

1 Molecular Structure

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Electron Delocalization

- Delocalized electrons result from π bonds
- The energy of the real molecule is lower than any resonance structure

Rules For Resonance

- # of unpaired electrons stays constant
- Only proper lewis structures allowed
- All resonance atoms must lie in the same plane
- The contribution made to the actual molecule by any given structure is roughly proportional to that structure's stability
- Separation of charges decreases stability

Two Conditions for Resonance to Occur

- a. A species must contain an atom either with a p orbital or an unshared pair of electrons
- b. That atom must be single bonded to an atom that possesses a double or triple bond
- c. Ring structures must also satisfy Huckel's Rule -- planary monocyclic rings with $4n + 2\pi$ electrons should be aromatic(must display resonance)

Dipole Moment

- $\mu = qd$
- A molecule with polar bonds may or may not have a dipole moment
- Intermolecular attractions- occur solely due to dipole moments
- Hydrogen Bond - strongest kind of intermolecular bond

Conformational Isomer

- Are not true isomers but are actually different spatial orientations
- Atoms rotate rapidly about their σ -bond
- Simplest way to distinguish between conformers is with Newman projections
- Gauche, antistaggered, fully eclipsed, eclipsed

Structural Isomer

- Have the same molecular formula but different bond-to-bond connectivity
 - Ex. isobutane and *n*-butane

Stereoisomers

- If two unique molecules have the same molecular formula and the same bond-to-bond connectivity, they are stereoisomers
- Unless they are geometric isomers, stereoisomers must each contain at least one chiral center in the same location
- Two types: enantiomers and diastereomers

Enantiomers

- Mirror images; must have opposite absolute configurations at each chiral carbon
- Resolution - separation of enantiomers
- Have same chemical and physical characteristics except for two cases: 1) reactions with other chiral compounds 2) reactions with polarized light

Diastereomers

- Have the same molecular formula, have the same bond-to-bond connectivity, are not mirror images to each other, and are not the same compound
- Geometric Isomers
 - exist due to hindered rotation about a bond
 - Cis - same-side substituents
 - ★ □ Have a dipole moment and therefore have stronger intermolecular bonds and higher boiling points
 - Due to their lower symmetry they don't form crystals as readily and thus have lower melting points

- Steric hindrance from groups crowding each other produce higher energy levels resulting in higher heats of combustion
 - Trans - opposite-side substituents
 - Do not have a dipole moment
 - Geometric isomers have different physical properties
 - E - unambiguous way to describe cis/trans for tri/tetra substituted alkenes
 - If highest priority substituent on each carbon are on opposite sides they are E
 - Z - same side
- Diastereomers have different physical properties(rotation of plane-polarized light, melting points, boiling points, solubilities, etc.). Their chemical properties also differ.
- The maximum number of optically active isomers a single compound can have = 2^n
- Meso Compounds
 - two chiral centers in a single molecule may offset each other creating an optically inactive molecule called meso compounds
 - Have a plane of symmetry through their centers which divides them into two halves that are mirror images to each other
- Epimers
 - Diastereomers that differ at only one chiral carbon
 - If ring closure occurs at the epimeric carbon then you have anomers

Chirality

- Any carbon is chiral when it is bonded with four different substituents

Absolute Configuration

- In order to determine the configuration of a given molecule the largest atomic weight is given the highest priority
- If two atoms have the same priority you look at the atoms attached to them
- Substituents on double and triple bonds are counted as two or three of those molecules...so a double bond to an oxygen counts as two single bonds to two oxygens
- THEN, rotate the molecule so the lowest priority is in the back
 - A clockwise circle is R, a counterclockwise circle is S
 - The mirror image of a chiral molecule always has the opposite absolute configuration

Relative Configuration

- Is not related to absolute configuration
- Two molecules have the same relative configuration about a carbon if they differ by only one substituent and the other substituents are oriented identically about the carbon. In an S_N2 reaction, it is the relative configuration that is inverted

Observed Rotation

- Direction and the degree to which a compound rotates plane-polarized light

Optically Inactive

- May be compounds with no chiral centers or may be compounds containing equal amounts of both stereoisomers

Optically Active

- Plane-polarized clockwise it is designated with a '+' or a 'D'
- Plane-polarized counterclockwise it is designated with a '-' or an 'L'

Observed Rotation

- Direction and number of degrees that the electric field in plane-polarized light rotates when it passes through a compound

Specific Rotation

- A standardized form of observed rotation that is arrived at through calculations using observed rotation and experimental parameters. Adjust for length of polarimeter, concentration of solution, temperature, and type of wavelength of light used

