Organic Chemistry 1
Lecture 3

Instructor: Prof. Duncan Wardrop

Time/Day: T & R, 12:30-1:45 p.m.

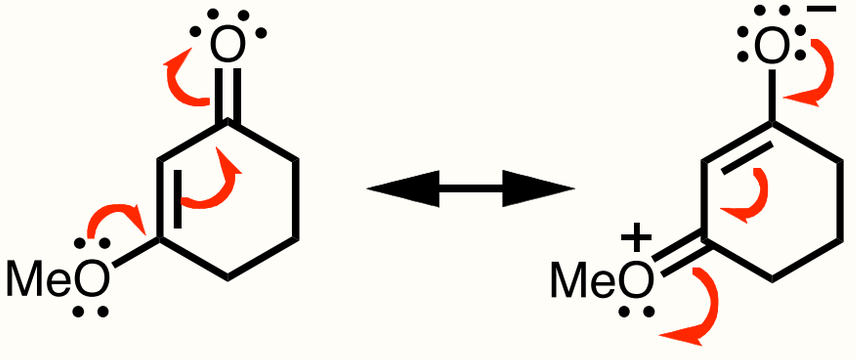
January 19, 2010

Lecture Summary

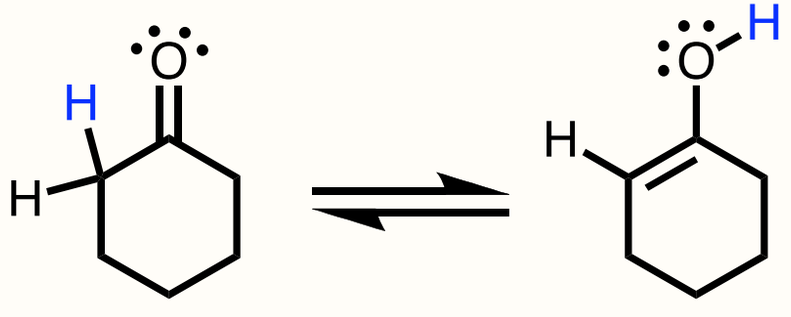
- ☑ Revision & Proof of Resonance
- ☑ Introduction to Hydrocarbons
  - ☑ Classification
  - ☑ Structure & Bonding
- ☑ Nomenclature

Revision of Resonance

Do not confuse equilibrium with resonance: double-headed arrows represent resonance contributors; two separate arrows represent the equilibrium of *distinct* chemical species....



Resonance
(electrons move)



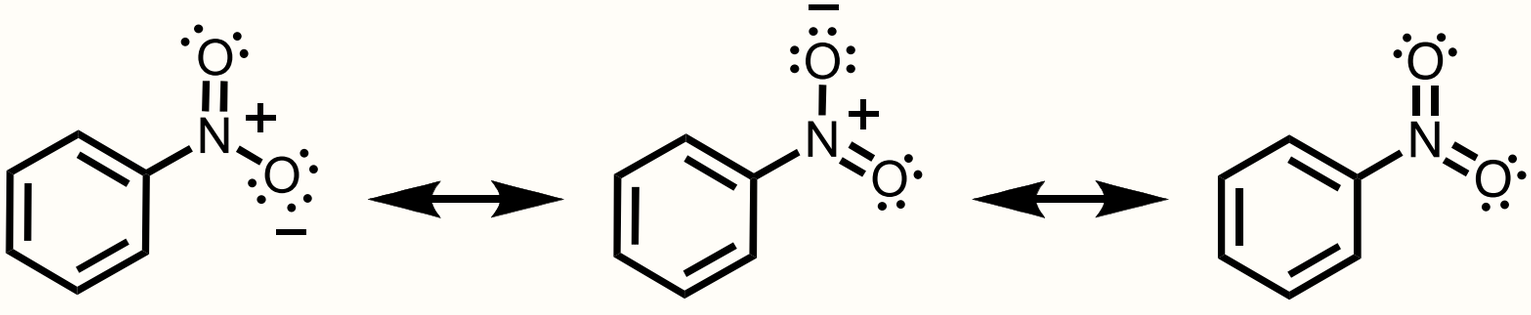
Equilibrium
(atoms move)

The first pair of structures are descriptions of the same molecule - the overall description is based on a weighted combination of the two extremes. The second pair of structures are distinct molecules: one is a ketone and the other an enol. For more details about this chemical transformation, see Chapter 18.

Prioritizing Resonance Contributors (How much Unicorn?!)

Priority 1

No first-row elements (B, C, N, O) can have more than eight electrons in its valence shell.....



Equal Contributor

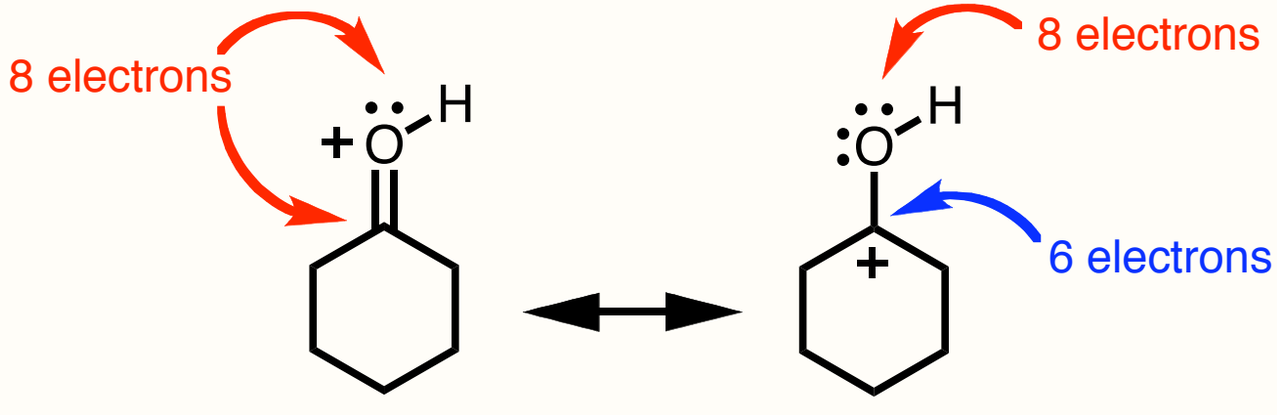
Equal Contributor

Non-Permissable Contributor (N has 10 elect.)

Prioritizing Resonance Contributors

Priority 2

Resonance structures in which all atoms are surrounded by an octet of electrons are almost always lower in energy than those resonance structures in which one or more atoms are electron deficient.



More Stable

C-O Bond Length
120 pm (C=O)
128 pm (calculated)
143 pm (C-O)

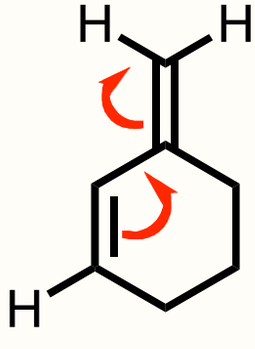
Prioritizing Resonance Contributors

Priority 3

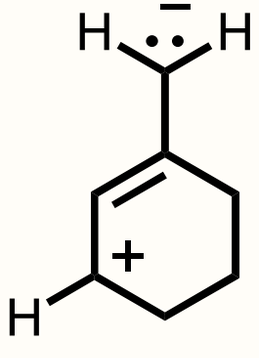
Resonance structures with charge separation are typically higher in energy than those without. If charge separation exists, then electropositive atoms (C, B) are better able to bear +ve charge...

Small Dipole Moment

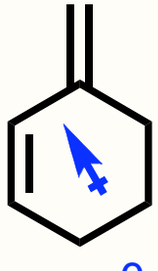
Major Contributor



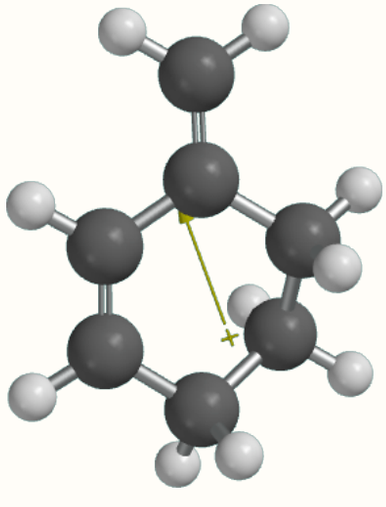
Unimportant Contributor



Physical Evidence



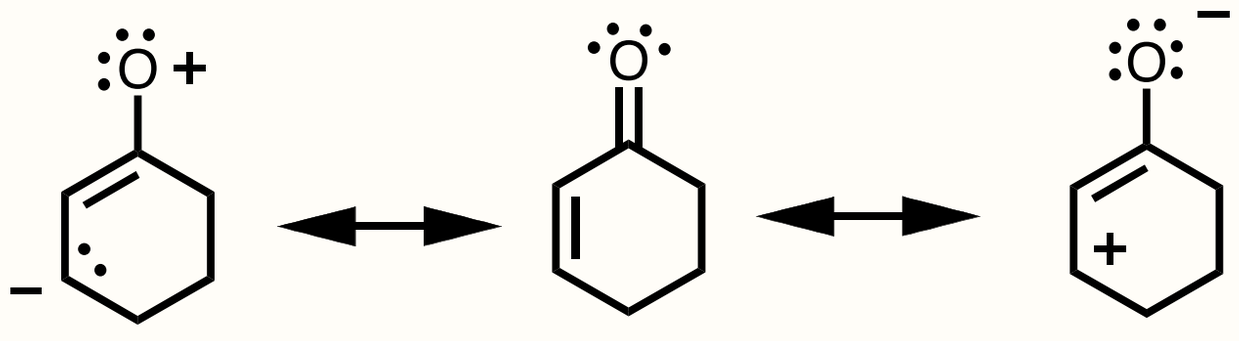
0.66 D



Prioritizing Resonance Contributors

Priority 4

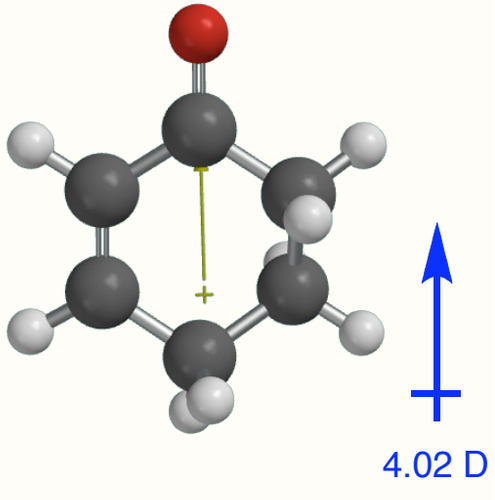
If charge separation exists in a resonance structure, then the electronegative atoms should gain the formal negative charge and vice versa:



Unimportant Contributor

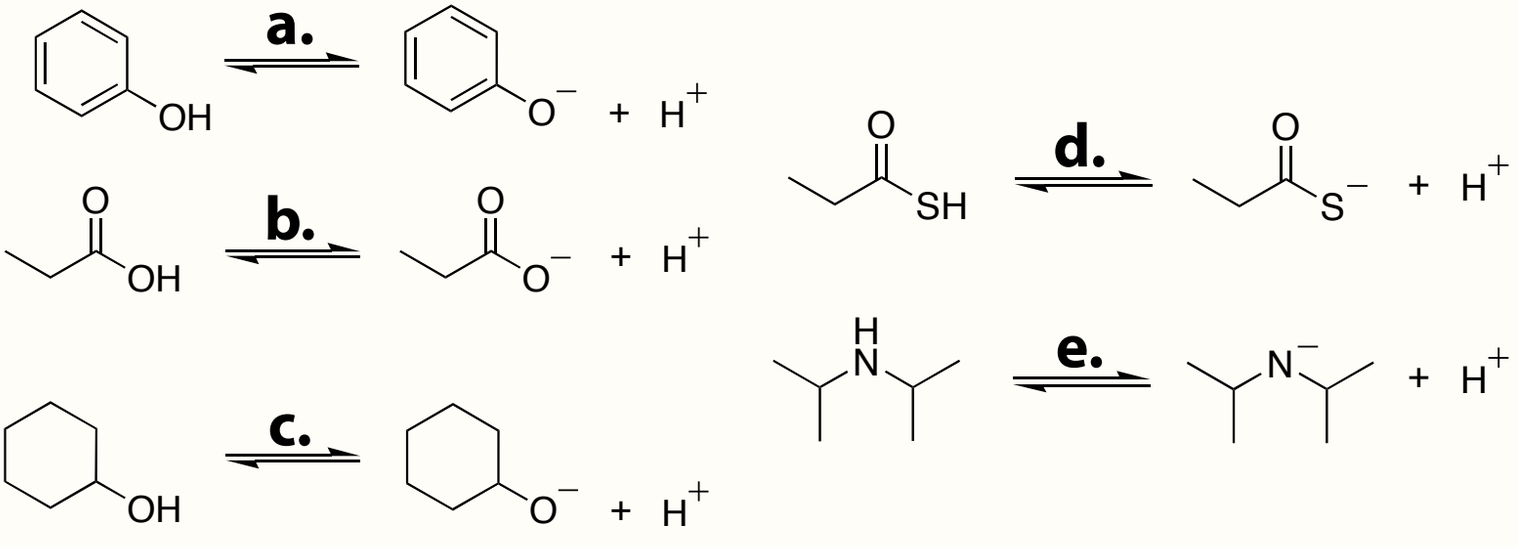
Major Contributor

Minor (but significant) Contributor



Self Test Question

Rank the following acids in order of increasing acidity.

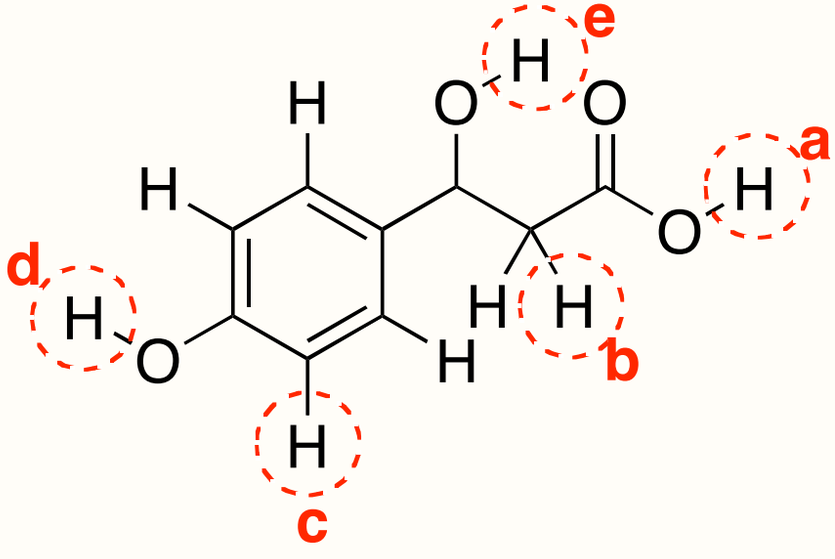


A. a, c, b, e, d
B. e, c, a, b, d
C. c, e, a, d, b
D. b, a, c, d, e
E. d, b, a, c, e

There are a number of structural features which effect the pKa of an acid: a) Electronegativity; b) The strength of the bond to the acidic hydrogen atom; c) Inductive effects; d) Resonance delocalization in conjugate base.

Self Text Question

Which is the *most* acidic proton in the molecule below?



A. a

B. b

C. c

D. d

E. e

Free Organic Chemistry Tutoring in the SLC

Where:
Science & Learning Center (201 SES)

Who:
Dr. Bob Widing

When:
Tuesday & Thursday, 1-5 p.m.
Monday & Wednesday afternoons

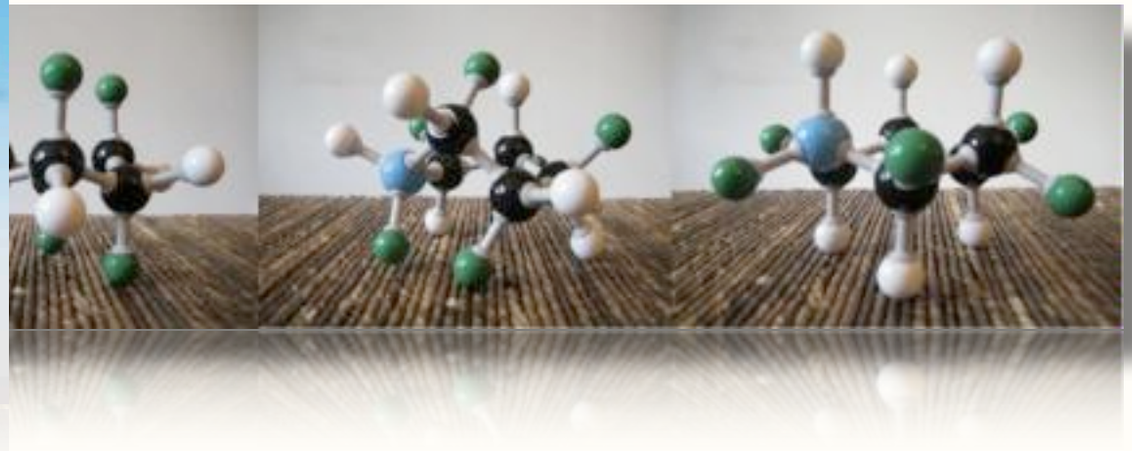
Look for a molecular model set and you'll know you've found the right person. If he's in the SLC, Dr. Widing is willing to help.

Quiz This Week

This will be the last notice about quizzes. You should expect a quiz in your discussion section every week.

- Quiz this week during your discussion section
- Topic = Chapter 1
- Only top ten quiz scores (25 points each) count
- No makeup quizzes; minimum 12 quizzes

Molecular Model Set



- A molecular model set is highly recommended
- Essential for Chapters 3 & 7
- Any set is fine; your preference; available in bookstore
- Bring your set to class and discussion section

Classes, Bonding & Structural Features of Hydrocarbons

Sections 2.1, 2.5-2.10

Classes of Hydrocarbons

Hydrocarbons

- only C & H atoms
- framework for funct. groups
- generally, non-reactive

Aliphatic

- *aleiphar* Greek for "fat"
- sources were fats and oils

Aromatic

- aka: arenes
- many isolated from plants; *impurities* can be fragrant
- aromaticity definiton: Ch. 12

Alkanes

- **only** single bonds
- nomenclature: -ane suffix

Alkenes

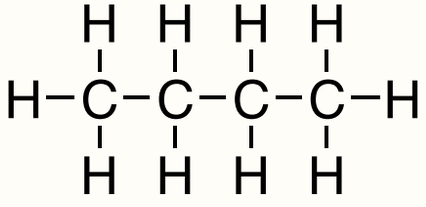
- contain a double bond
- nomenclature: -ene suffix

Alkynes

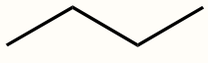
- contain a triple bond
- nomenclature: -yne suffix

Examples of Aliphatic Hydrocarbons

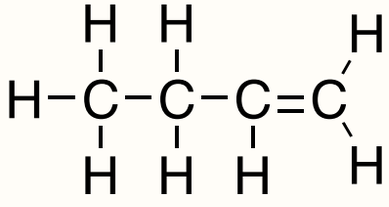
butane



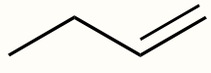
$CH_3CH_2CH_2CH_3$



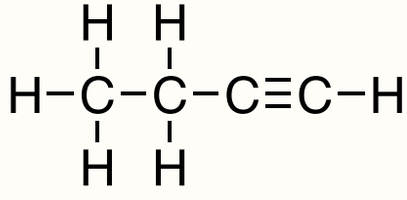
1-butene



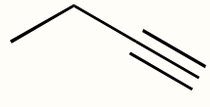
$CH_3CH_2CHCH_2$



1-butyne



CH_3CH_2CCH



Alkanes

- **only** single bonds
- C_nH_{2n+2}
- nomenclature: -ane suffix

Alkenes

- contain a double bond
- C_nH_{2n} (1 double bond)
- nomenclature: -ene suffix

Alkynes

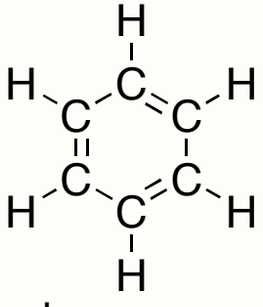
- contain a triple bond
- C_nH_{2n-2} (1 triple bond)
- nomenclature: -yne suffix

Examples of Aromatic Hydrocarbons

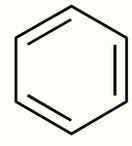
Aromatic

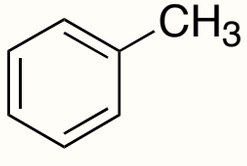
- aka: arenes
- many isolated from plants; impurities were fragrant
- aromaticity definiton: Ch. 12

- many are derivatives of benzene
- resonance: delocalized electrons
- adjacent double bonds
- planar (120° bond angles)
- polyaromatic hydrocarbons (PAHs) contain two or more aromatic rings; highly carcinogenic and environmental toxin

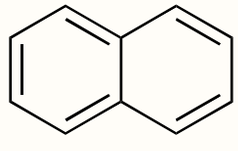


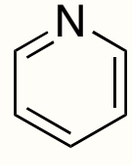
benzene


benzene



toluene

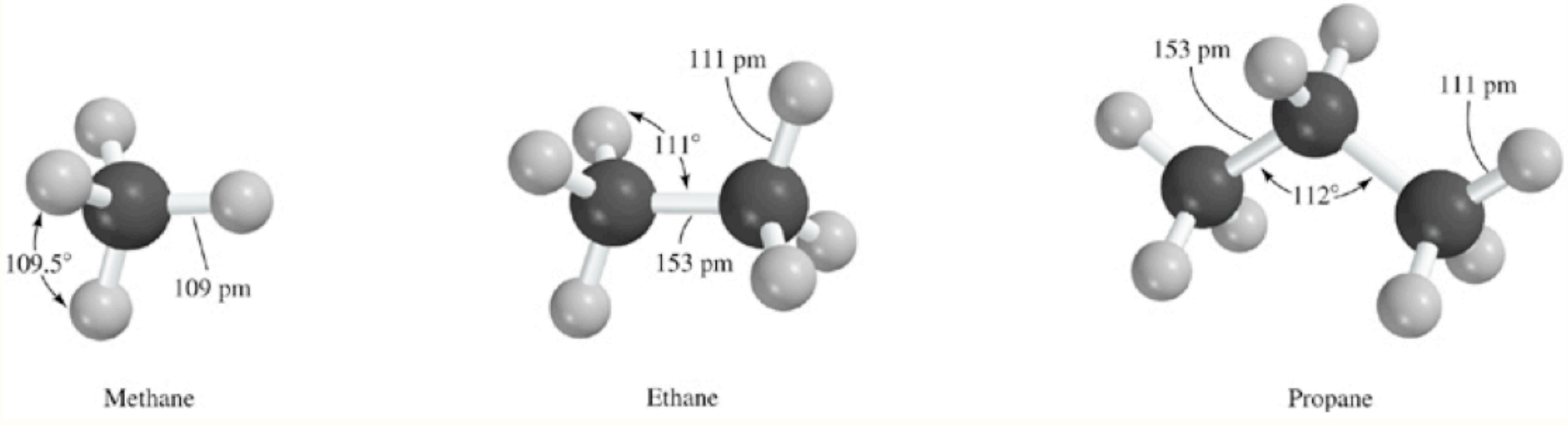

napthalene



pyridine

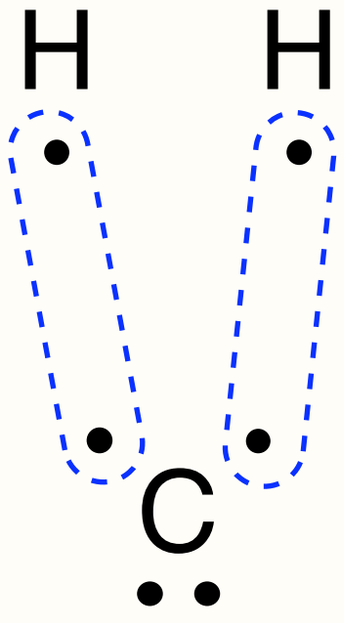
furan

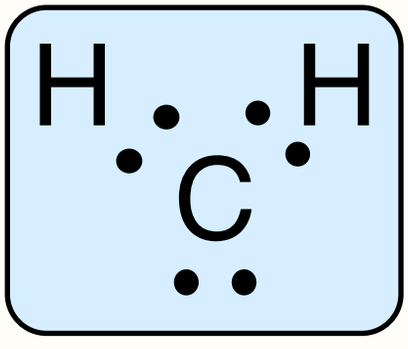
Structural Features of Simple Alkanes

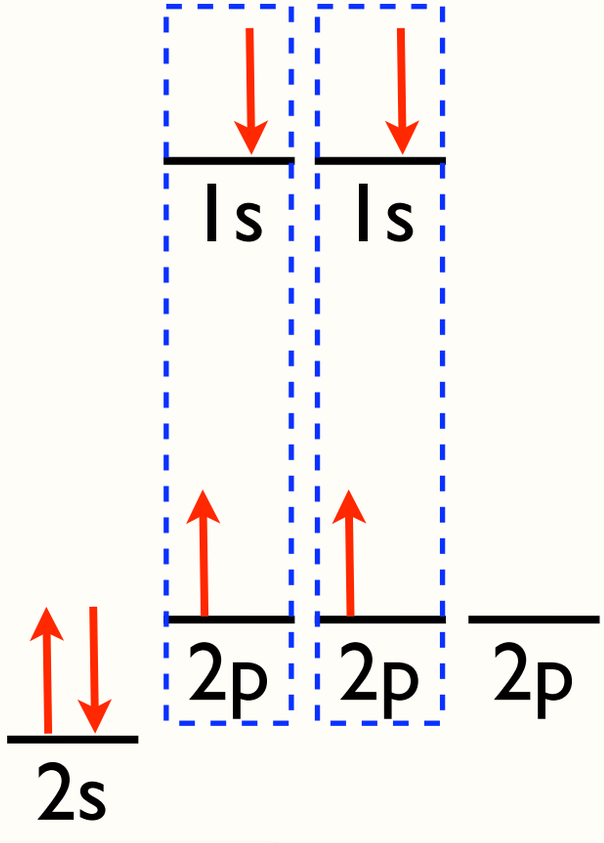


- 4 bonds to carbon, 1 bond to H
- C–H bond length ~ 110 pm
- C–C bond length ~ 153 pm
- all bond angles are nearly tetrahedral

Initial Valence Bond Model of Carbon

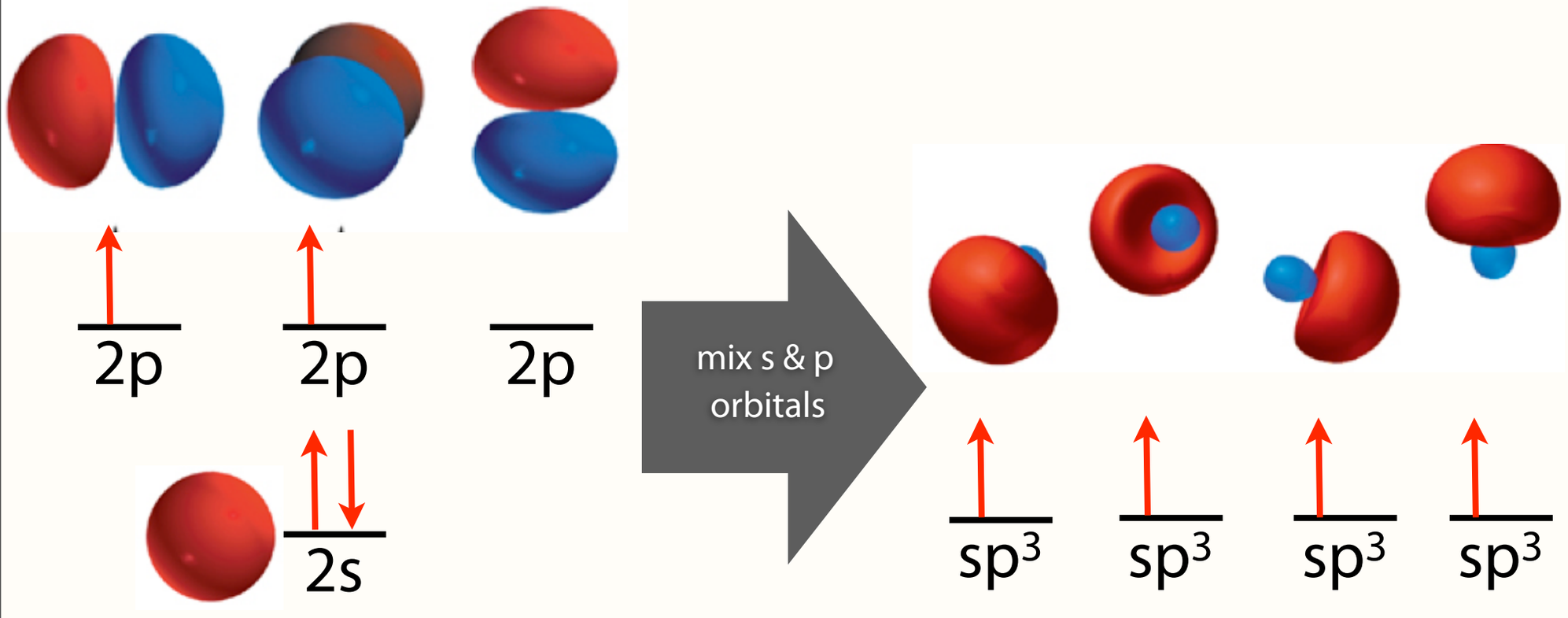






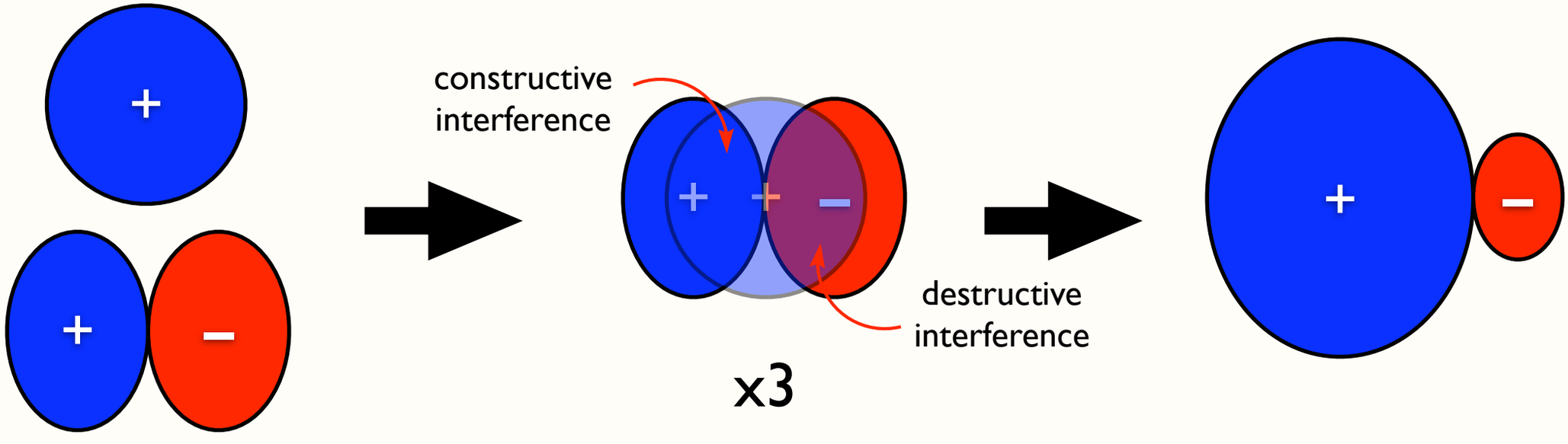
- carbon only has *two* half-filled orbitals
- should, then, form two bonds
- actually forms 4 bonds!?!?

Valence Bond Model: Hybridization



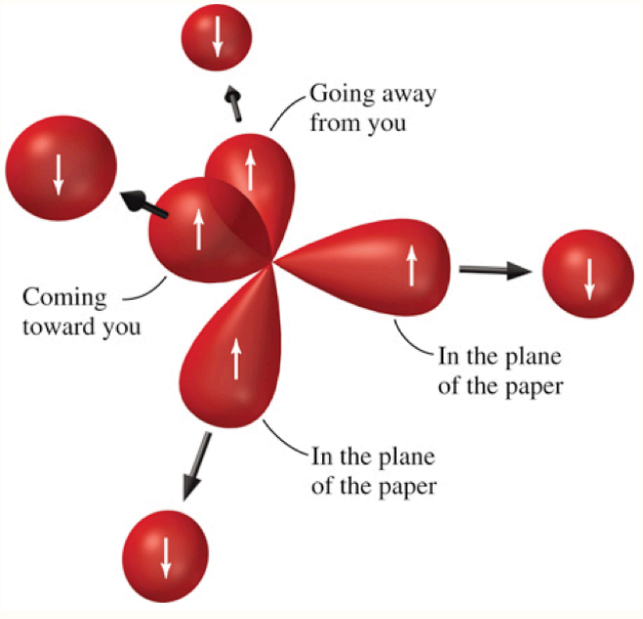
- hybrids: mixture of s & p; sp^3 lower in energy than *p*
- 25% *s*-character and 75% *p*-character
- 4 degenerate orbitals = equal in energy
- each half-filled, can form 4 bonds
- VSEPR: tetrahedral (bond angles = 109.5°)

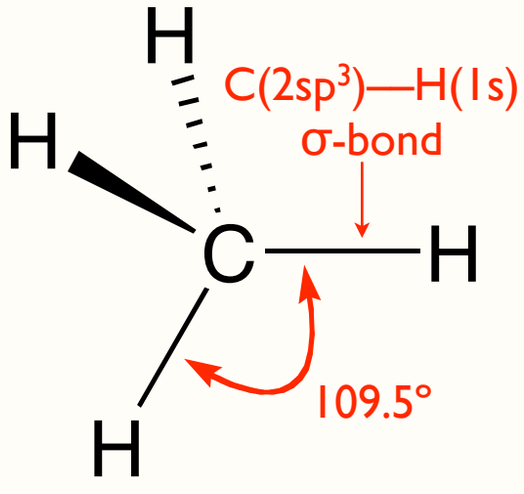
Understanding the Shape of sp^3 Orbitals



- constructive interference: reinforce electron wave where sign is the same
- destructive interference: cancel out wave where sign is opposite
- higher probability of finding an electron on one side of the nucleus

Sigma Bonds (σ-bond) in Methane





= group is pointing toward you, in front of the plane of paper

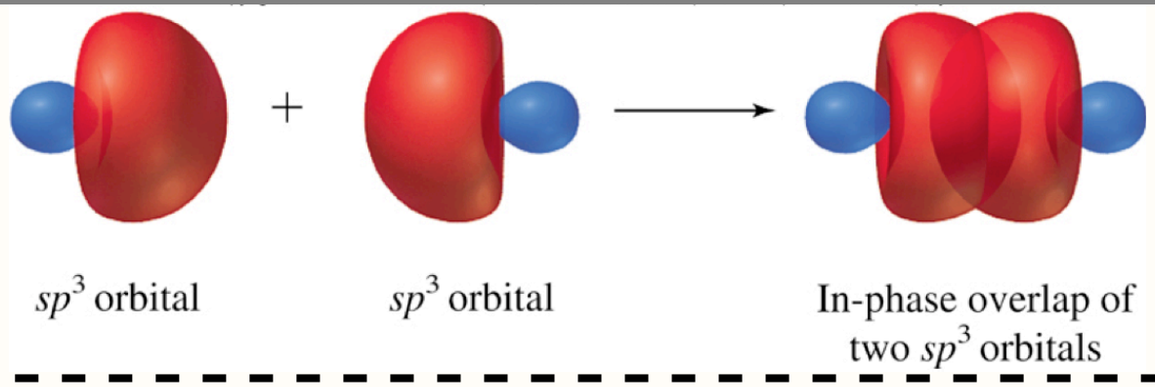
= group is pointing away from you, behind the plane of paper

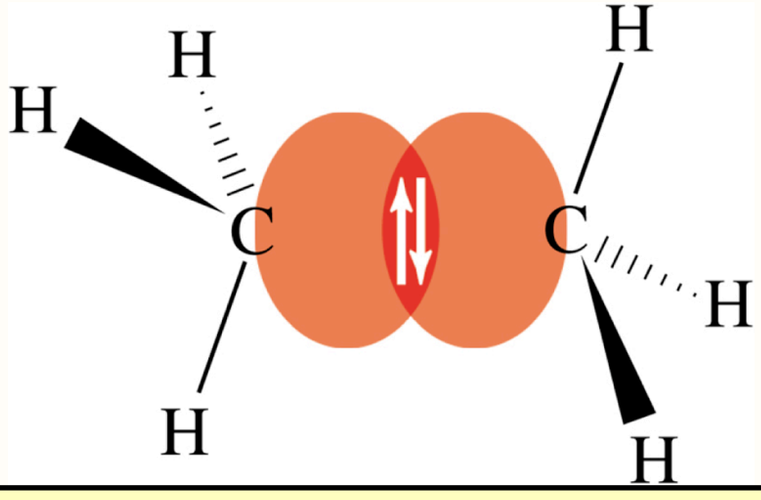
= group is *either* toward or away from you, usually denotes mixtures

= group lies in the plane of the drawing surface

- σ-bond: head-to-head overlap of orbitals; strongest bond type
- hybridization increases bond strength of σ-bonds since electrons are concentrated on one side of nucleus
- only larger lobe of sp^3 involved in bonding
- typically ignore (don't draw) smaller lobe

The C–C σ-bond in Ethane



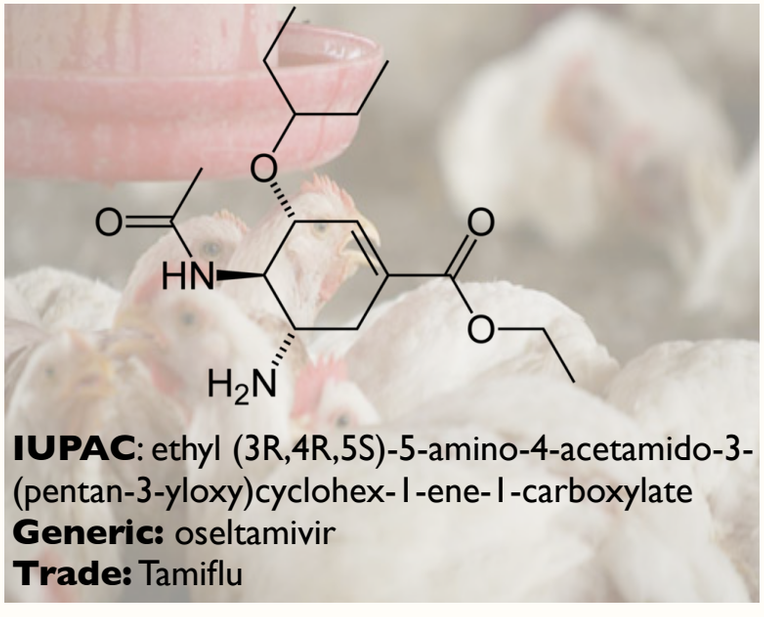


- in-phase overlap of an sp^3-hybridized orbital from each carbon atom
- overlap is along internuclear axis (σ-bond)
- VSEPR: tetrahedral around each carbon atom

Nomenclature of Hydrocarbons

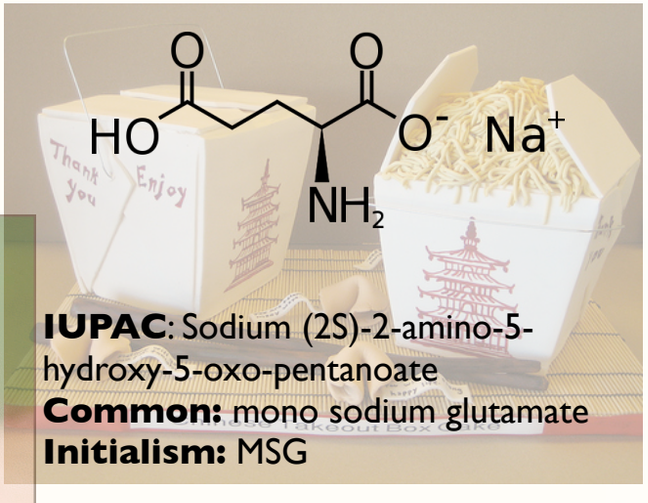
Sections: 2.11-2.15

What's In a Name?

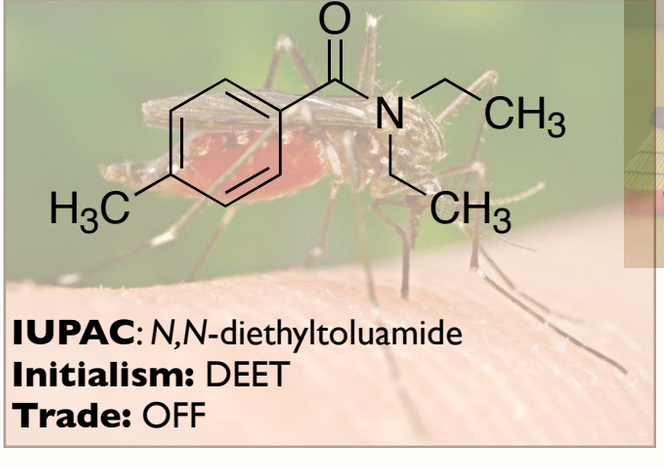


IUPAC: ethyl (3R,4R,5S)-5-amino-4-acetamido-3-(pentan-3-yloxy)cyclohex-1-ene-1-carboxylate
Generic: oseltamivir
Trade: Tamiflu

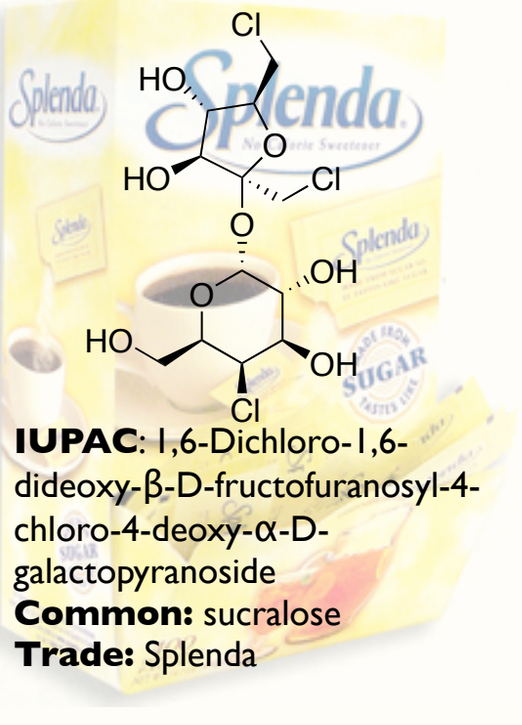
IUPAC: sodium dodecyl sulfate
Common: sodium lauryl sulfate
Trade: SDS



IUPAC: Sodium (2S)-2-amino-5-hydroxy-5-oxo-pentanoate
Common: mono sodium glutamate
Initialism: MSG



IUPAC: *N,N*-diethyltoluamide
Initialism: DEET
Trade: OFF



IUPAC: 1,6-Dichloro-1,6-dideoxy-β-D-fructofuranosyl-4-chloro-4-deoxy-α-D-galactopyranoside
Common: sucralose
Trade: Splenda

IUPAC: Alkanes with NO Substituents

IUPAC: International Union of Pure and Applied Chemistry

TABLE 2.2 IUPAC Names of Unbranched Alkanes

Number of carbon atoms	Name	Number of carbon atoms	Name	Number of carbon atoms	Name
1	Methane	11	Undecane	21	Henicosane
2	Ethane	12	Dodecane	22	Docosane
3	Propane	13	Tridecane	23	Tricosane
4	Butane	14	Tetradecane	24	Tetracosane
5	Pentane	15	Pentadecane	30	Triacontane
6	Hexane	16	Hexadecane	31	Hentriacontane
7	Heptane	17	Heptadecane	32	Dotriacontane
8	Octane	18	Octadecane	40	Tetracontane
9	Nonane	19	Nonadecane	50	Pentacontane
10	Decane	20	Icosane*	100	Hectane

common name retained

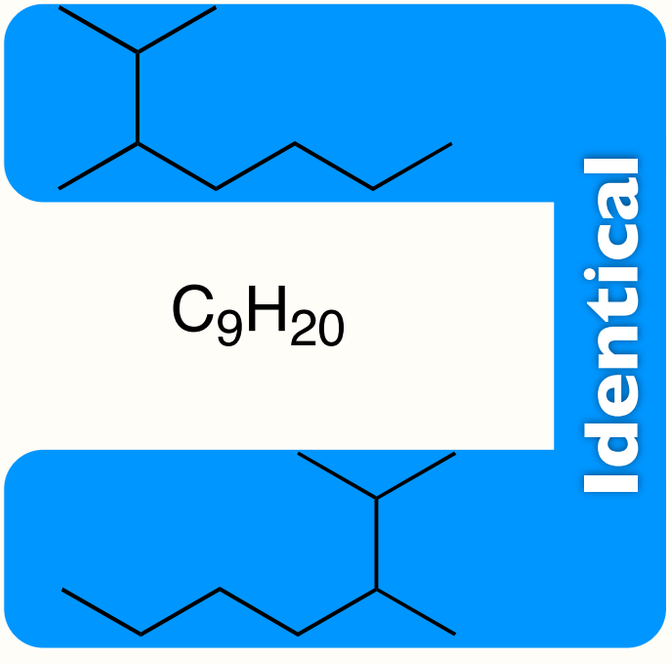
Greek prefixes

Constitutional (Structural) Isomers

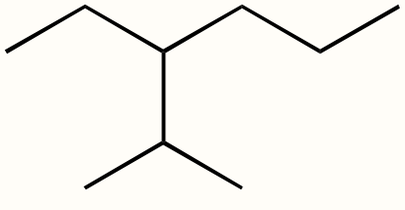
constitutional isomers: same molecular formula; different connectivity

connectivity: order in which the atoms are bonded

C_9H_{20}



C_9H_{20}



C_9H_{20}

C_9H_{20}

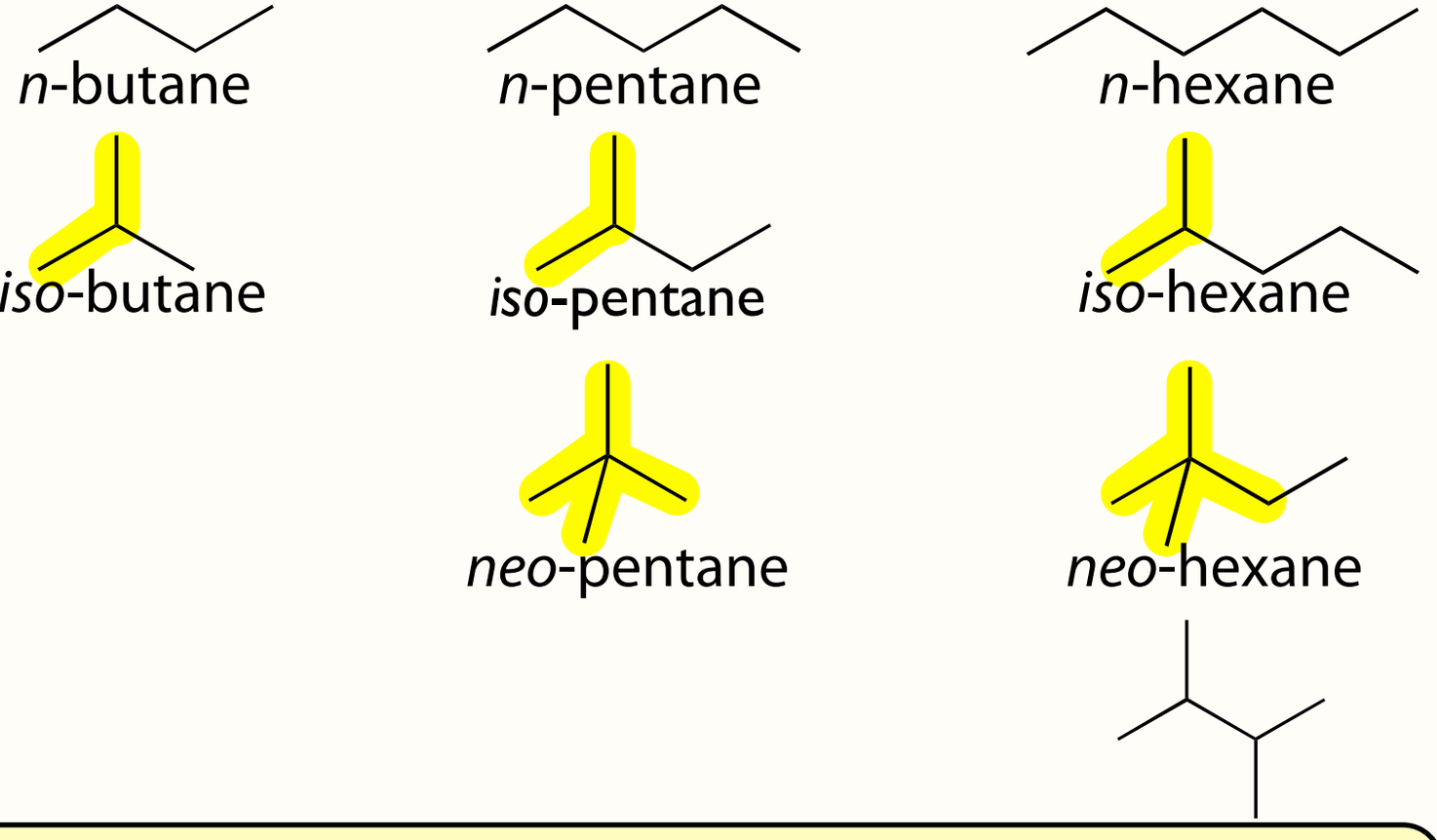
Common Names for Branched Isomers of Simple Alkanes

homologous series: succesive members differ by a $–CH_2–$ group

methyl: CH_3

methylene: CH_2

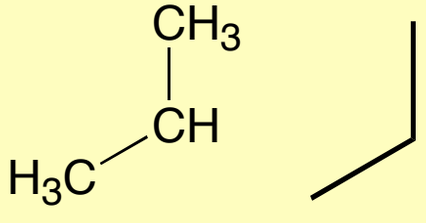
methine: CH



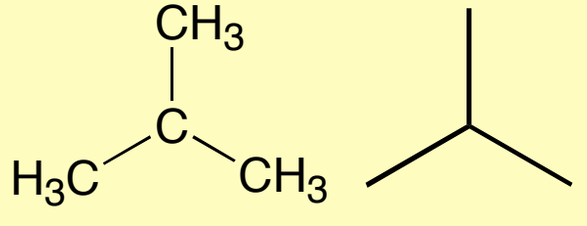
n

"normal" straight chain

iso



neo



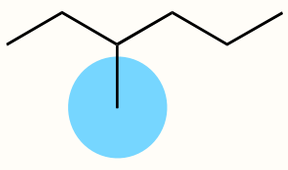
Common Names Become Too Complex: Systematic Method of Naming is Needed

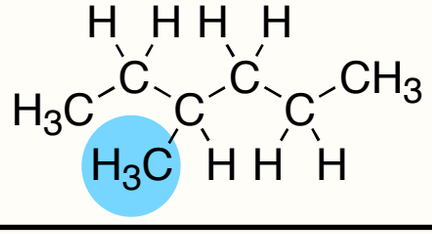
TABLE 2.1 The Number of Constitutionally Isomeric Alkanes of Particular Molecular Formulas

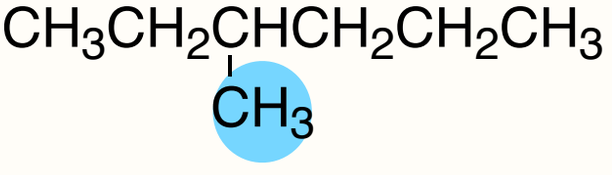
Molecular formula	Number of constitutional isomers
CH_4	1
C_2H_6	1
C_3H_8	1
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{15}H_{32}$	4,347
$C_{20}H_{42}$	366,319
$C_{40}H_{82}$	62,491,178,805,831

IUPAC: Naming Alkyl Substituent Groups

substituent: atom or group other than H bonded to carbon
alkyl group: one H atom less than an alkane





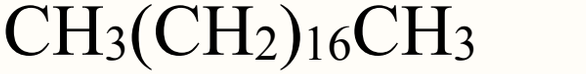


Steps:

1. Identify longest continuous chain of carbon atoms.
2. Locate substituents attached to the longest continuous chain of carbon atoms.
3. Name alkane substituent by replacing *-ane* of parent alkane with *-yl*

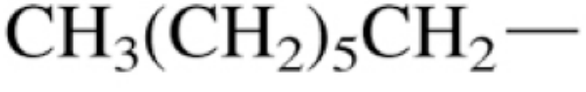
Ethane

Heptane

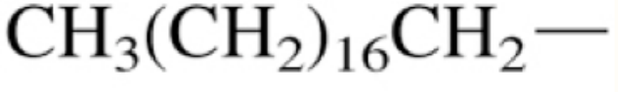


Octadecane

Ethyl group



Heptyl group

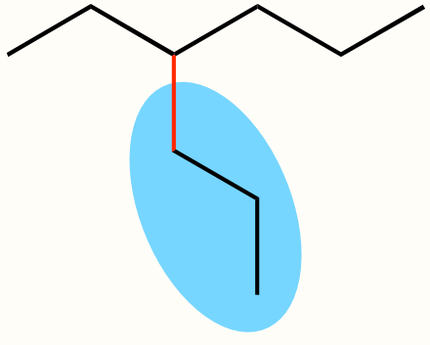


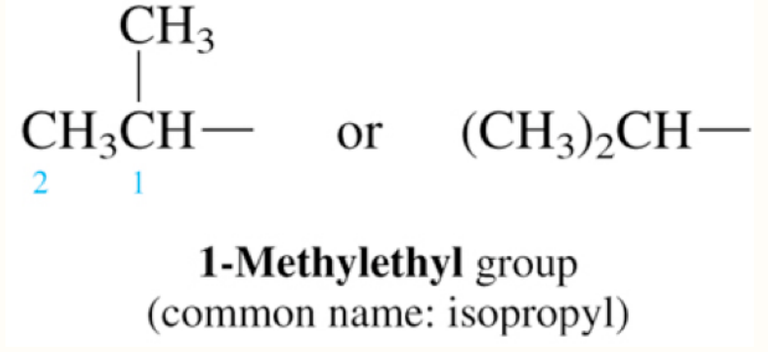
Octadecyl group

Common & IUPAC Names of 3-Carbon Alkyl Groups

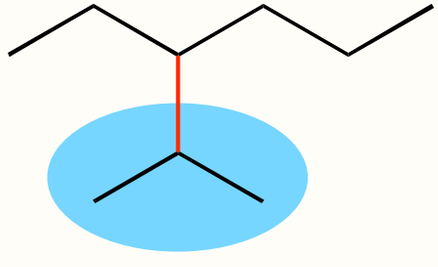
$CH_3CH_2CH_2—$

Propyl group
(common name: *n*-propyl)





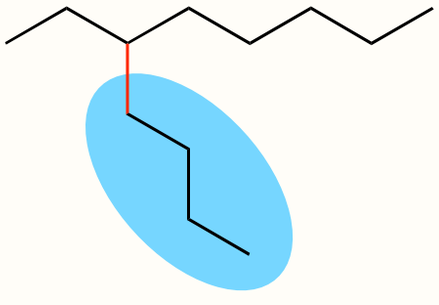
1-Methylethyl group
(common name: isopropyl)

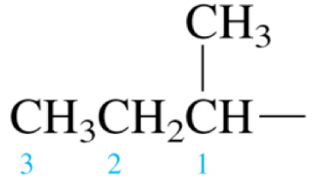


Common & IUPAC Names of 4-Carbon Alkyl Groups

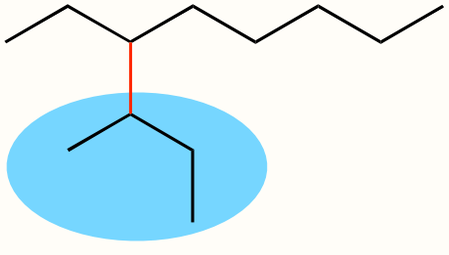
$CH_3CH_2CH_2CH_2-$

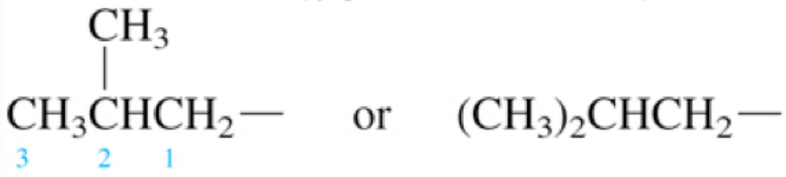
Butyl group
(common name: *n*-butyl)



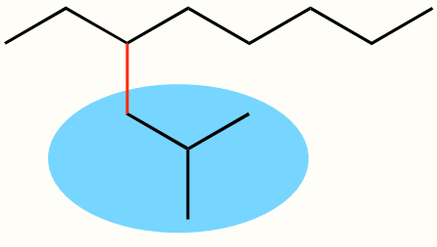


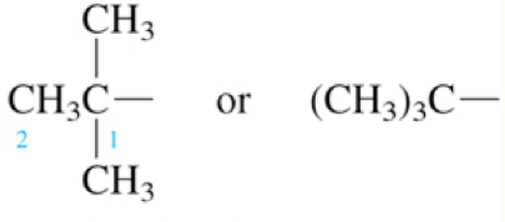
1-Methylpropyl group
(common name: *sec*-butyl)



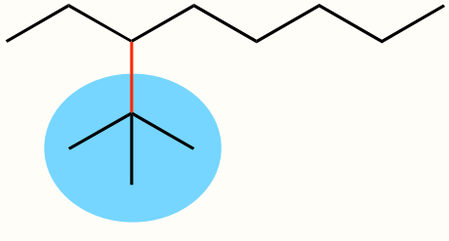


2-Methylpropyl group
(common name: isobutyl)

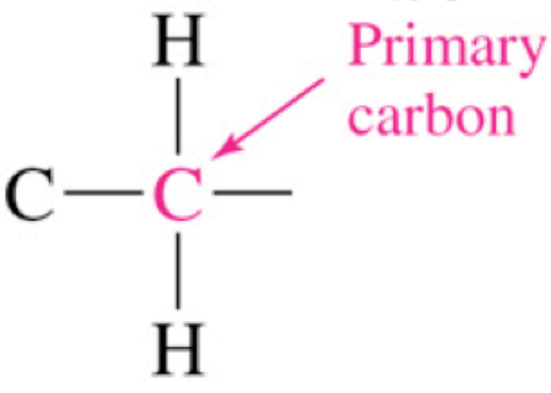




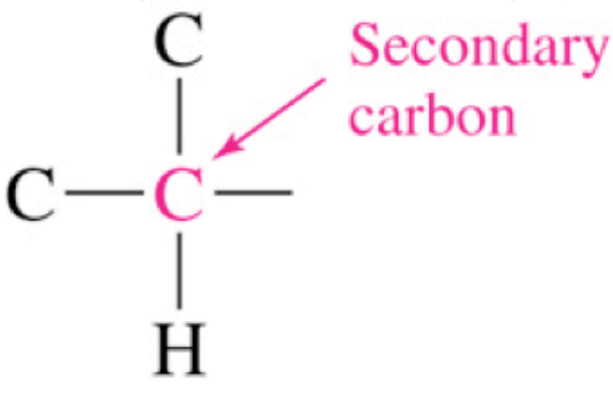
1,1-Dimethylethyl group
(common name: *tert*-butyl)



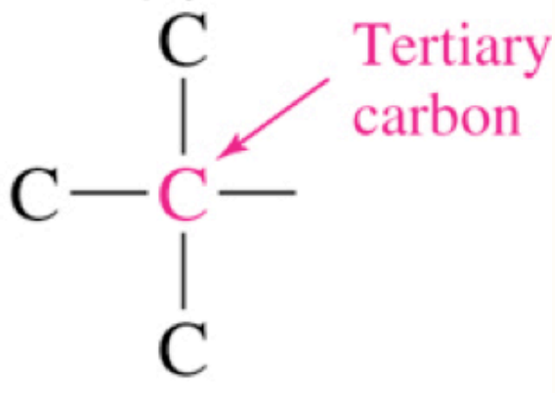
Carbon Classification



Primary alkyl group

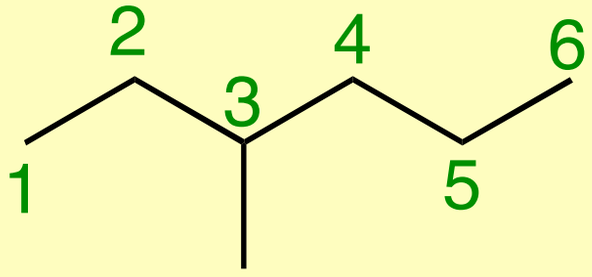


Secondary alkyl group



Tertiary alkyl group

IUPAC: Alkanes with One substituent (Monosubstituted)



$CH_3CH_2CHCH_2CH_2CH_3$
CH_3

3-methylhexane

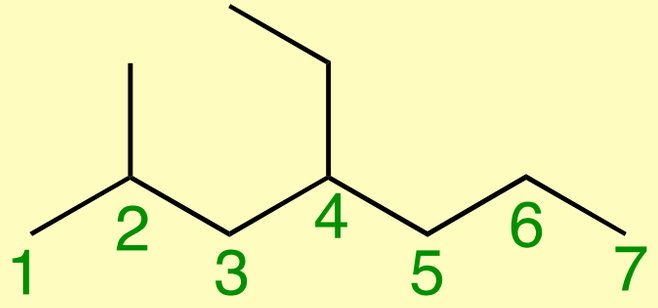
Steps:

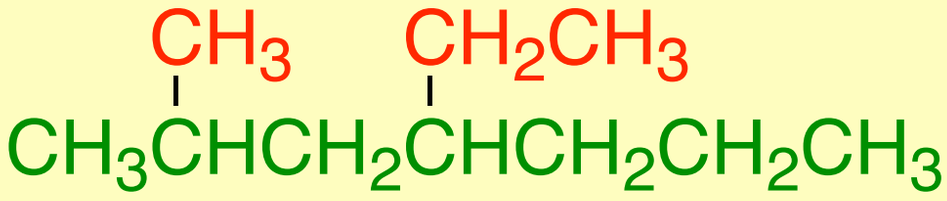
1. Identify the longest continuous chain of carbons.
2. Identify substituent group (group not part of the longest continuous chain).
3. Number the longest chain so that substituent has the lowest number.
4. Name the compound according to the figure below.

Conventions:

- *locant* refers to the numerical location of a substituent
- numbers and letters are always separated by a dash (-)

IUPAC: Alkanes with Two or More Different Substituents





4-ethyl-2-methylheptane

Steps:

1. Identify the longest continuous chain of carbons.
2. Identify substituent groups (groups not part of the longest continuous chain).
3. Number the longest chain so that substituents have the lowest locants.
4. Name the compound according to the figure below.

Conventions:

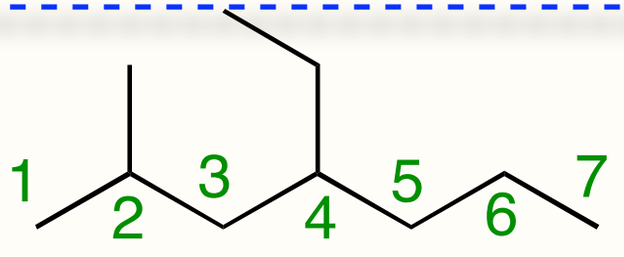
- if two numbering give same parent, number chain to maximize number of substituent groups.
- order the substituents in the name alphabetically
- Follow First Point of Difference Rule: Number the chain so that the locant at the first point of difference has the lowest value (e.g. 2,2,4 better than 4,2,2) if two numberings give same locants, choose numbering that gives lower locant to first in alphabet

locant — **substituent name first in alphabet** — **locant** — **substituent name 2nd in alphabet** **parent alkane**

IUPAC: First Point of Difference Rule

Number the chain (or ring) so that the locant at the first point of difference in the name has the lowest value

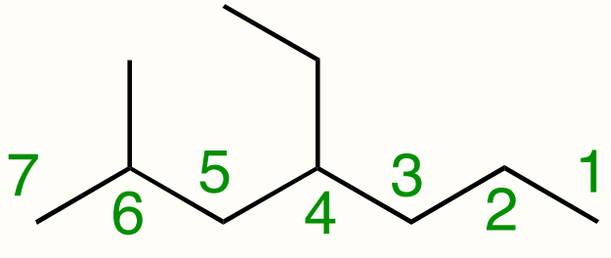
The correct set of locants is NOT the one with the lowest sum!



Correct Name

4-ethyl-2-methylheptane

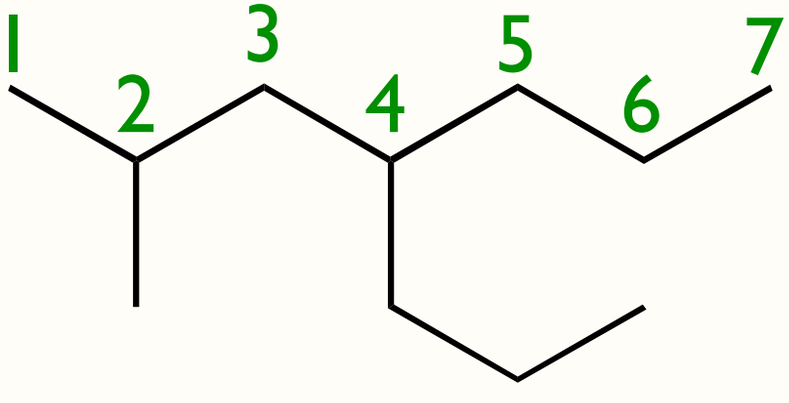
first point of difference



4-ethyl-6-methylheptane

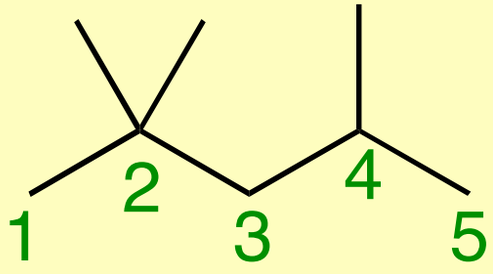
Self Test Question

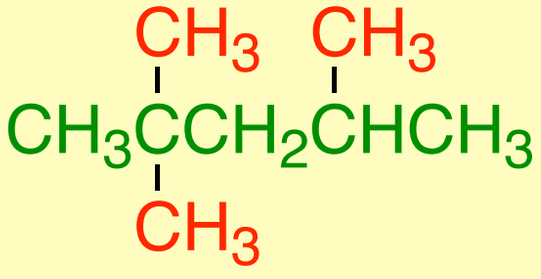
What is the IUPAC name for the molecule below?



A. 2-methyl-4-propylheptane
B. 4-propyl-6-methylhexane
C. 2-methyl-4-butylhexane
D. 2,4-methylethylheptane
E. 4-propyl-2-methylheptane

IUPAC: Alkanes with Repeating Substituents





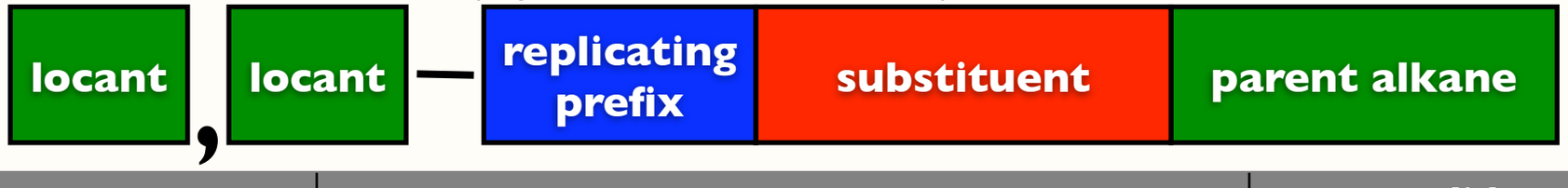
2,2,4-trimethylpentane

Steps:

1. Identify and number the longest continuous chain of carbons to provide lowest values of locants.
2. Identify substituent groups (groups not part of the longest continuous chain).
3. Use replicating prefixes (e.g. di, tri, tetra) to indicate total number of substituents on parent
4. Name the compound according to the figure below.

Conventions:

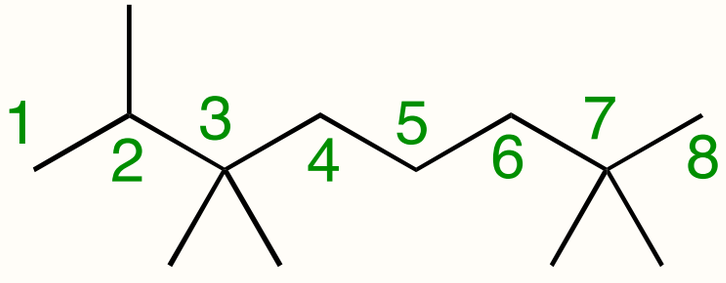
- List each locant separately. Separate numbers with a comman, no space.
- Prefixes are not considered when alphabetizing substituent names.
- Follow First Point of Difference Rule: Number the chain so that the locant at the first point of difference has the lowest value (e.g. 2,2,4 better than 4,2,2)



IUPAC: First Point of Difference Rule

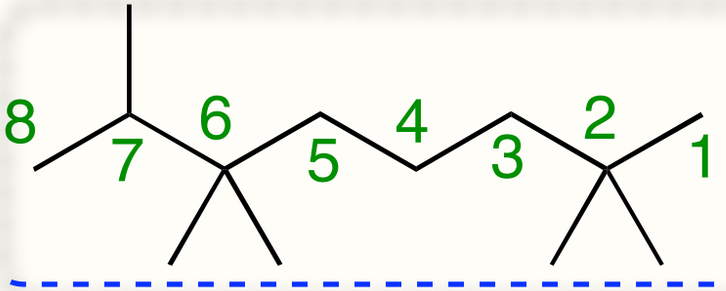
Number the chain (or ring) so that the locant at the first point of difference in the name has the lowest value

The correct set of locants is NOT the one with the lowest sum!



2,3,3,7,7-Pentamethyloctane

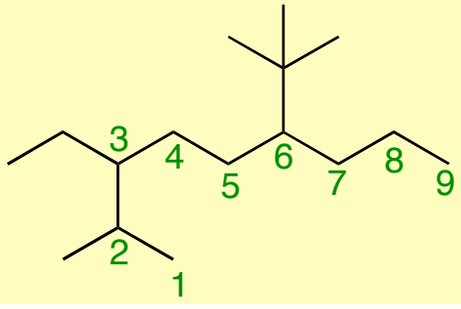
first point of difference

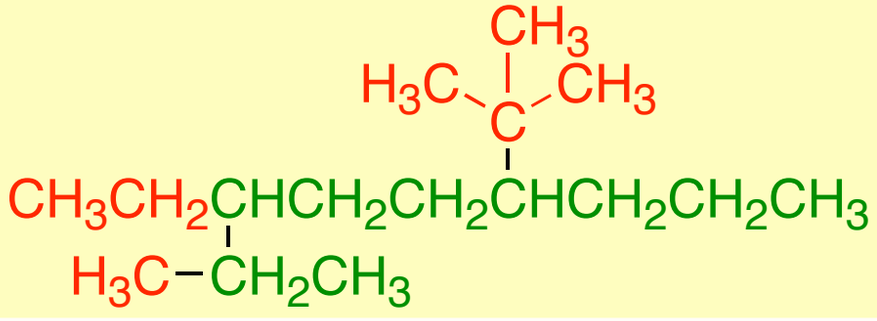


2,2,6,6,7-Pentamethyloctane

Correct Name

IUPAC: Alkanes with Branched Substituents (Using Common Substituent Names)





2-methyl-3-ethyl-6-*tert*-butylnonane

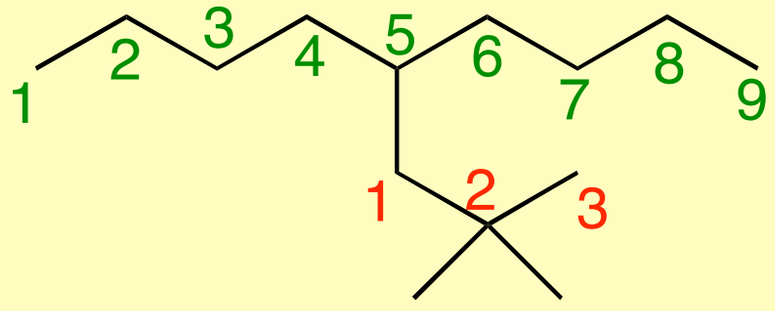
Steps:

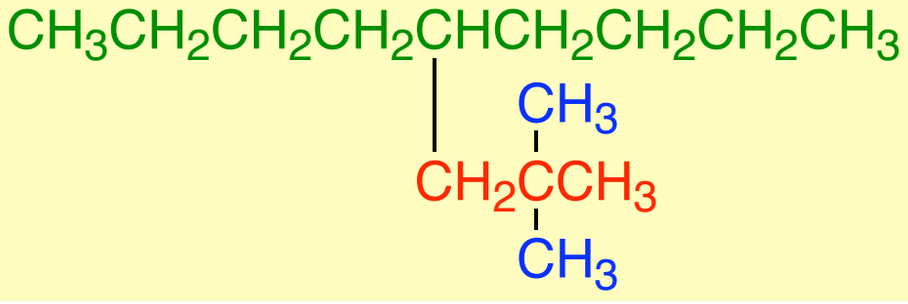
1. Identify and number the longest continuous chain of carbons to provide lowest values of locants.
2. Identify common substituent groups (isopropyl, *sec*-butyl, isobutyl, *tert*-butyl).
3. Name the compound according to the figure below.

Conventions:

- List each locant separately. Separate numbers with a comman, no spaces.
- Prefixes are not considered when alphabetizing substituent names.
- Always follow first point of difference rule.
- *Neo*-pentyl is not used as a common substituent name

IUPAC: Alkanes with Branched Substituents (Using IUPAC Substituent Names)





5-(2,2-dimethylpropyl)-nonane

Steps:

1. Identify and number the longest continuous chain of carbons to provide lowest values of locants.
2. Identify and number longest chain is substituent group beginning with point of attachment to parent.
3. Name the compound according to the figure below.

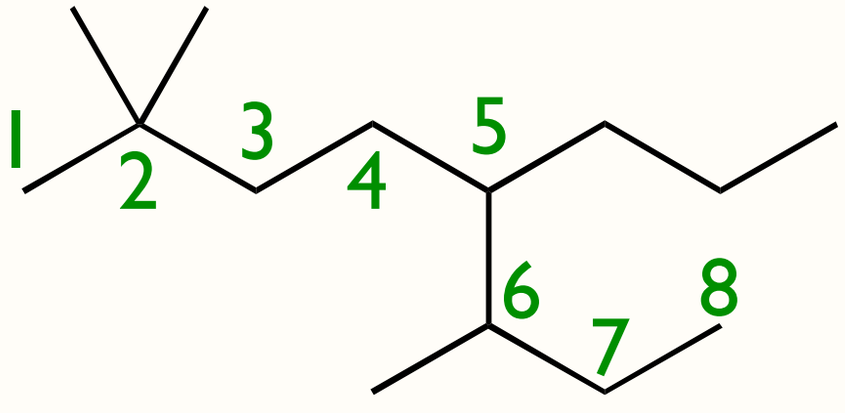
Conventions:

- Follow all other steps and conventions for both chains.
- Substituent name is placed within parentheses when preceded by locants of its own.
- Parentheses are separated from outside words by a dash, no spaces.

parent locant – (**2nd chain locant** – **substituent** **2nd chain name**) – **parent chain name**

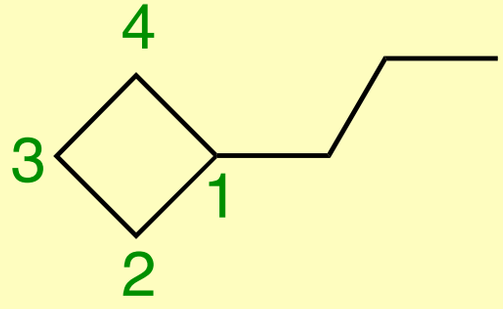
Self Test Question

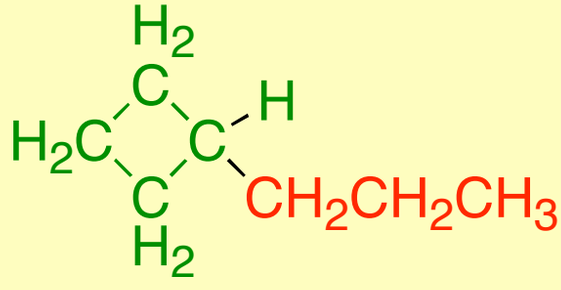
What is the IUPAC name for the molecule below?



A. 5-(1-methylpropyl)-2,2-dimethyloctane
B. 2,2-dimethyl-5-*sec*-butyloctane
C. 4-*sec*-butyl-7-*tert*-butyloctane
D. 2,2,6-trimethyl-5-propyloctane
E. 2-methyl-5-butyloctane

IUPAC: Monosubstituted Cycloalkanes





propylcyclobutane

Steps:

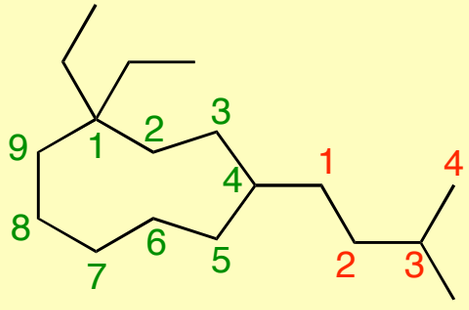
1. Count the number of carbons in the ring. Precede the parent name with *cyclo*.
2. Identify straight chain, common or branched substituent groups.
3. Name the compound according to the figure below.

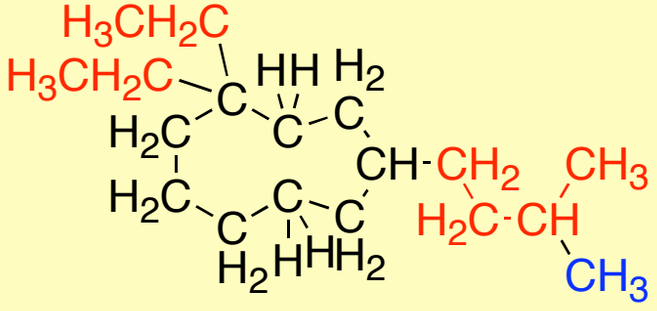
Conventions:

- If the number of carbons in the substituent is greater, name the ring as the substituent as a cycloaklyl substituent (e.g. cyclobutyl)
- If the ring is monosubstituted, no locant is neccessary; substituent locant is assumed to be 1.

substituent	"cyclo"	parent ring name

IUPAC: Disubstituted Cycloalkanes





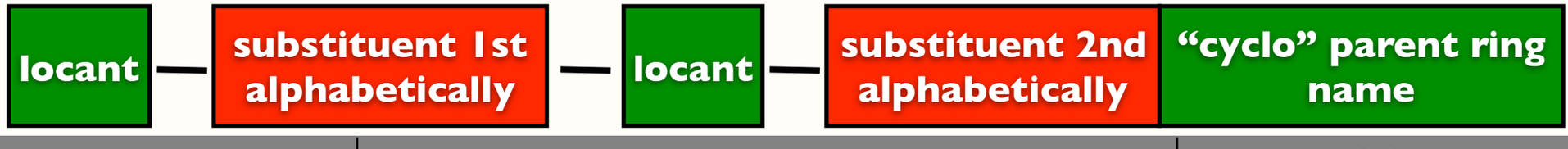
1,1-diethyl-4-(3-methylbutyl)cyclononane

Steps:

1. Count the number of carbons in the ring. Precede the parent name with *cyclo*.
2. Identify straight chain, common or branched substituent groups.
3. Name the compound according to the figure below.

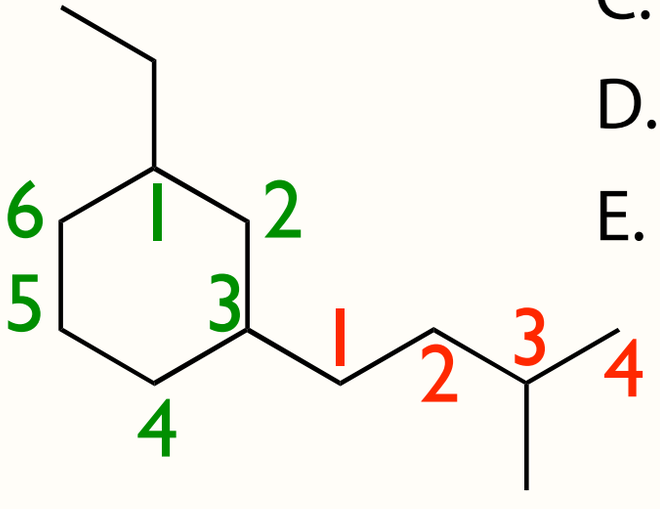
Conventions:

- If the number of carbons in the substituent is greater, name the ring as the substituent as a cycloaklyl substituent (e.g. cyclobutyl). Follow all previous steps and conventions for naming substituents.
- List substituents in alphabetical order. Ignore replicating prefixes.
- Follow first point of difference rule.



Self Test Question

What is the IUPAC name for the molecule below?



A. 1-ethyl-3-pentylcyclohexane
B. 3-ethyl-1-pentylcyclohexane
C. 1-ethyl-3-(3-methylbutyl)cyclohexane
D. 1-butyl-3-ethylcycloheptane
E. 1-(2-methylbutyl)-3-ethylcyclohexane

Next Lecture. . .

Chapter 2, Sections: 2.16-2.22
Chapter 3, Sections: 3.1-3.3