Amine			

<i>Alkyl group</i>	<u>a portion of an alkane molecule bonded to something else</u>
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- Ex) $-CH_3$ (methyl), $-CH_2CH_3$ (ethyl), and $-CH(CH_3)_2$ (2-propyl)
- Use *R* to designate any alkyl group
- If there are two or more different alkyl groups, we use *R*, *R'*, *R''* or *R*₁, *R*₂, *R*₃

<i>Electronegativity</i>	<u>tendency of an atom in a molecule to attract bonding electron density</u>
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BONDS IN MOLECULES ARRANGED IN 3D

<i>Valence bond theory</i>	<u>a model that focuses on the formation of individual chemical bonds, such as the formation of a σ bond between two atoms within a polyatomic molecule</u>
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- How atomic orbitals change and combine when a molecule forms
- VSEPR model is *not* accurate

<i>Hybrid orbital</i>	<u>combinations of valence atomic orbitals that emphasize concentration of electron density in specific directions</u>
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- A hybrid orbital's greater e^- density in a specific direction provides greater overlap with an orbital from another atom when forming a σ bond

sp hybrid orbitals...

- Two of these (degenerate) form when combining the valence s AO with one p AO
- Oriented at 180° from each other; linear geometry
- Leaves two unhybridized p orbitals
- 50% s character, 50% p character; 1: 1

sp^2 hybrid orbitals...

- Three of these (degenerate) form when combining the valence s AO with two p AOs
- The three sp^2 hybrid orbitals are oriented in trigonal planar with each other (120°) on the same plane
- Leaves one unhybridized p orbital
- 33% s character, 67% p character; 1: 2

sp^3 hybrid orbitals...

- Four of these (degenerate) form when combining the valence s AO with all three p AOs
- The four sp^3 hybrid orbitals are oriented as a tetrahedron (109.5°)
- No unhybridized p orbitals
- 25% s character, 75% p character; 1: 3

Formation of σ and π bonds...

- σ bonds form when a hybrid orbital with one unpaired e^- from one atom overlaps with a hybrid orbital with one unpaired e^- from another atom creating a σ bond containing a pair of e^-
- Hybrid orbitals are derived from combining two or more AOs from valence shells of a single AO
 - AOs are the most stable arrangements of e^- in isolated atoms
 - Hybrid orbitals are important in molecules because they result in stronger (lower energy) σ bonds
- Most σ bonds form from overlaps of hybrid orbitals; most π bonds form from overlap of unhybridized p orbitals
- # of hybrid orbitals = # valence AOs that were combined to produce the hybrid orbital
- Since π bonds are formed by unhybridized p AOs, an atom that's involved in π bonding cannot be sp^3 hybridized
- If a hybrid orbital on an atom in a molecule has a pair of e^- but is not pointing at another atom, the filled hybrid orbital is *not* in bonding. This corresponds to a lone pair on an atom in Lewis structure

Determining hybridization...

- (1) Determine the number of valence AOs that *are* hybridized n_{hyb}
- (2) Count the number of σ bonds n_σ the atom forms
 - o Double bond $\rightarrow 1 \sigma, 1 \pi$
 - o Triple bond $\rightarrow 1 \sigma, 2 \pi$
- (3) Are there any lone pairs?
 - a. YES: $n_{hyb} = n_\sigma + 1$
 - b. NO: $n_{hyb} = n_\sigma$
- (4) Using n_{hyb} , determine the hybridization...
 - a. $n_{hyb} = 2$: atom is sp hybridized (two AOs are hybridized)
 - b. $n_{hyb} = 3$: atom is sp^2 hybridized (three AOs are hybridized)
 - c. $n_{hyb} = 4$: atom is sp^3 hybridized (four AOs are hybridized)
 - d. SPECIAL CASE: If $n_{hyb} = 1$ or H atom, *NOT* hybridized

Applying and interpreting hybridization...

MOLECULAR TYPE	n_σ	n_{hyb}	ELECTRON REGION GEOMETRY	MOLECULAR GEOMETRY	IDEAL BOND ANGLES	HYBRIDIZATION OF THE CENTRAL ATOM
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AX_2	2	2	Linear	Linear	180°	sp
Wedge-dash notation			straight lines represent bonds on plane of page; solid wedges represent coming <i>out</i> of page and dashed wedges represent bonds going <i>away</i> , <i>in</i> the page			
Bendt's rule			a hybrid orbital on a central atom has greater <i>p</i> character, the greater the electronegativity of the other atom forming a bond			

- ➔ A lone pair is assigned zero electronegativity since there is no atom attracting electrons in the bond away from the central atom

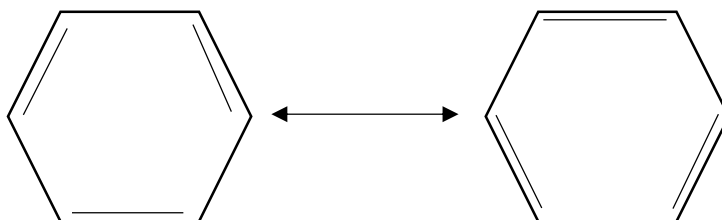
CONSEQUENCES OF 3D STRUCTURES: ORBITAL OVERLAP AND ELECTRON DELOCALIZATION

<i>Resonance structure</i>	<u>weighted average of a set of Lewis structures</u>
<i>Resonance hybrid</i>	<u>the actual electronic structure of the molecule</u>

- A molecule does *NOT* fluctuate between resonance structures, instead the actual electronic structure is *ALWAYS* the weighted average of the resonance structures
- Guidelines...
- Each resonance structure should have the name # e^- ; formal charge is useful to help with this
 - Between resonance structures, atom locations are fixed: only the locations where the e^- are shown changes; can be drawn from *any* perspective
 - Double headed arrow (\leftrightarrow) is used to denote a set of resonance structures

<i>Aromatic compounds</i>	<u>contain ring structures and exhibit bonding that much be described using resonance structures</u>
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Ex) Benzene C_6H_6



CONSEQUENCES OF 3D STRUCTURES: FLUXIONALITY AND STEREOISOMERISM

<i>Conformers</i>	<u>structures that differ only because of rotations around single bonds</u>
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- Conformers represent the same chemical compound, same name, same physical properties
- The energy needed for rotation about a single bond is relatively small because the MO of a σ covalent bond has cylindrical symmetry along the internuclear axis

<i>Stereoisomers</i>	<u>molecules that have the same molecular formula and same atomic connectivity, but differ in orientation of atoms in 3D space</u>
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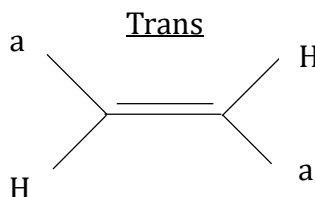
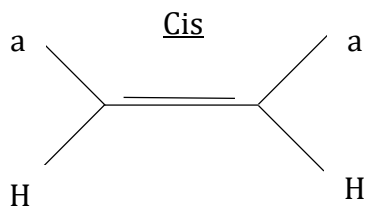
- Two carbon atoms as $C = C$ double bond cannot freely rotate with respect to each other because such rotation would break the π bond; when this bond is broken it is free to rotate

<i>Geometric isomers</i>	<u>stereoisomers that differ in orientation of the groups connected to the two carbons in a $C = C$ bond</u>
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- Caused by rigid characteristic of $C = C$ bond
- Two types: cis and trans

<i>Cis isomer</i>	<u>two groups on the same side causing restricted rotation; type of geometric isomer</u>
<i>Trans isomer</i>	<u>two groups on the opposite side; type of geometric isomer</u>

Ex) General alkane



<i>Enantiomers</i>	<u>isomers that are mirror images of each other but cannot be superimposed; exhibit chirality</u>
<i>Chirality</i>	<u>property of a molecule that is not superimposable on its mirror image</u>
<i>Chiral center</i>	<u>atom bonded to four different groups; can be marked by an asterisk (*)</u>

- A carbon atom that is a chiral center is referred to as an asymmetric carbon atom or chiral carbon atom
- Enantiomeric structures represent different substances that can be separated from one another and would not readily convert from one another

<i>Intermolecular forces</i>	<u>any attractive forces between molecules</u>
<i>Viscosity</i>	<u>measure of liquids resistance to flow</u>

CONSEQUENCES OF 3D STRUCTURE: UNEVEN DISTRIBUTIONS OF ELECTRON DENSITY

Polarity...

<i>Pure covalent bond</i>	<u>shared e^- have an equal probability of being near each nucleus</u>
<i>Polar covalent bond</i>	<u>bonding e^- are attracted by one atom more than the other atom</u>
<i>Bond dipole moment</i>	<u>unequal distribution of electron density on two bonded atoms</u>

$$\mu = Qr$$

- ➔ Polarity can be estimated by the difference between the electronegativities of the bonded atoms
- ➔ \uparrow polarity, $\uparrow \Delta EN$, $\uparrow Q$

<i>Dipole-dipole attraction</i>	<u>attractive electrostatic force between polar molecules</u>
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- ➔ The positive end of one molecular dipole interacts with the negative end of another molecular dipole
- ➔ More polar, stronger dipole-dipole attractions

<i>Polar molecules</i>	<u>molecules that have a molecular dipole moment</u>
<i>Nonpolar molecules</i>	<u>molecules that have a zero (or near zero) molecular dipole moment</u>

Functional groups...

<i>Carbonyl group</i>	<u>a carbon atom double bonded to an oxygen</u>
<i>Aldehyde</i>	<u>functional group which the carbonyl carbon is also bonded to a hydrogen</u>
<i>Ketone</i>	<u>functional group consisting of solely the carbonyl group</u>
<i>Ether</i>	<u>functional group centering the $-O-$ bond between two different R groups</u>
<i>Ester</i>	<u>functional group containing a carbonyl group with a second oxygen atom single bonded to the carbonyl carbon and also single bonded to another carbon atom</u>
<i>Alcohol</i>	<u>functional group containing a hydroxyl group ($-OH$) covalently bonded to a carbon atom</u>
<i>Addition reaction</i>	<u>all atoms contained in the reactant molecules are contained in the product molecule</u>

Hydrogen bonding...

<i>Hydrogen bonding</i>	<u>the interaction between an $X-H$ covalent bond (X is a highly electronegative atom) and the lone pair on an electron rich atom Z</u>
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- ➔ Strong hydrogen bonding occurs between $F-H$, $O-H$, $N-H$, and an e^- lone pair on another F , O , N atom (these are among the most electronegative atoms on the periodic table)
- ➔ Has about 5 – 10% the strength of a typical covalent bond

More functional groups...

<i>Carboxylic acid</i>	<u>functional group $-COOH$; hydroxyl group linked to a carbonyl carbon atom</u>
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- ➔ Different from an ester because its bonded to a hydrogen atom and is found at the end of a molecule

<i>Amine</i>	<u>functional group that's a derivative of ammonia that contains one or more carbon-nitrogen bonds</u>
<i>Amide</i>	<u>functional group that contains a nitrogen atom connected to the carbon atom of the carbonyl group</u>

POLYMERS ARE MACROMOLECULES

<i>Polymers</i>	<u>large molecules made by covalently linking many small molecules</u>
<i>Monomer</i>	<u>the small molecules that link to form a polymer</u>
<i>Addition polymer</i>	<u>made by addition reactions, where two molecules combine to form a single product molecule</u>
<i>Cross-link</i>	<u>a covalent σ bond between two separate polymer strands; <i>not</i> at the end of either strand</u>

- ➔ Increase molecular weight and limits motions of polymer strands with respect to one another
- ➔ Since they are covalent bonds, they are typically stronger than IMFs between polymer chains and therefore amplify the effect of increasing IMFs on polymer properties

Examples of addition reaction...








Monomer	Common Name	Polymer	Physical Property	Some Typical Uses
	Ethylene	Polyethylene	Varied depending on branching/density	Packaging films, toys, bottles, coatings, water pipes
	Propylene	Polypropylene (Herculon)	Usually tough and flexible, similar to HDPE	Hinges, molding, rope, outdoor carpeting
	Styrene	Polystyrene (Styrofoam, Styron)	Hard and rather brittle	Transparent containers (such as Petri dish), plastic glasses, styrofoam
	Vinyl chloride	Polyvinyl chloride (PVC)	Hard, moderately tough, can be rigid or flexible	Pipe and tubing, raincoats, phonograph records, floor tiles
	Tetrafluoroethylene	Polytetrafluoroethylene (Teflon)	Hard and tough	Nonstick pan coatings, bearings, gaskets
	Vinyl acetate	Polyvinyl acetate	Highly branched, not solid at room temperature	Elmer's glue, wood glue
	Methyl methacrylate	Polymethyl methacrylate (Plexiglass, Lucite)	Hard and brittle, but can be modified to be more shatter-resistant	Stiff plastic sheets, blocks, tubing, and other shapes

Table: Monomers for Some Common Addition Polymers

Copolymers and condensation polymers...

<i>Copolymers</i>	<u>made by polymerizing a mixture of two or more monomers</u>
<i>Condensation polymer</i>	<u>a polymer formed in a condensation reaction</u>
<i>Polyester</i>	<u>a polymer where the individual units are held together by ester linkages</u>
<i>Polyamide</i>	<u>a polymer where the individual units are held together by amide linkages</u>

BIOLOGICALLY RELEVANT MOLECULES

Proteins...

<i>Proteins</i>	<u>condensation polymers amino acids</u>
<i>Amino acids</i>	<u>carbon atom bonded to a hydrogen atom, amine group, carboxylic acid group, and an R group often on the side of the chain; referred to the protein backbone</u>
<i>Primary structure</i>	<u>sequence in which the amino acids are linked</u>
<i>Secondary structure</i>	<u>pattern of hydrogen bonds between non-adjacent backbone amide group</u>
<i>α-helix</i>	<u>regular pattern of hydrogen bonding between backbone amide group</u>
<i>β-sheet</i>	<u>structures of pattern chain connected side-by-side by hydrogen bonds between backbone amide group</u>
<i>Tertiary structure</i>	<u>overall 3D shape of the protein</u>

Primary forces that stabilize a proteins 3D structure...

- ➔ Keeping hydrophobic side chains away from water as much as possible
- ➔ Maximizing LDFs by minimizing open spaces in the interior of the proteins
- ➔ Maximizing hydrogen bonding
- ➔ Attractions between negatively and positively charged sites formed when acidic and basic side chains lose or gain H^+ ions
- ➔ Formation of *d*-sulfide bonds

DNA and Lipids...

<i>Deoxyribonucleic acid (DNA)</i>	<u>two polymer strands that coil around each other forming a double helix</u>
<i>Nucleotides</i>	<u>monomer units of DNA strands; a phosphate group and nucleo-base attached to a sugar (deoxyribose)</u>
<i>Glycolipids</i>	<u>composed of glycerol and fatty acids</u>
<i>Glycerol</i>	<u>three C atoms each bonded to $-OH$ (hydroxyl group)</u>
<i>Fatty acids</i>	<u>long, unbranched hydrocarbon chains with a carboxylic acid and atomic end</u>
<i>Fats</i>	<u>glycolipids with higher melting points usually solid at room temperature (also called waxes)</u>
<i>Oils</i>	<u>glycolipids with lower melting points usually liquid at room temperature</u>

PHASE CHANGES AND ENERGY FLOWS

Energy and enthalpy...

<i>Thermal energy</i>	<u>kinetic energy associated with random motion of atoms and molecules</u>
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- When thermal energy is transferred into an object, its atoms move faster on average (higher KE_{avg}), the objects temperature increases

<i>Heating</i>	<u>q; transfer of thermal energy between two samples of matter at different temperatures</u>
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- Heat transfer occurs until thermal equilibrium is achieved

<i>Specific heat capacity</i>	<u>c; heating required to move the temperature of 1g of substance by 1°C</u>
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$$q = mc\Delta T = mc(T_f - T_i)$$

- $\Delta T < 0 \rightarrow q < 0 \rightarrow$ substance is being cooled
 → $\Delta T > 0 \rightarrow q > 0 \rightarrow$ substance is being heated

<i>System</i>	<u>the substance undergoing a physically or chemical change</u>
<i>Surrounding</i>	<u>everything else that can exchange energy with the system</u>
<i>Exothermic process</i>	<u>heat transfer from the system to the surroundings</u>
<i>Endothermic process</i>	<u>heat transfer from the surroundings to the system</u>
<i>Enthalpy</i>	<u>H; energy transfer that accumulate physical and chemical changes</u>

- If pressure is constant, $\Delta H = q$

Solutions...

<i>Solution</i>	<u>homogenous mixture of two or more substances</u>
<i>Miscible</i>	<u>infinite mutual solubility</u>

- For gases, molecules are so far apart so IMFs are negligible

<i>Immiscible</i>	<u>do not mix completely but instead form two separate liquid layers</u>
<i>Hydrophobic</i>	<u>intermolecular attractions of its molecules with water are weak</u>
<i>Hydrophilic</i>	<u>capable of strong intermolecular attractions to water</u>