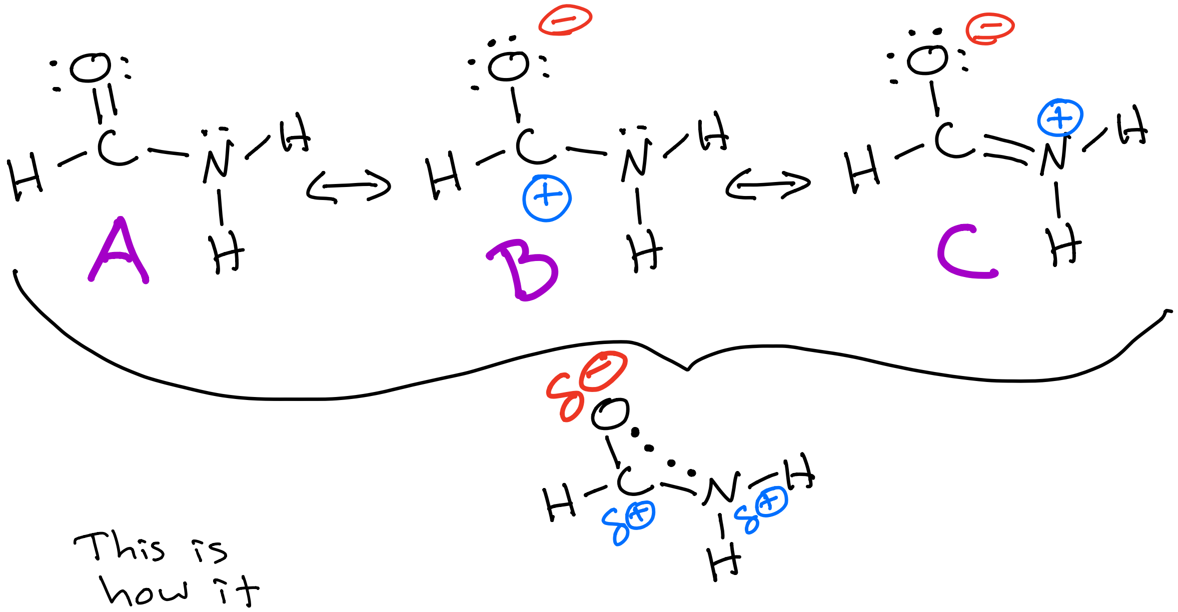
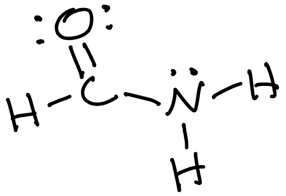
# Amide contributing structures revisited

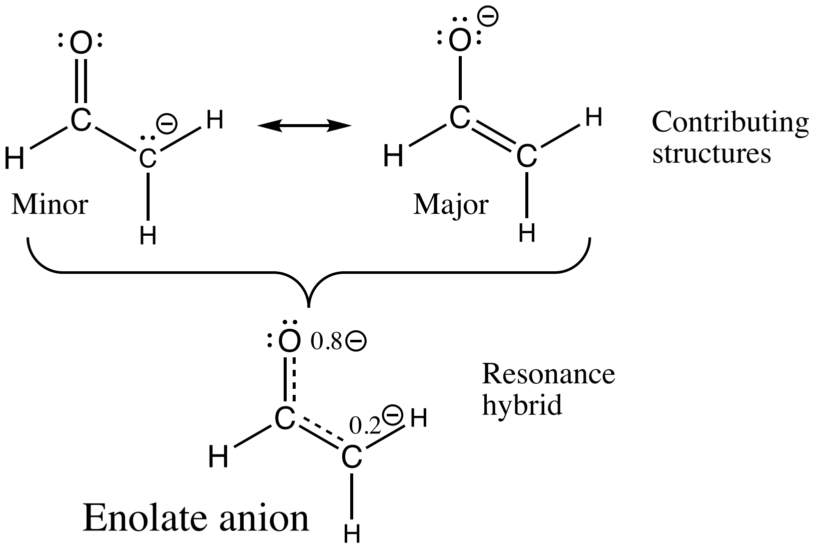


This is how it is drawn, but all 3 contributing structures must be considered ⇒



**5. Delocalization of charge over a larger area is stabilizing.** The majority of molecules you will encounter will be neutral, but some carry negative or positive charges because they contain an imbalance in their total number of electrons and protons. In general, charges are destabilizing (higher Gibbs free energy), increasing the reactivity of the molecules that possess them. Localized charges are the most destabilizing (highest Gibbs free energy). Delocalizing the charge over a larger area through interactions such as resonance, inductive effects, and hyperconjugation is stabilizing (lowering the Gibbs free energy). In addition, it is more stabilizing to have more negative charge on a more electronegative atom (e.g. O), and more positive charge on a less electronegative atom (e.g. C).

**7. Delocalization of pi electron density over a larger area is stabilizing.** Pi electron density delocalization occurs through overlapping 2*p* orbitals, so to take part in pi electron density delocalization atoms must be *sp2* or *sp* hybridized and reside in the same plane. Pi electron delocalization can involve even large numbers of such atoms. Pi electron density cannot delocalize onto or through *sp3* hybridized atoms because an *sp3* atom has no 2*p* orbital. Aromaticity is a special type of pi electron density delocalization involving rings and a specific number of pi electrons, and is the most stabilizing form of pi electron density delocalization.



Enolate anion

**Molecular Orbital Theory** approach to bonding: Just add the individual orbital wave functions:

$$\Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz} + \Psi_{O1s} + \Psi_{O2s} + \Psi_{O2px} + \Psi_{O2py} + \Psi_{O2pz}$$

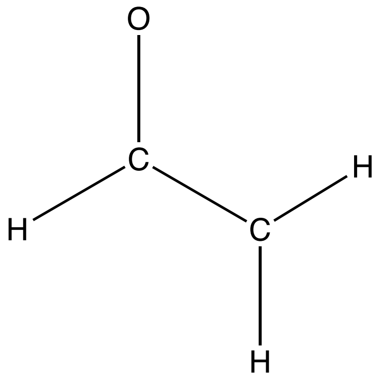
**Valence Bond Theory** approach to bonding: Hybridize the atomic orbitals on atoms first, then look for overlap with remaining orbital wave functions:

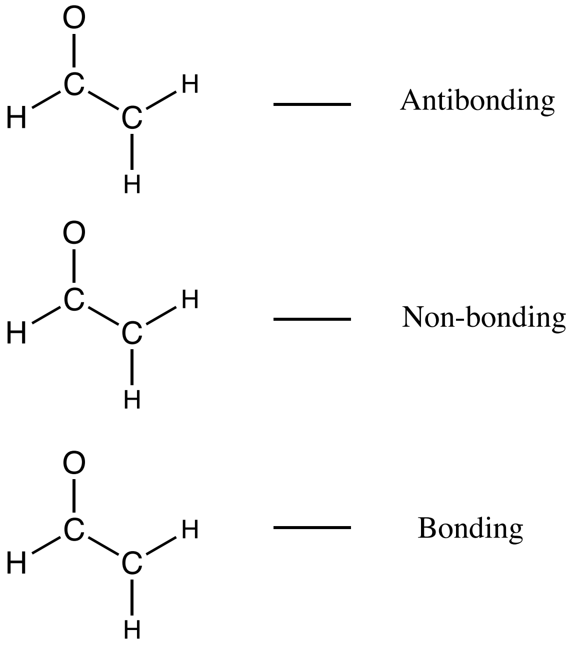
$$\Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py}) + \Psi_{C2pz} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py}) + \Psi_{C2pz} + \Psi_{O1s} + (\Psi_{O2s} + \Psi_{O2px} + \Psi_{O2py}) + \Psi_{O2pz}$$

Sigma (σ) bonding - overlap of hybridized orbitals

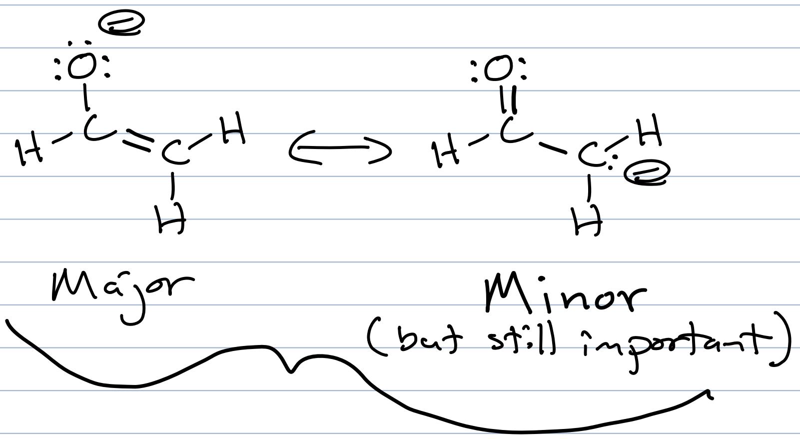
π-way bonding - overlap of 3 adjacent unhybridized 2p orbitals

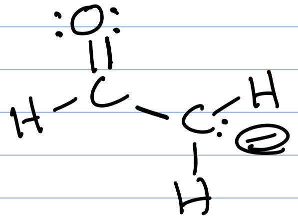
$$\Psi_{C2pz} + \Psi_{C2pz} + \Psi_{O2pz}$$

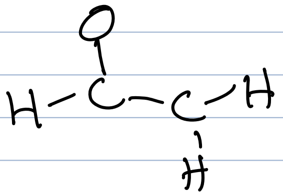




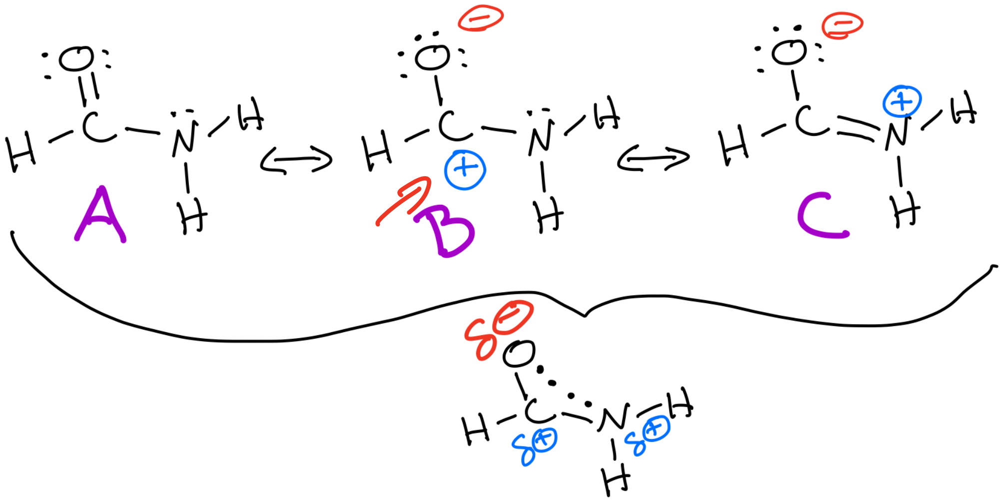
# Enolate ion contributing structures

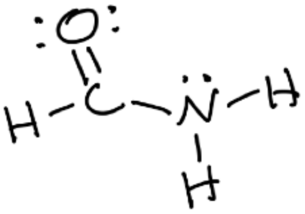






# Amide contributing structures

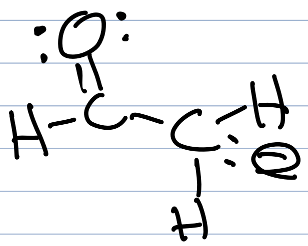


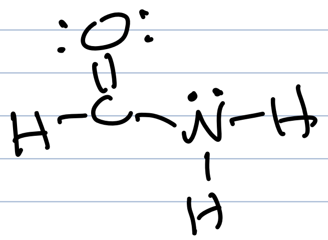


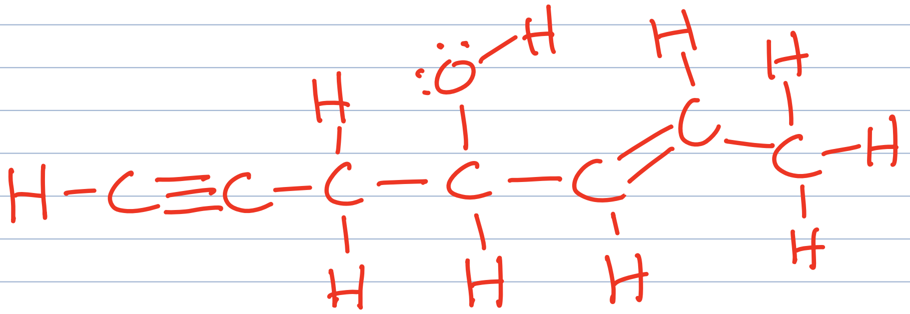
Survival skill in OChem

↳ Identify hybridization state of atoms in molecules

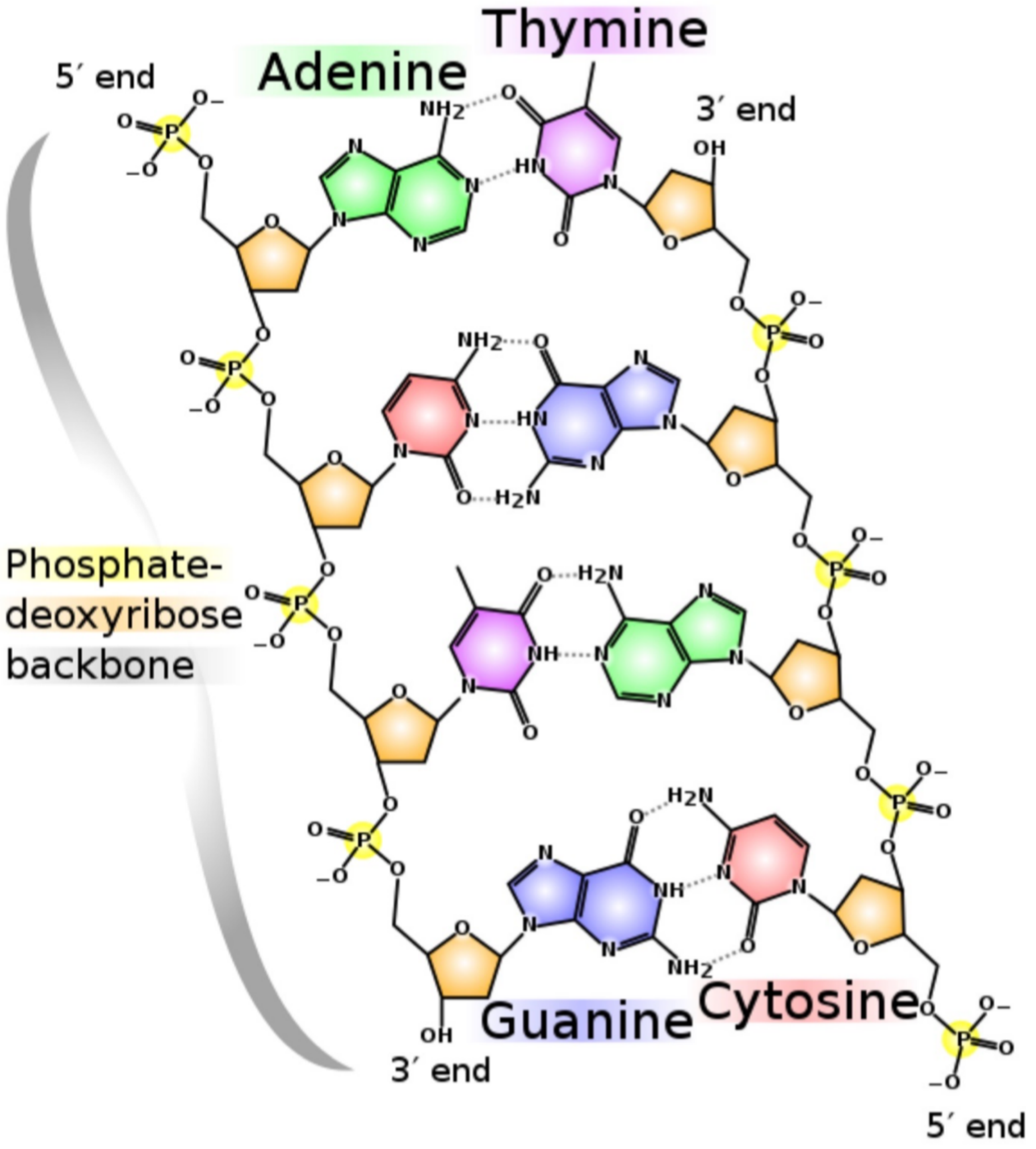
⇒ An atom counts as having a π bond



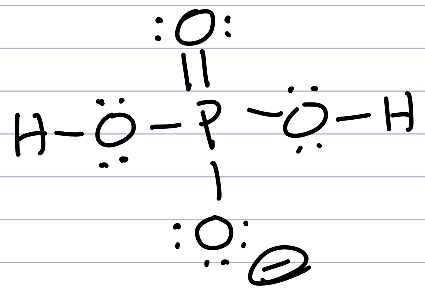




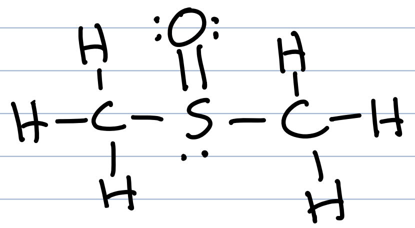
From Wikipedia 9/2020



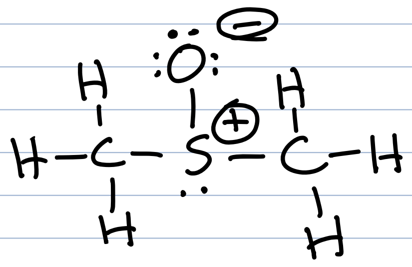
Chemical structure of DNA; hydrogen bonds shown as dotted lines



vs.



vs.



All of these
are
$C_5H_{12}$

Constitutional isomers →

$C_4H_{10}O$ → Constitutional Isomers

# Nomenclature of molecules

2 systems → Common names → existed
before systematic names

IUPAC → systematic naming process
for structures

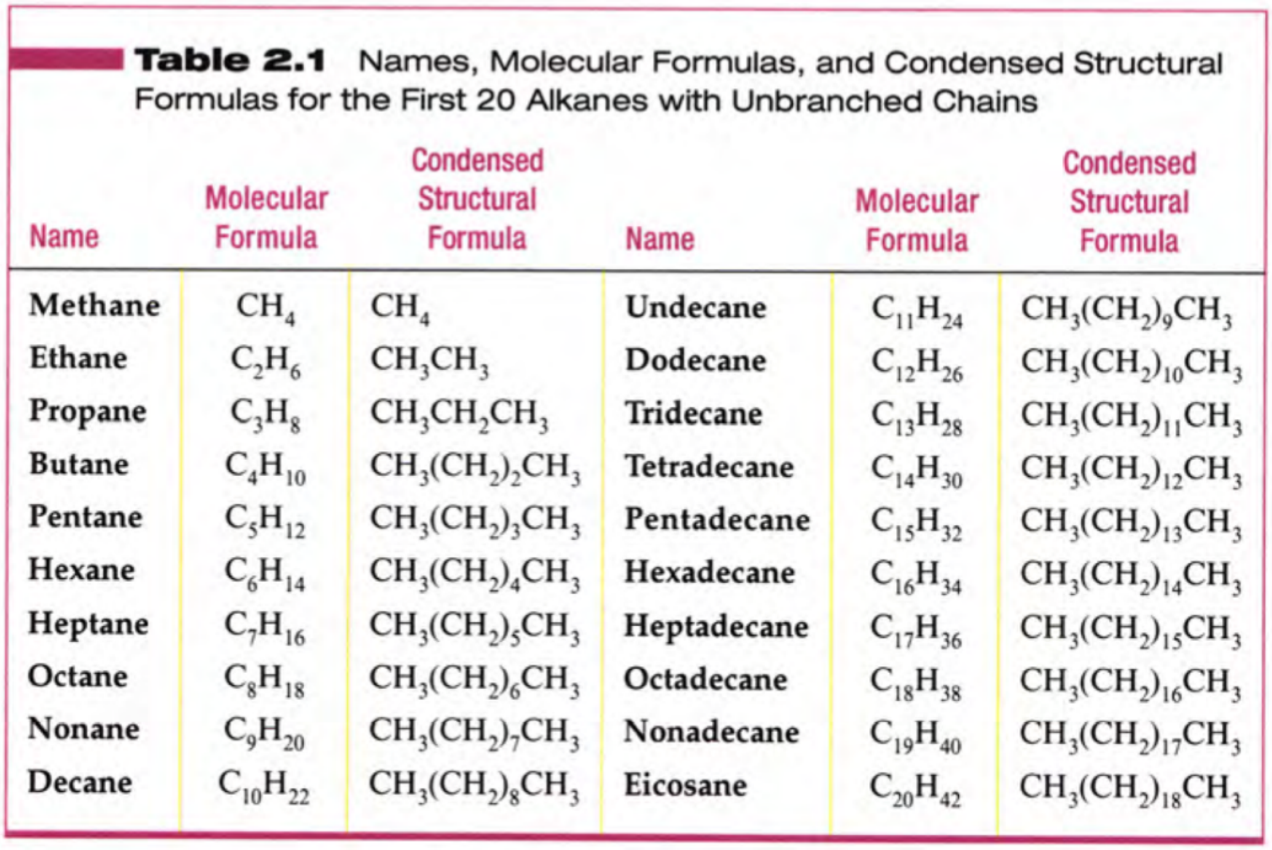


**Table 2.1** Names, Molecular Formulas, and Condensed Structural Formulas for the First 20 Alkanes with Unbranched Chains

| Name | Molecular Formula | Condensed Structural Formula | Name | Molecular Formula | Condensed Structural Formula |
|---|---|---|---|---|---|
| **Methane** | $CH_4$ | $CH_4$ | **Undecane** | $C_{11}H_{24}$ | $CH_3(CH_2)_9CH_3$ |
| **Ethane** | $C_2H_6$ | $CH_3CH_3$ | **Dodecane** | $C_{12}H_{26}$ | $CH_3(CH_2)_{10}CH_3$ |
| **Propane** | $C_3H_8$ | $CH_3CH_2CH_3$ | **Tridecane** | $C_{13}H_{28}$ | $CH_3(CH_2)_{11}CH_3$ |
| **Butane** | $C_4H_{10}$ | $CH_3(CH_2)_2CH_3$ | **Tetradecane** | $C_{14}H_{30}$ | $CH_3(CH_2)_{12}CH_3$ |
| **Pentane** | $C_5H_{12}$ | $CH_3(CH_2)_3CH_3$ | **Pentadecane** | $C_{15}H_{32}$ | $CH_3(CH_2)_{13}CH_3$ |
| **Hexane** | $C_6H_{14}$ | $CH_3(CH_2)_4CH_3$ | **Hexadecane** | $C_{16}H_{34}$ | $CH_3(CH_2)_{14}CH_3$ |
| **Heptane** | $C_7H_{16}$ | $CH_3(CH_2)_5CH_3$ | **Heptadecane** | $C_{17}H_{36}$ | $CH_3(CH_2)_{15}CH_3$ |
| **Octane** | $C_8H_{18}$ | $CH_3(CH_2)_6CH_3$ | **Octadecane** | $C_{18}H_{38}$ | $CH_3(CH_2)_{16}CH_3$ |
| **Nonane** | $C_9H_{20}$ | $CH_3(CH_2)_7CH_3$ | **Nonadecane** | $C_{19}H_{40}$ | $CH_3(CH_2)_{17}CH_3$ |
| **Decane** | $C_{10}H_{22}$ | $CH_3(CH_2)_8CH_3$ | **Eicosane** | $C_{20}H_{42}$ | $CH_3(CH_2)_{18}CH_3$ |

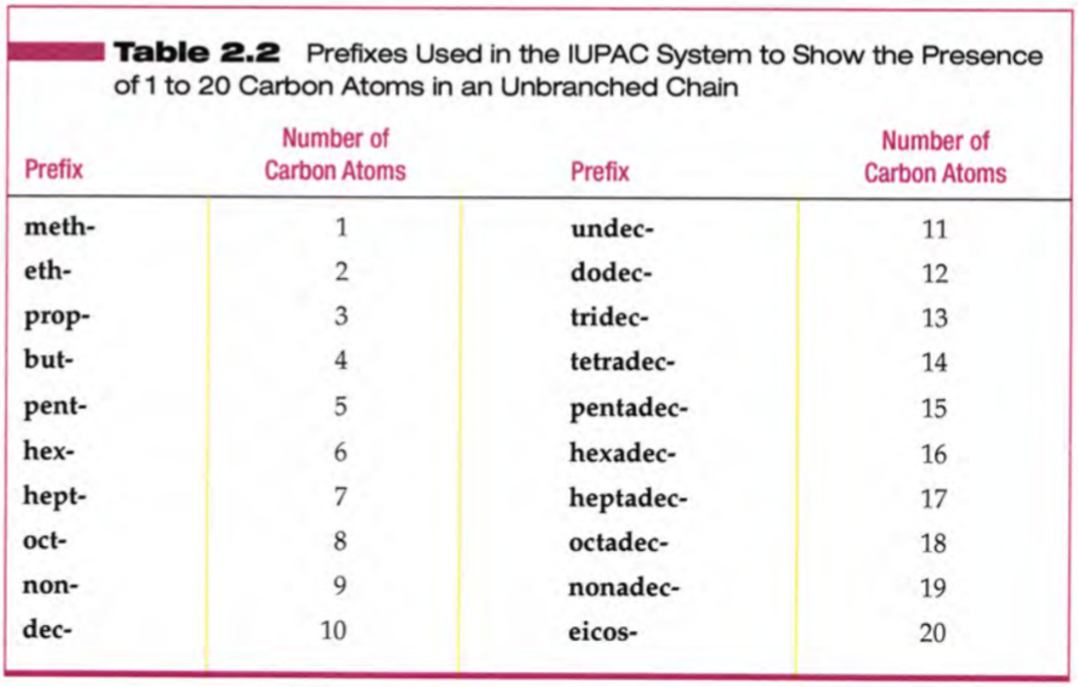


**Table 2.2** Prefixes Used in the IUPAC System to Show the Presence of 1 to 20 Carbon Atoms in an Unbranched Chain

| Prefix | Number of Carbon Atoms | Prefix | Number of Carbon Atoms |
|---|---|---|---|
| meth- | 1 | undec- | 11 |
| eth- | 2 | dodec- | 12 |
| prop- | 3 | tridec- | 13 |
| but- | 4 | tetradec- | 14 |
| pent- | 5 | pentadec- | 15 |
| hex- | 6 | hexadec- | 16 |
| hept- | 7 | heptadec- | 17 |
| oct- | 8 | octadec- | 18 |
| non- | 9 | nonadec- | 19 |
| dec- | 10 | eicos- | 20 |

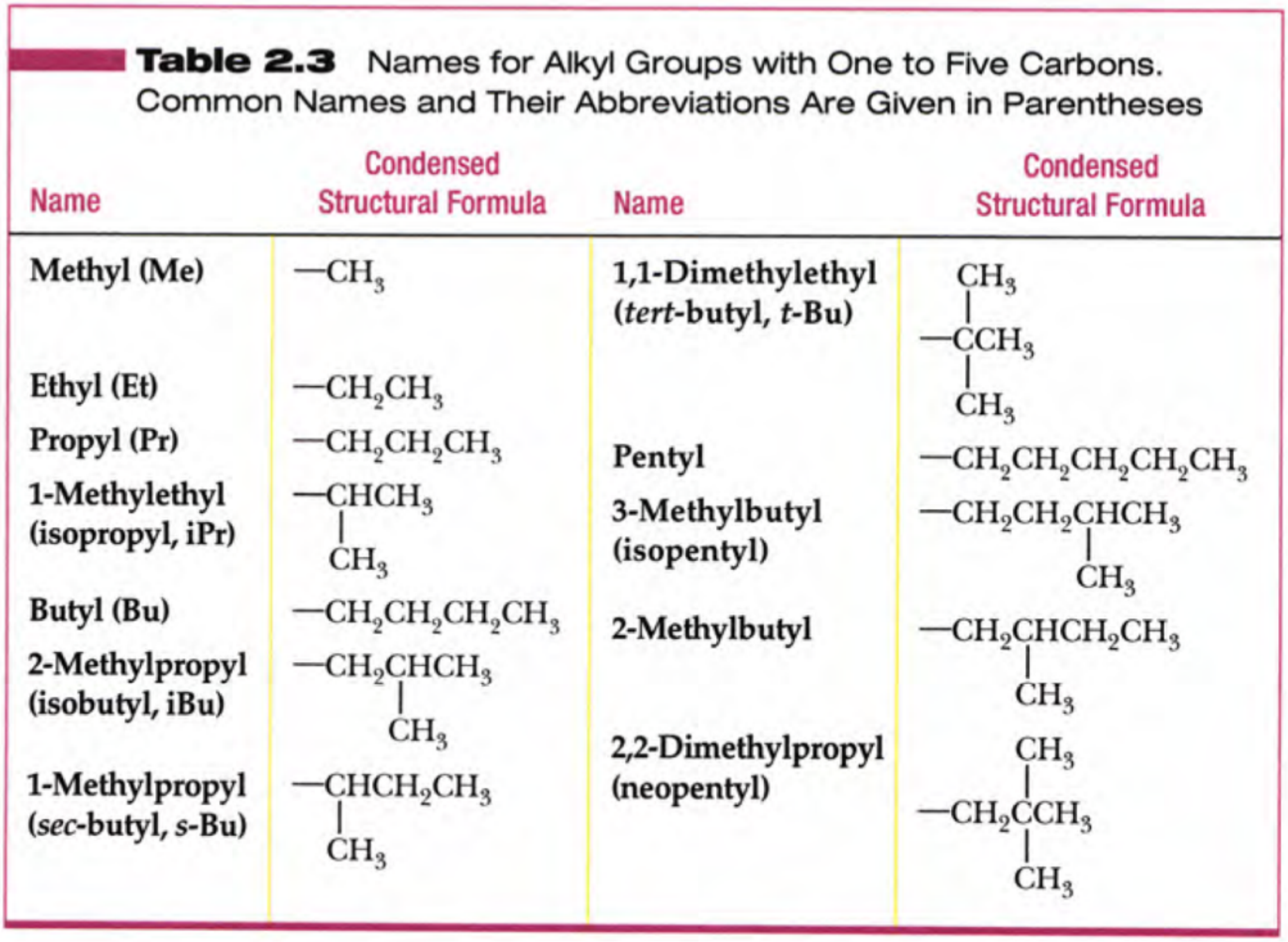


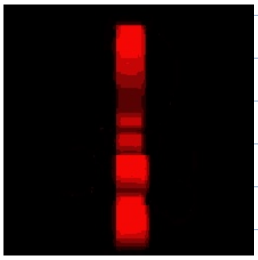
**Table 2.3** Names for Alkyl Groups with One to Five Carbons. Common Names and Their Abbreviations Are Given in Parentheses

| Name | Condensed Structural Formula | Name | Condensed Structural Formula |
|---|---|---|---|
| **Methyl (Me)** | $-CH_3$ | **1,1-Dimethylethyl (*tert*-butyl, *t*-Bu)** | $-\overset{\underset{\vert}{CH_3}}{\underset{\overset{\vert}{CH_3}}{C}}CH_3$ |
| **Ethyl (Et)** | $-CH_2CH_3$ | | |
| **Propyl (Pr)** | $-CH_2CH_2CH_3$ | **Pentyl** | $-CH_2CH_2CH_2CH_2CH_3$ |
| **1-Methylethyl (isopropyl, iPr)** | $-\underset{\overset{\vert}{CH_3}}{C}HCH_3$ | **3-Methylbutyl (isopentyl)** | $-CH_2CH_2\underset{\overset{\vert}{CH_3}}{C}HCH_3$ |
| **Butyl (Bu)** | $-CH_2CH_2CH_2CH_3$ | **2-Methylbutyl** | $-CH_2\underset{\overset{\vert}{CH_3}}{C}HCH_2CH_3$ |
| **2-Methylpropyl (isobutyl, iBu)** | $-CH_2\underset{\overset{\vert}{CH_3}}{C}HCH_3$ | **2,2-Dimethylpropyl (neopentyl)** | $-CH_2\overset{\underset{\vert}{CH_3}}{\underset{\overset{\vert}{CH_3}}{C}}CH_3$ |
| **1-Methylpropyl (*sec*-butyl, *s*-Bu)** | $-\underset{\overset{\vert}{CH_3}}{C}HCH_2CH_3$ | | |

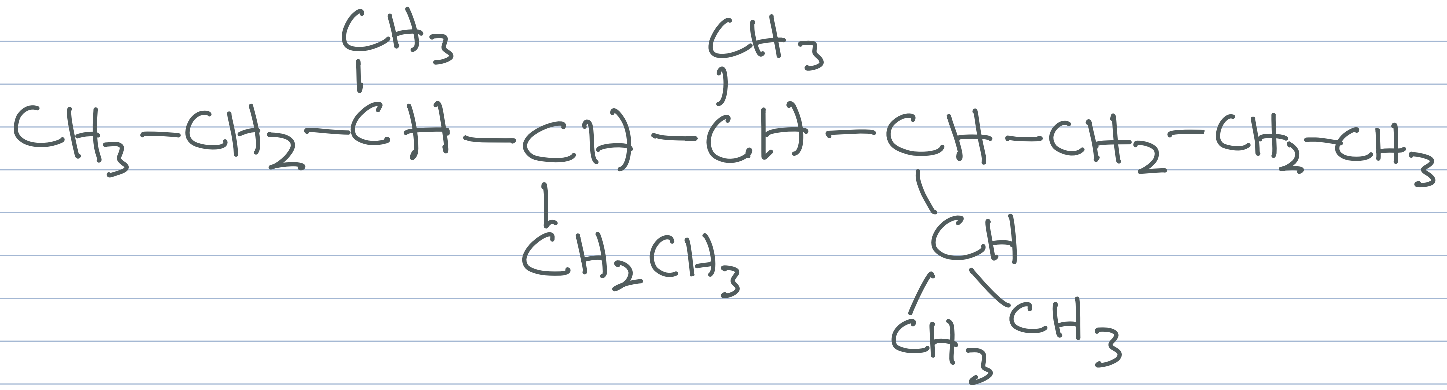
<u>Step 2</u> → Identify the parent chain then number it.

Step 3 → Name the substituents →
changing "ane" to "yl"
see Table 2.3

Step 4 → Alphabetize substituents and
list in alphabetical order

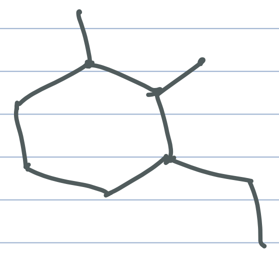


Putting it all together:



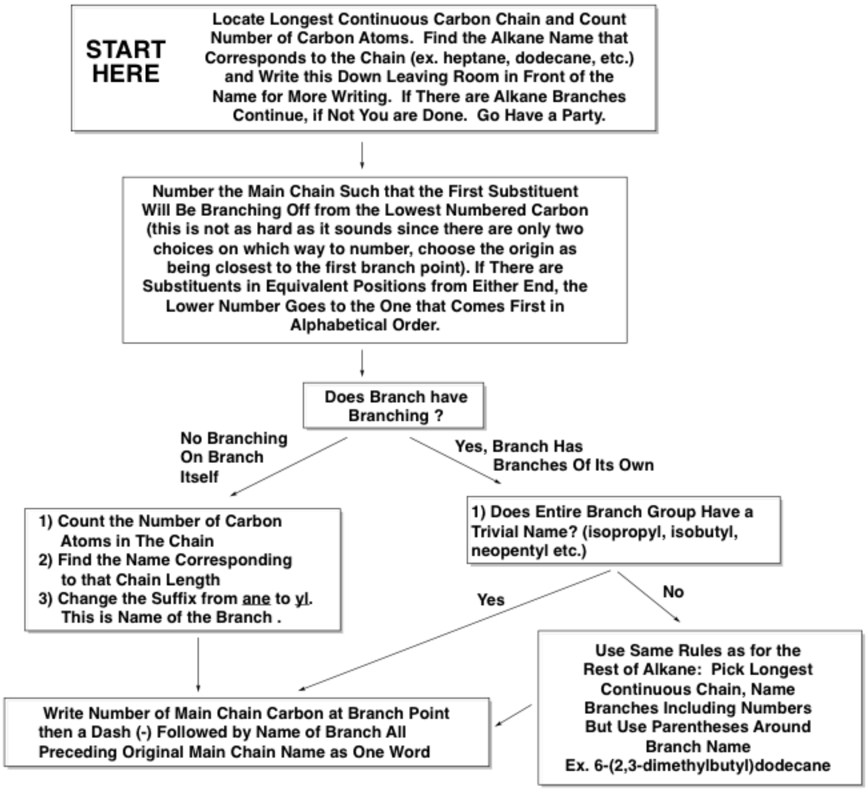
$$CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}H-\underset{CH_2CH_3}{\underset{|}{C}}H-\overset{CH_3}{\overset{|}{C}}H-\underset{\underset{CH_3 \quad CH_3}{CH}}{\underset{|}{C}}H-CH_2-CH_2-CH_3$$

# Cyclic Structures



## IUPAC PROCEDURE FOR NAMING ALKANES

Before you begin you must:
1) Memorize alkane chain names (Table 2.1)
2) Memorize substituent names (Tables 2.2 and 2.3)
*[I apologize on behalf of all chemists for the crazy names you have to memorize. I wish I knew an easier way, but I do not]*



**START HERE**

Locate Longest Continuous Carbon Chain and Count Number of Carbon Atoms. Find the Alkane Name that Corresponds to the Chain (ex. heptane, dodecane, etc.) and Write this Down Leaving Room in Front of the Name for More Writing. If There are Alkane Branches Continue, if Not You are Done. Go Have a Party.

Number the Main Chain Such that the First Substituent Will Be Branching Off from the Lowest Numbered Carbon (this is not as hard as it sounds since there are only two choices on which way to number, choose the origin as being closest to the first branch point). If There are Substituents in Equivalent Positions from Either End, the Lower Number Goes to the One that Comes First in Alphabetical Order.

Does Branch have Branching ?

No Branching On Branch Itself

1) Count the Number of Carbon Atoms in The Chain
2) Find the Name Corresponding to that Chain Length
3) Change the Suffix from <u>ane</u> to <u>yl</u>. This is Name of the Branch .

Yes, Branch Has Branches Of Its Own

1) Does Entire Branch Group Have a Trivial Name? (isopropyl, isobutyl, neopentyl etc.)

Yes

No

Use Same Rules as for the Rest of Alkane: Pick Longest Continuous Chain, Name Branches Including Numbers But Use Parentheses Around Branch Name
Ex. 6-(2,3-dimethylbutyl)dodecane

Write Number of Main Chain Carbon at Branch Point then a Dash (-) Followed by Name of Branch All Preceding Original Main Chain Name as One Word

**ADDITIONAL RULES**

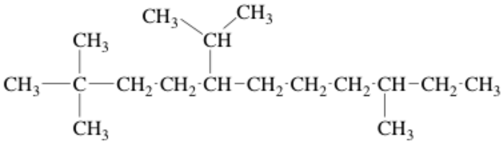
1) If a Molecule Contains Two of the Same Branching Alkyl Groups Use the Prefix <u>di</u>, if Three Use <u>tri</u>, if Four Use <u>tetra</u>, if Five Use <u>penta</u>, if Six Use <u>hexa</u> etc.
Ex. 2,3,4-trimethylhexane

2) If Structure Contains a Ring That Has More Carbon Atoms Than Any Other Open Chain, the Main Chain <u>is the Ring</u> and is Named by Adding <u>cyclo</u> to the Name of the Alkane with the Same Number of Carbon Atoms as the Ring. The Rest is the Same as for Normal Alkane Except You Need to Keep the Total Numbers as Small as Possible When Numbering.
Ex. 1,2-dimethylcyclohexane

3) If More Than One Branch, List Them in Alphabetical Order, NOT Numerical Order.
Ex. 5-ethyl-3,4-diisopropyl-7-methyldecane

4) DO NOT Include the Italicized Prefixes *n*-, *sec*-, and *tert*- OR the Mulitplying Prefixes di, tri, tetra, etc. When Alphabetizing Simple Substitutents. All Other Prefixes (iso, neo, etc.) are Included When Alphabetizing Simple Substituents. No Need to Argue, I Did Not Invent TheseRules!
Ex. 5-*tert*-butyl-2-methyldecane

Big Old Hairy Example:



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2{\cdot}CH_2{\cdot}\overset{CH(CH_3)_2}{CH}-CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}\underset{CH_3}{CH}-CH_2{\cdot}CH_3$$

**5-Isopropyl-2,2,9-trimethylundecane**

What you need to know

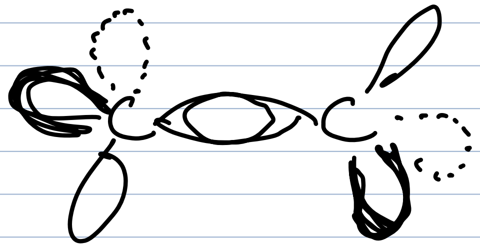
Important concept → Energy and stability are relative terms that are related to each other →

A molecule

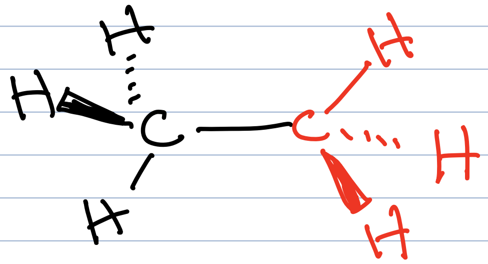
A molecule

<u>Strain</u>

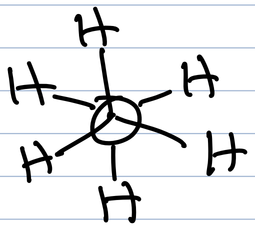
Carbon-Carbon sigma bonds rotate rapidly at room temperature

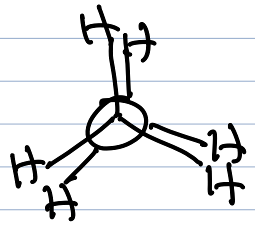


Newman Projection



Two extremes





Torsional Strain ⟶