

# Chapter 24 From Petroleum to Pharmaceuticals

24.1 Petroleum Refining and the Hydrocarbons

24.2 Functional Groups and Organic Synthesis

24.3 Pesticides and Pharmaceuticals

IR Tutor and Infrared Spectroscopy

*Hydrocarbons*

```
graph TD; A[Hydrocarbons] --- B[Aliphatic]; A --- C[Aromatic];
```

*Aliphatic*

*Aromatic*

*Hydrocarbons*

```
graph TD; A[Hydrocarbons] --> B[Aliphatic]; A --> C[Aromatic]; B --> D[Alkanes]; B --> E[Alkenes]; B --> F[Alkynes];
```

Aliphatic

Aromatic

Alkanes

Alkenes

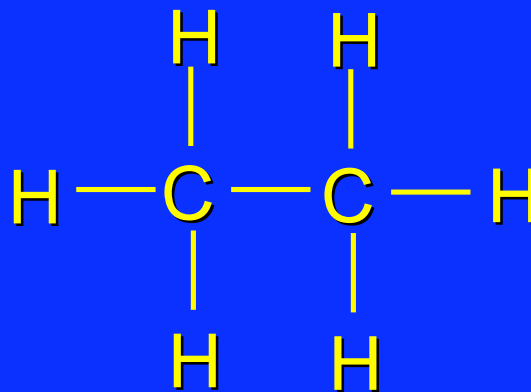
Alkynes

# Hydrocarbons

Aliphatic

Alkanes

Alkanes are hydrocarbons in which all of the bonds are *single* bonds.

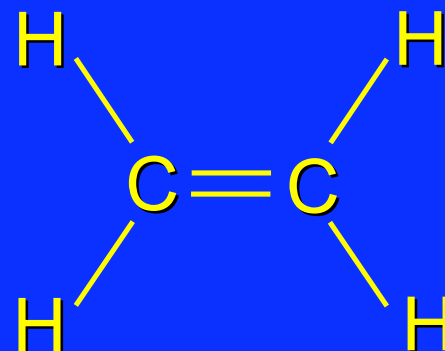


# Hydrocarbons

Aliphatic

Alkenes

Alkenes are hydrocarbons that contain a carbon-carbon *double bond*.



# Hydrocarbons

```
graph TD; A[Hydrocarbons] --> B[Aliphatic]; A --> C[Alkynes]; B --> D[Alkynes]; C --- E[Alkynes are hydrocarbons that contain a carbon-carbon triple bond.]; D --- F[HC≡CH];
```

Aliphatic

Alkynes are hydrocarbons that contain a carbon-carbon *triple bond*.

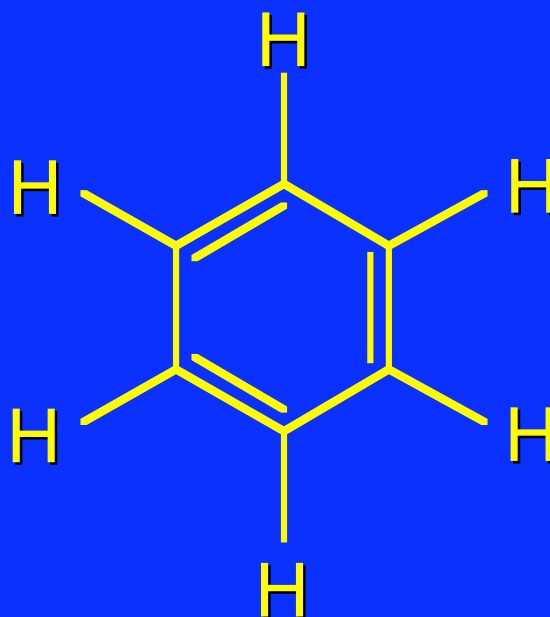
Alkynes



## Hydrocarbons

The most common aromatic hydrocarbons are those that contain a benzene ring.

Aromatic



# Reactive Sites in Hydrocarbons

## The Functional Group Concept

## *Functional Group*

a structural unit in a molecule responsible for its  
characteristic chemical behavior and its

IR spectroscopic characteristics

## Alkanes



functional group is a hydrogen atom

the reaction that takes place is

termed a substitution

one of the hydrogens is substituted

by some other atom or group, X

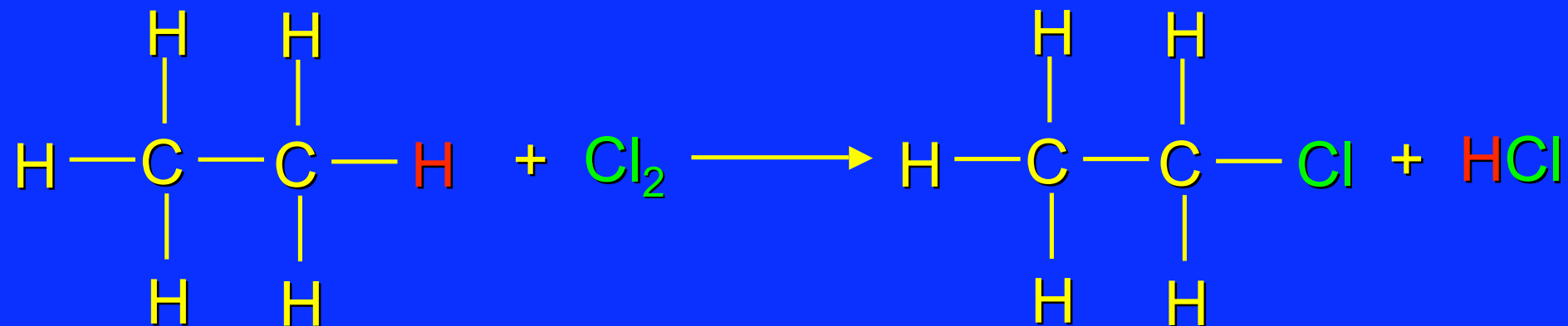
## Alkanes



functional group is a hydrogen

the reaction that takes place is substitution

one of the hydrogens is substituted  
by some other atom or group



## *Functional Groups in Hydrocarbons*

alkanes

RH

alkenes

RH, double bond

alkynes

RH, triple bond

aromatics

ArH, double bond

# Some Key Functional Groups

## *Families of organic compounds and their functional groups*

Alcohols

ROH

Alkyl halides

RX (X = F, Cl, Br, I)

Amines

primary amine:  $\text{RNH}_2$

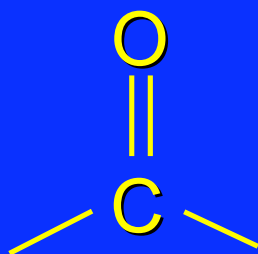
secondary amine:  $\text{R}_2\text{NH}$

tertiary amine:  $\text{R}_3\text{N}$

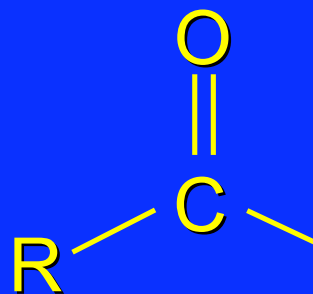
Ethers

ROR

*Many classes of organic compounds  
contain a carbonyl group*

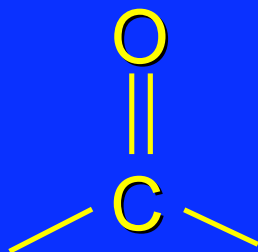


Carbonyl group

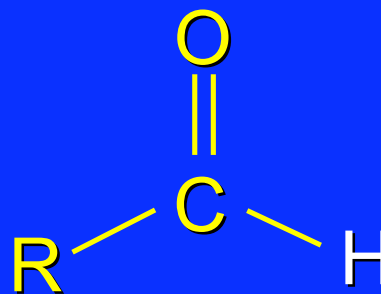


Acyl group

*Many classes of organic compounds  
contain a carbonyl group*

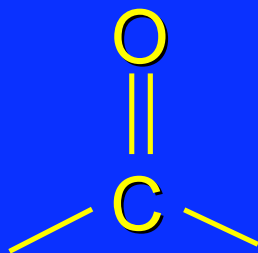


Carbonyl group

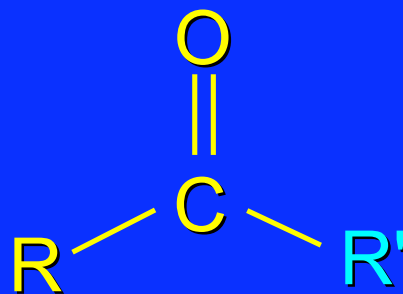


Aldehyde

*Many classes of organic compounds  
contain a carbonyl group*

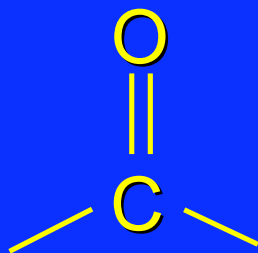


Carbonyl group

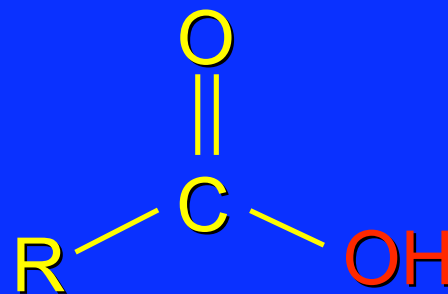


Ketone

*Many classes of organic compounds  
contain a carbonyl group*

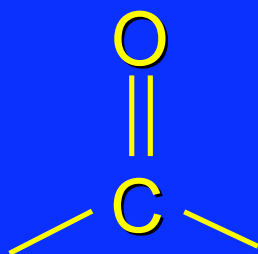


Carbonyl group

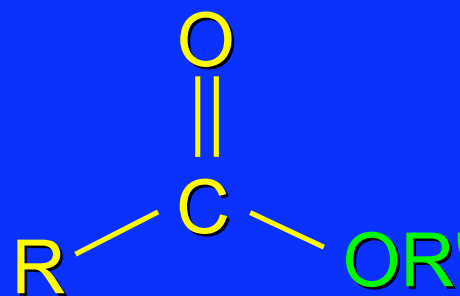


Carboxylic acid

*Many classes of organic compounds  
contain a carbonyl group*

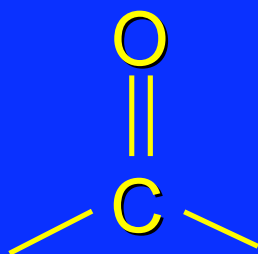


Carbonyl group

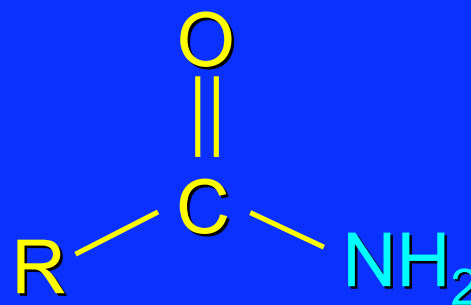


Ester

*Many classes of organic compounds  
contain a carbonyl group*



Carbonyl group



Amide

General formula for an alkane



Introduction to Alkanes:

Methane,  $\text{CH}_4$

Ethane,  $\text{C}_2\text{H}_6$

Propane,  $\text{C}_3\text{H}_8$

## *The simplest alkanes*

Methane (CH<sub>4</sub>)

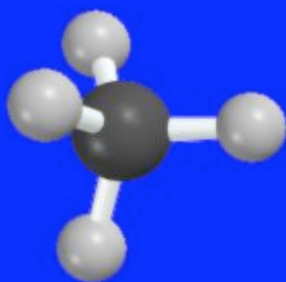
CH<sub>4</sub>

Ethane (C<sub>2</sub>H<sub>6</sub>)

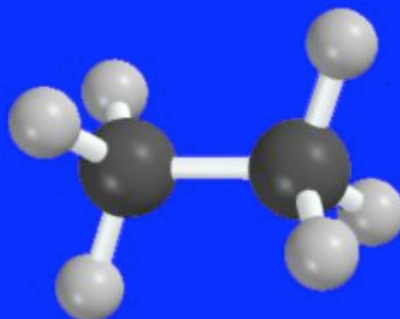
CH<sub>3</sub>CH<sub>3</sub>

Propane (C<sub>3</sub>H<sub>8</sub>)

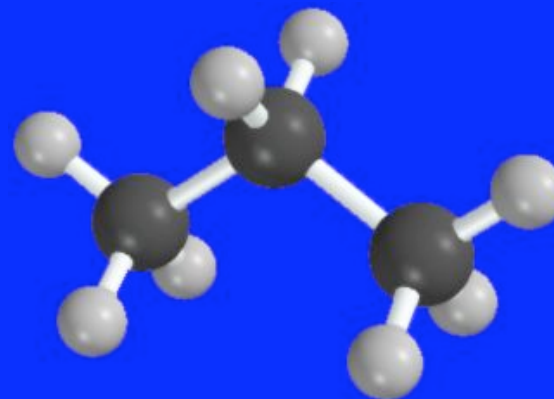
CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>



bp -160°C



bp -89°C



bp -42°C

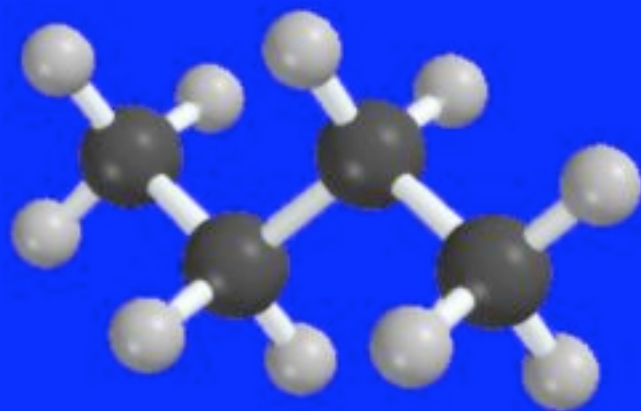
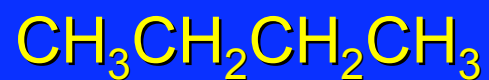
No isomers possible for C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> hydrocarbons

# Isomeric Alkanes: The Butanes



General formula for any butane

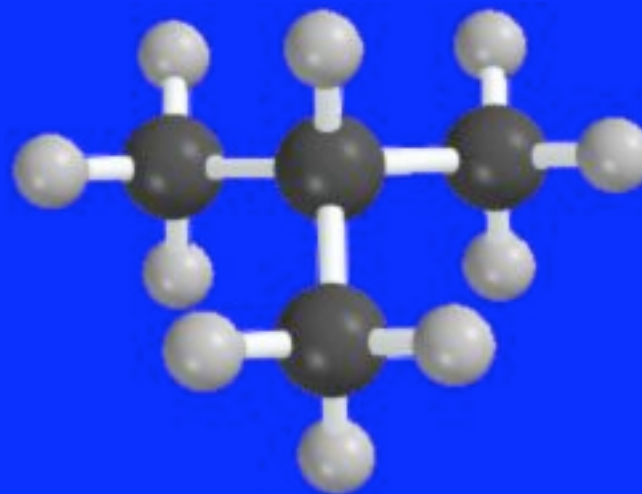
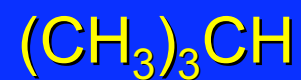
*n*-Butane



bp  $-0.4^\circ\text{C}$

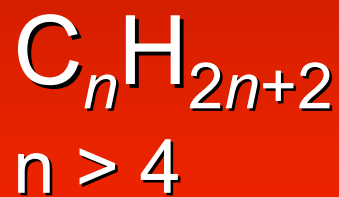


Isobutane



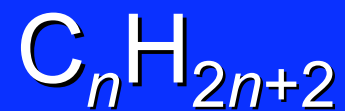
bp  $-10.2^\circ\text{C}$

# Higher *n*-Alkanes Pentane (C<sub>5</sub>H<sub>12</sub>) and Beyond

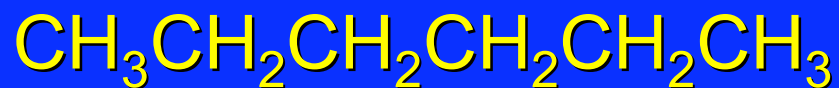




*n*-Pentane



$$n > 4$$

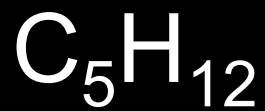


*n*-Hexane



*n*-Heptane

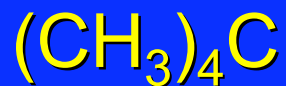
# The C<sub>5</sub>H<sub>12</sub> Isomers



*n*-Pentane



Isopentane



Neopentane

## *How many isomers?*

The number of isomeric alkanes increases as the number of carbons increase.

There is no simple way to predict how many isomers there are for a particular molecular formula.

*Table 2.3*  
*Number of Constitutionally Isomeric Alkanes*

$\text{CH}_4$       1

$\text{C}_2\text{H}_6$       1

$\text{C}_3\text{H}_8$       1

$\text{C}_4\text{H}_{10}$      2

$\text{C}_5\text{H}_{12}$      3

$\text{C}_6\text{H}_{14}$      5

$\text{C}_7\text{H}_{16}$      9

*Table 2.3*  
*Number of Constitutionally Isomeric Alkanes*

$\text{CH}_4$	1	$\text{C}_8\text{H}_{18}$	18
$\text{C}_2\text{H}_6$	1	$\text{C}_9\text{H}_{20}$	35
$\text{C}_3\text{H}_8$	1	$\text{C}_{10}\text{H}_{22}$	75
$\text{C}_4\text{H}_{10}$	2	$\text{C}_{15}\text{H}_{32}$	4,347
$\text{C}_5\text{H}_{12}$	3	$\text{C}_{20}\text{H}_{42}$	366,319
$\text{C}_6\text{H}_{14}$	5	$\text{C}_{40}\text{H}_{82}$	62,491,178,805,831
$\text{C}_7\text{H}_{16}$	9		

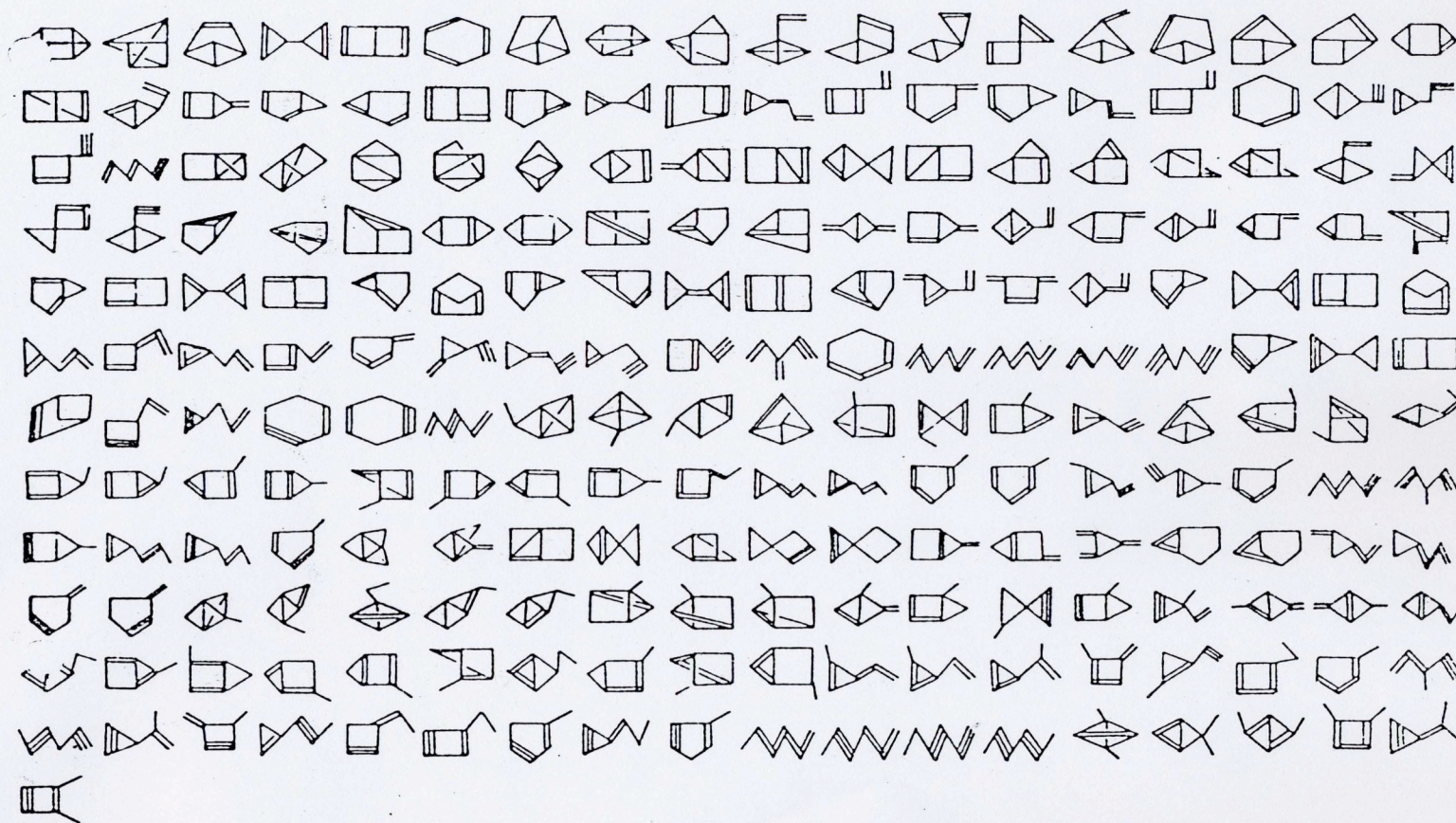
# $C_6H_6$ Isomers

How many isomers with the  
composition

$C_6H_6$  can you draw?

# $C_6H_6$ Isomers: How many isomers with the composition

## $C_6H_6$ can you draw?



THE  $C_6H_6$  ISOMERS

# Structure and Bonding in Alkenes

## Structure of Ethylene

bond angles:

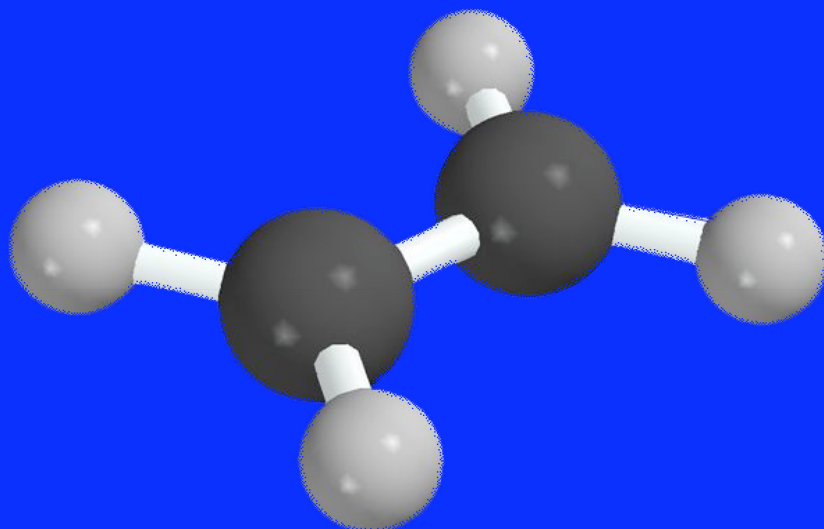
$$\text{H-C-H} = 117^\circ$$

$$\text{H-C-C} = 121^\circ$$

bond distances:

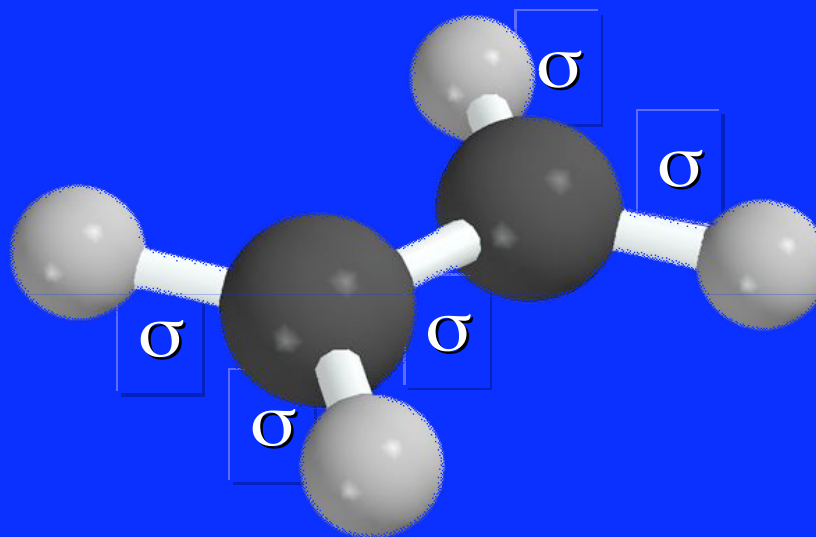
$$\text{C-H} = 110 \text{ pm}$$

$$\text{C=C} = 134 \text{ pm}$$



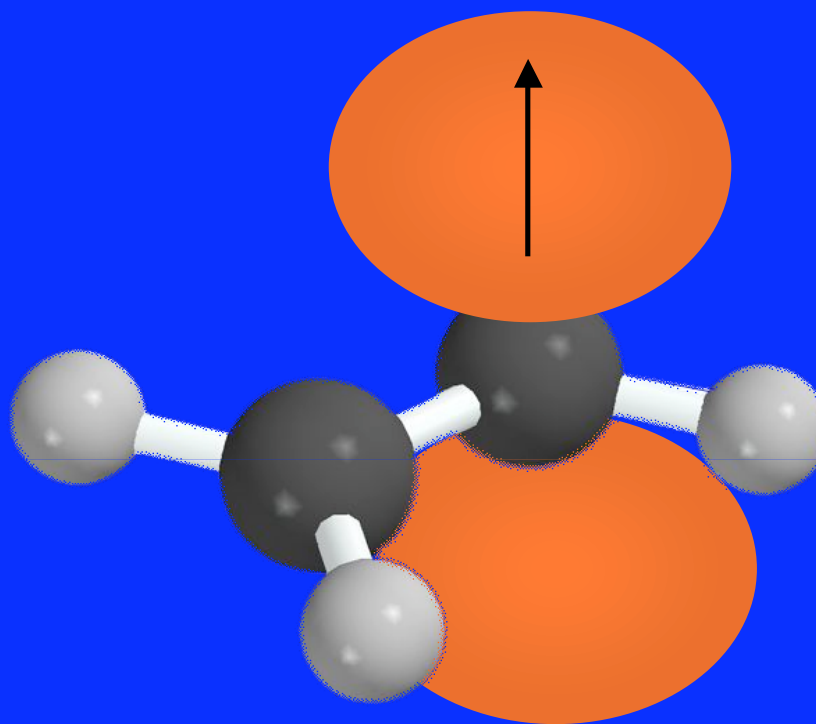
planar

## Bonding in Ethylene



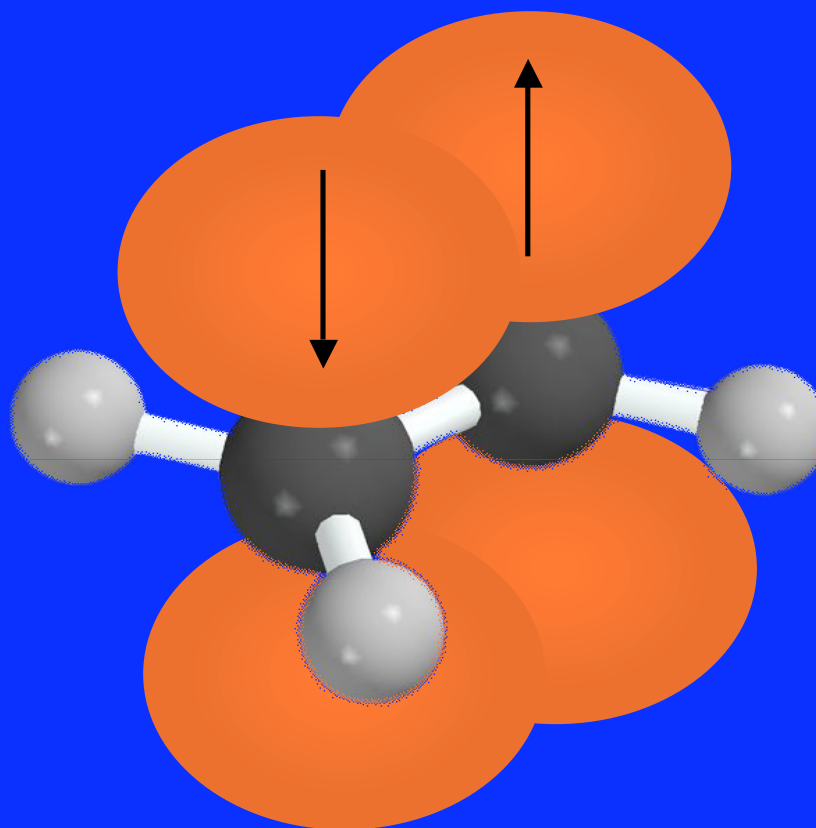
Framework of  $\sigma$  bonds  
Each carbon is  $sp^2$  hybridized

## Bonding in Ethylene



Each carbon has a half-filled  $p$  orbital

## Bonding in Ethylene



Side-by-side overlap of half-filled  $p$  orbitals gives a  $\pi$  bond

# Isomerism in Alkenes

## *Isomers*

Isomers are different compounds that have the same molecular formula (composition).

*Isomers*

```
graph TD; A[Isomers] --> B[Constitutional isomers]; A --> C[Stereoisomers];
```

The diagram is a simple tree structure. At the top is a box with a red diagonal hatched pattern containing the word 'Isomers'. A vertical line descends from this box, then a horizontal line branches out to the left and right. From the left end of this horizontal line, a vertical line goes down to a solid red box containing the text 'Constitutional isomers'. From the right end of the horizontal line, a vertical line goes down to a solid brown box containing the text 'Stereoisomers'. All text is in a yellow, sans-serif font.

Constitutional isomers

Stereoisomers

# Isomers

```
graph TD; A[Isomers] --- B[Constitutional isomers]; A --- C[Stereoisomers];
```

Constitutional isomers

different connectivity

Stereoisomers

same connectivity;  
different arrangement  
of atoms in space

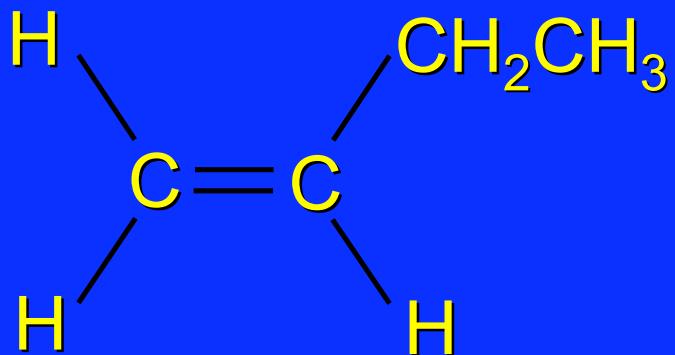
*Isomers*

```
graph TD; A[Isomers] --> B[Constitutional isomers]; A --> C[Stereoisomers];
```

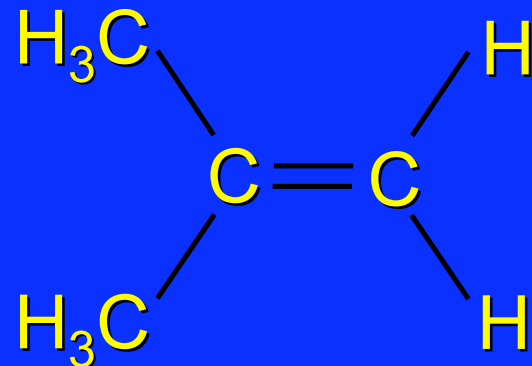
Constitutional isomers

Stereoisomers

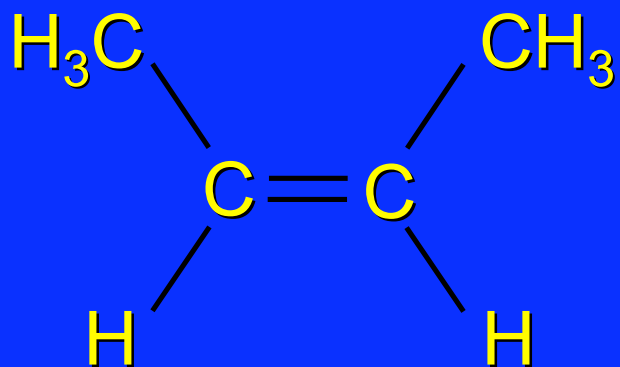
consider the isomeric alkenes of  
molecular formula  $C_4H_8$



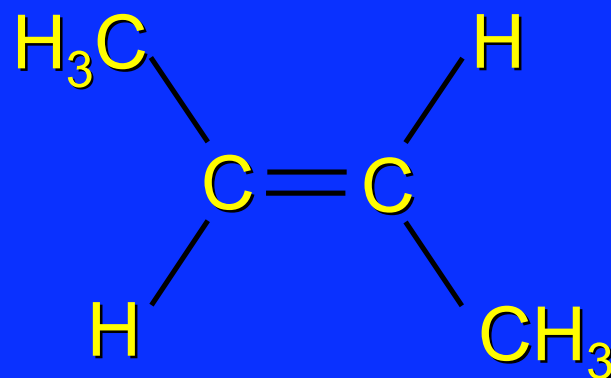
1-Butene



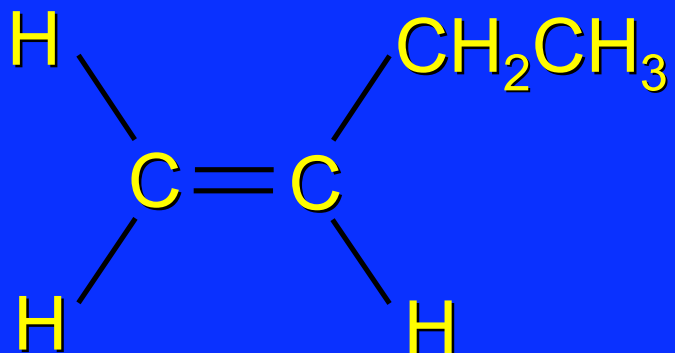
2-Methylpropene



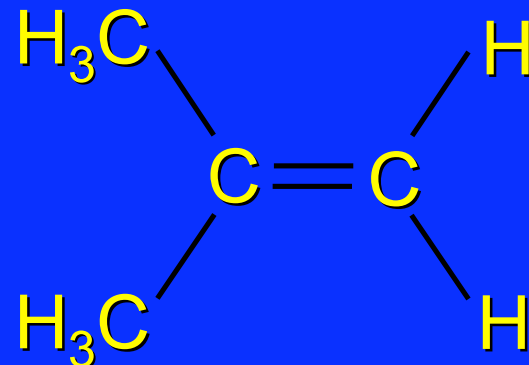
*cis*-2-Butene



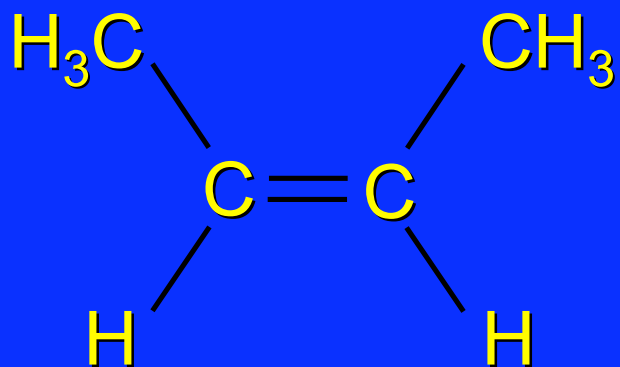
*trans*-2-Butene



1-Butene

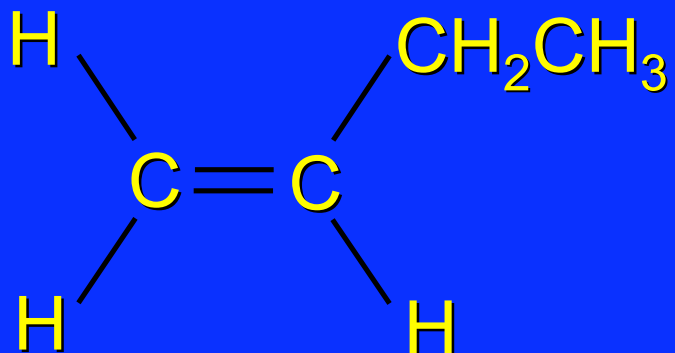


2-Methylpropene

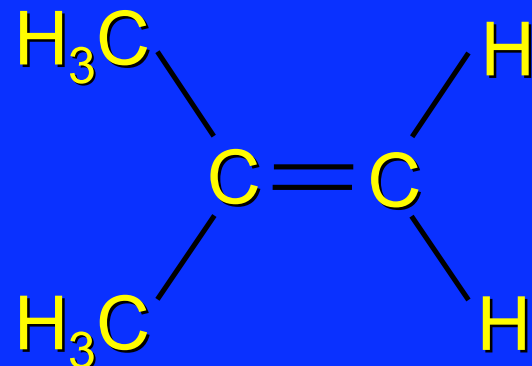


*cis*-2-Butene

Constitutional isomers

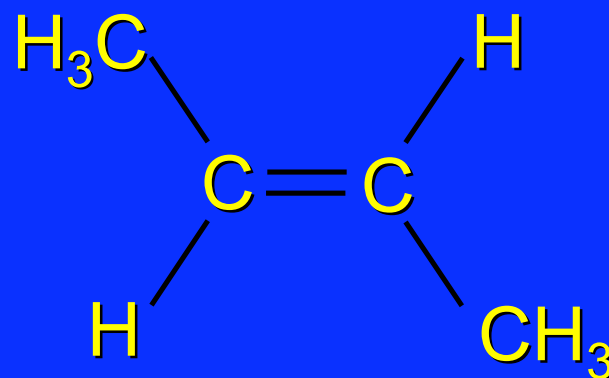


1-Butene



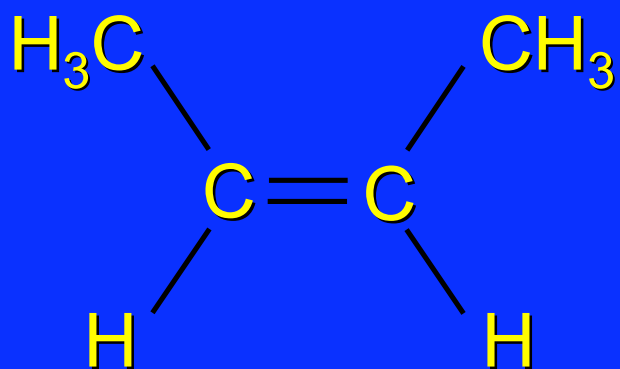
2-Methylpropene

Constitutional isomers

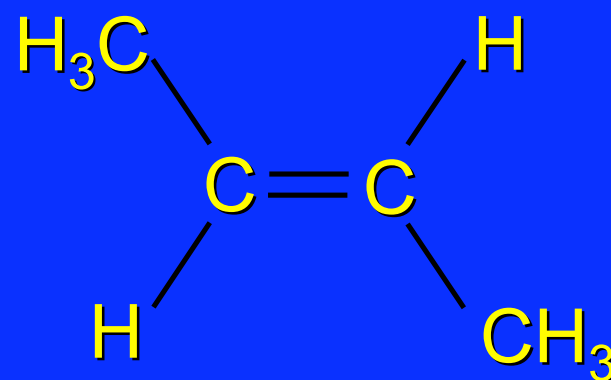


*trans*-2-Butene

## Stereoisomers



*cis*-2-Butene



*trans*-2-Butene

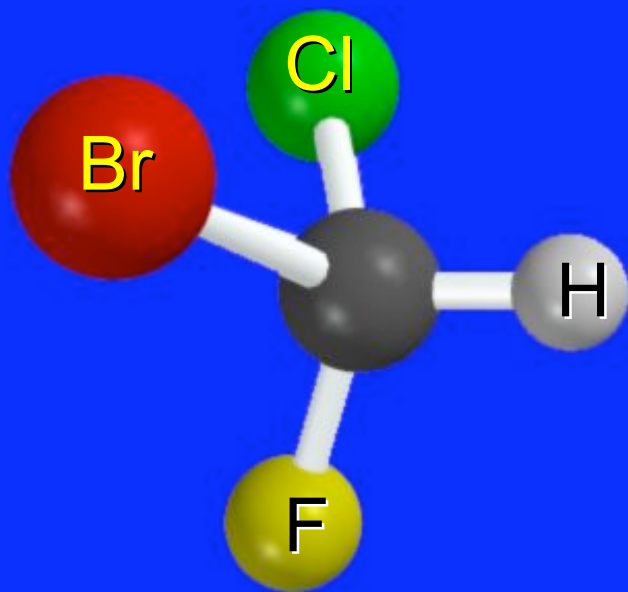
# Molecular Chirality: Enantiomers

## Chirality

A molecule is chiral if its two mirror image forms are not superposable upon one another.

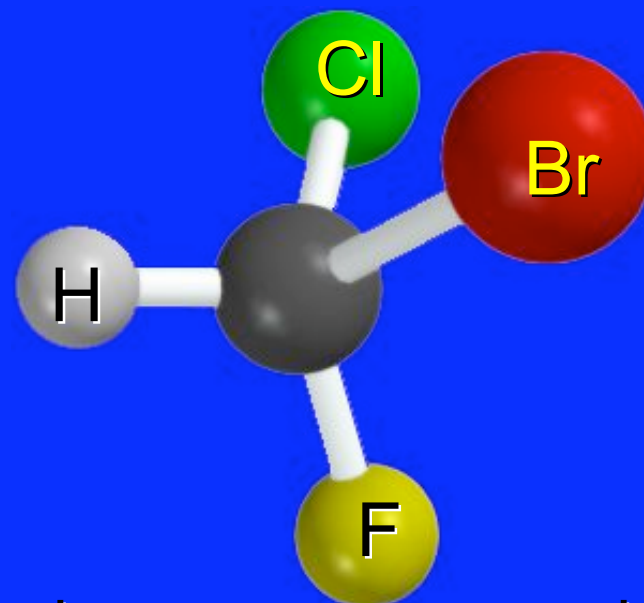
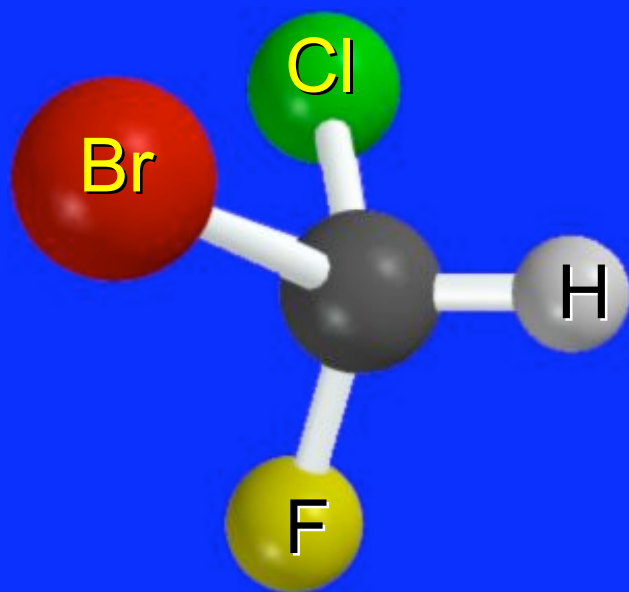
A molecule is achiral if its two mirror image forms are superposable.

## Bromochlorofluoromethane is chiral



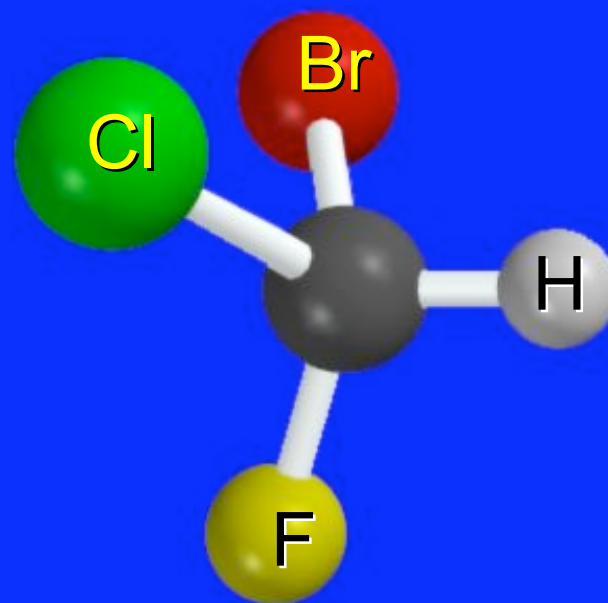
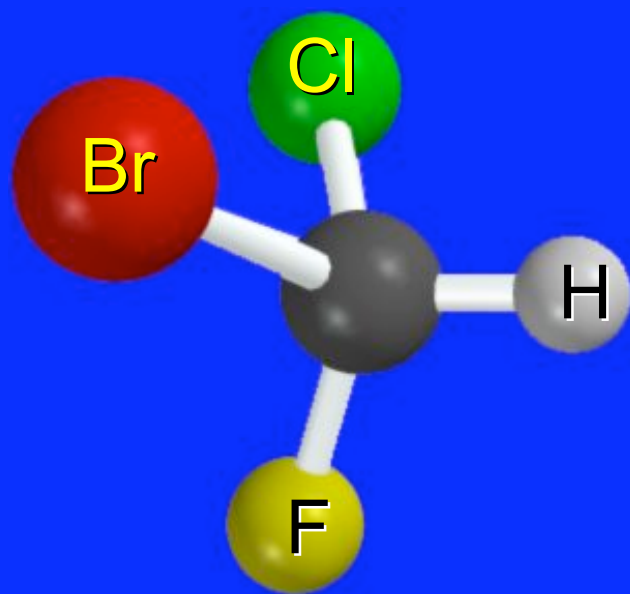
It cannot be superposed point for point on its mirror image.

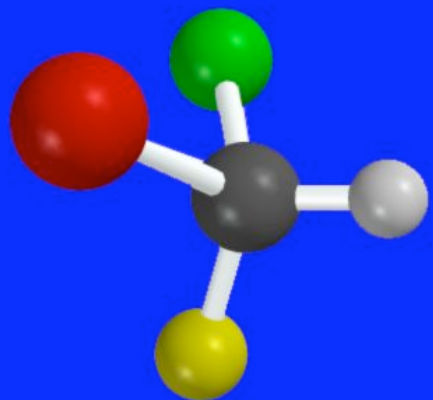
## Bromochlorofluoromethane is chiral



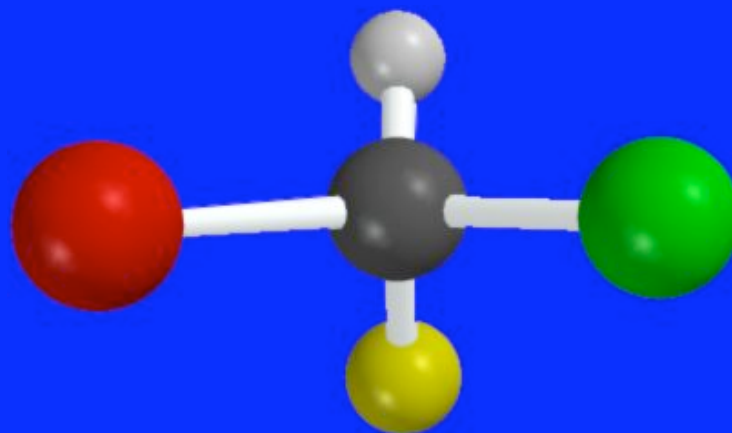
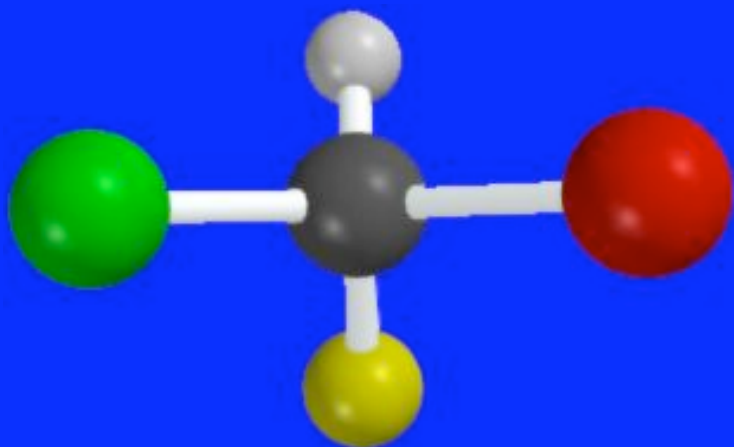
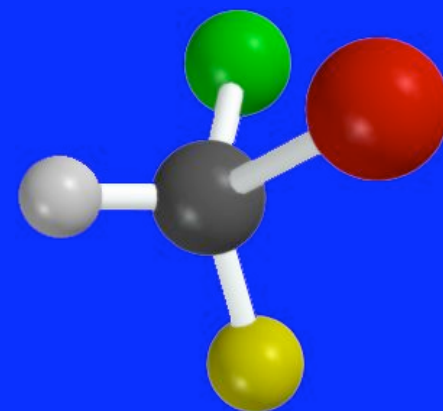
To show nonsuperposability, rotate this model 180° around a vertical axis.

Bromochlorofluoromethane is chiral



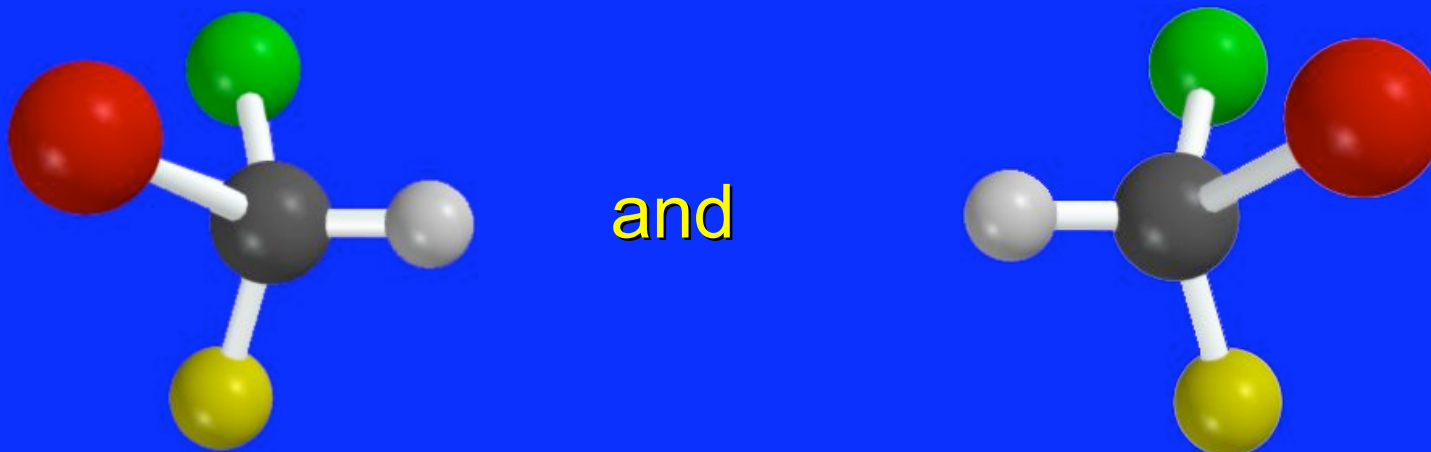


*Another look*



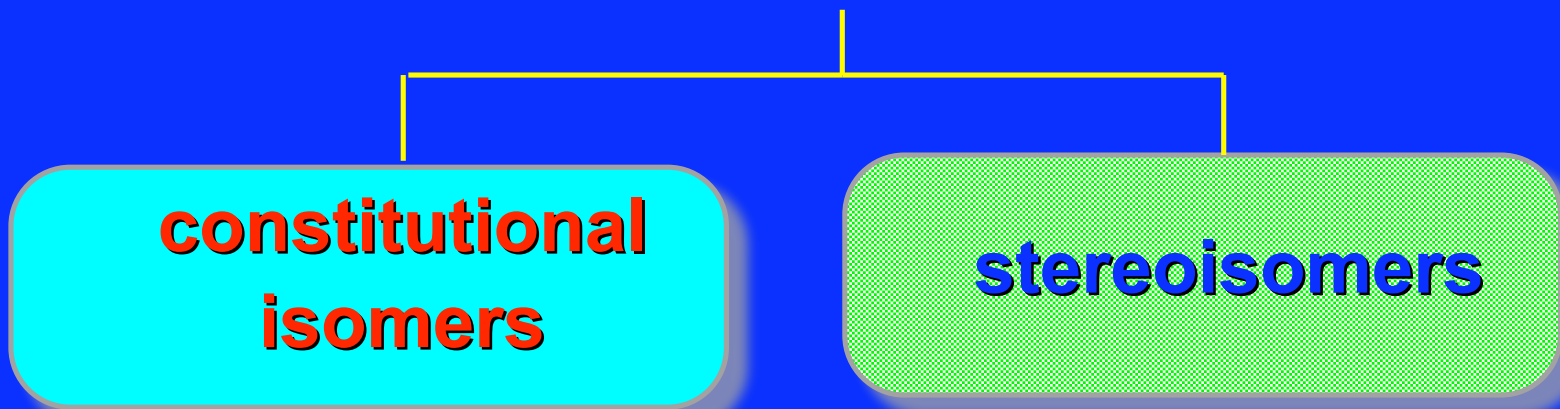
## *Enantiomers*

nonsuperposable mirror images are called enantiomers

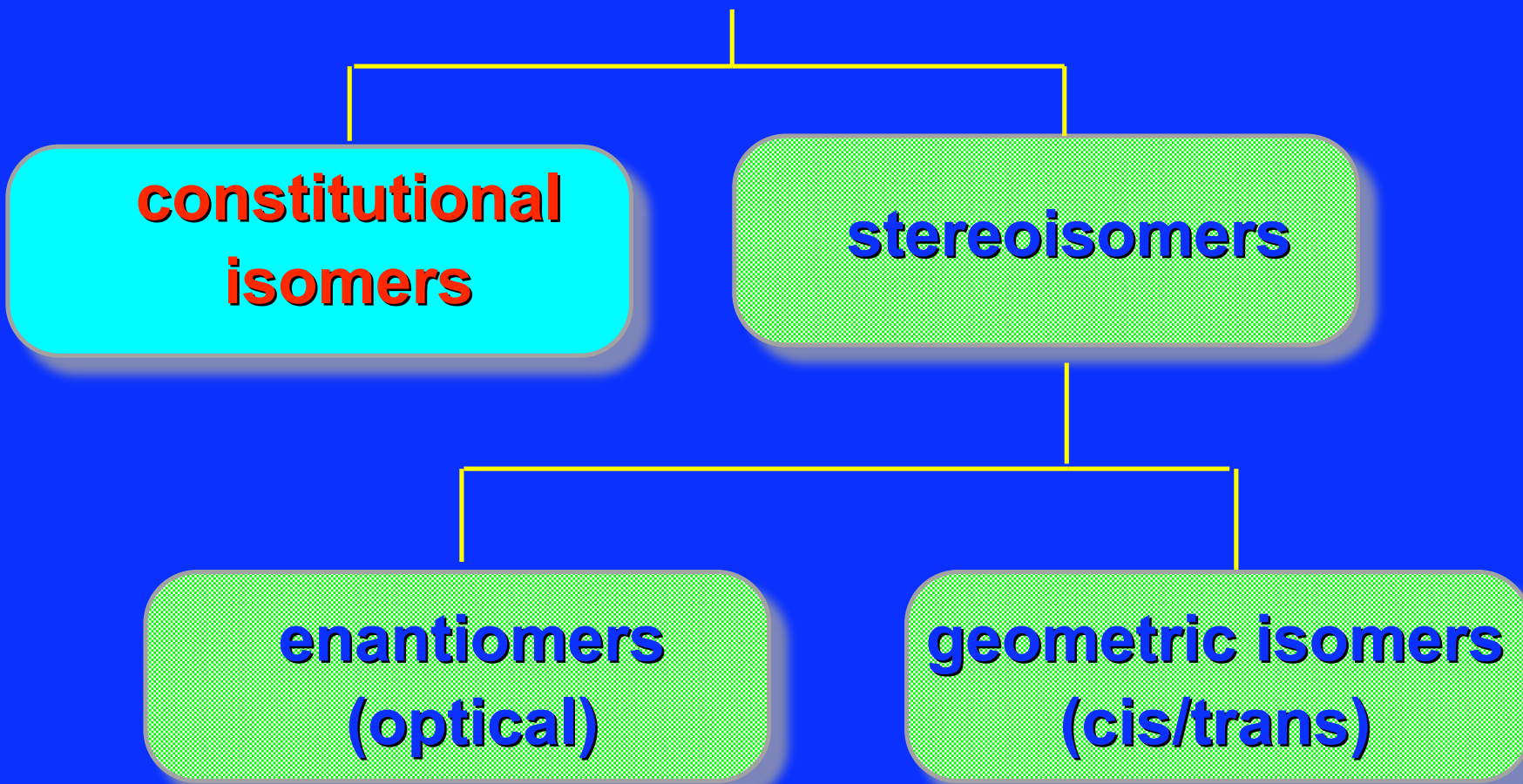


are enantiomers with respect to each other

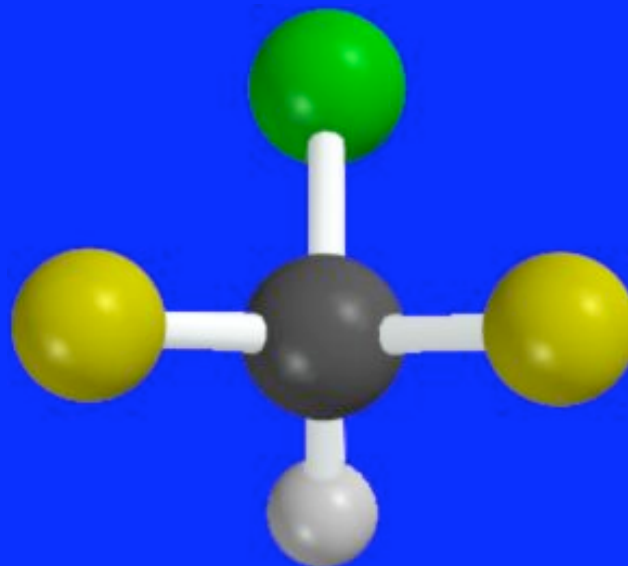
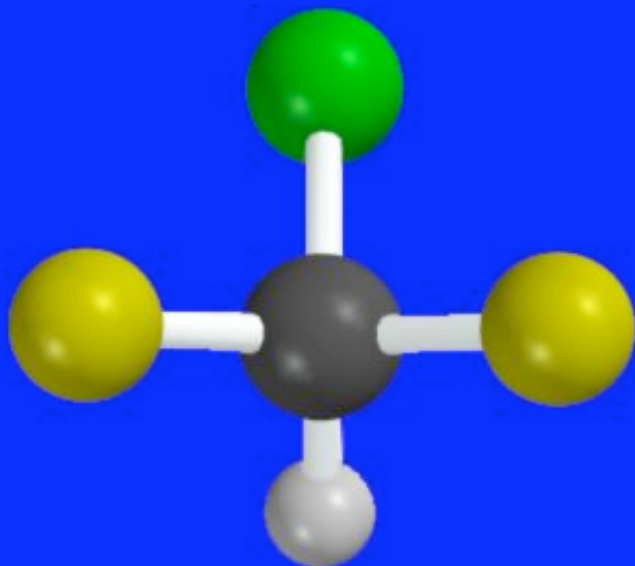
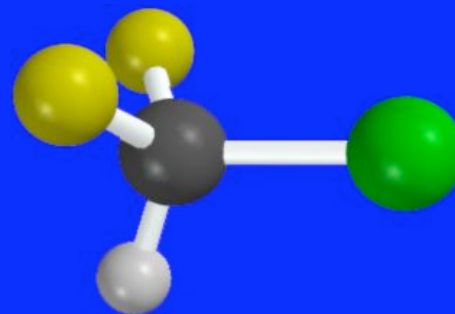
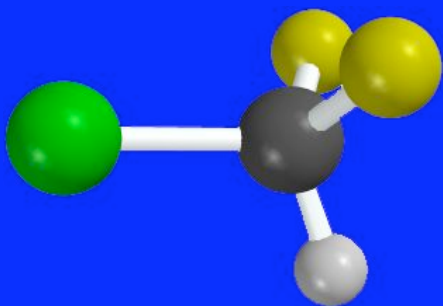
# *Isomers*

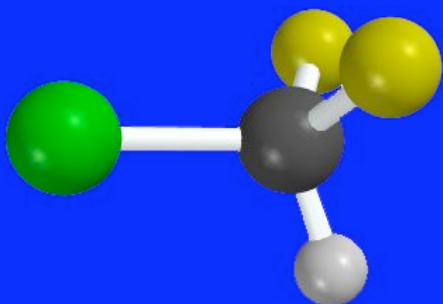


# *Isomers*

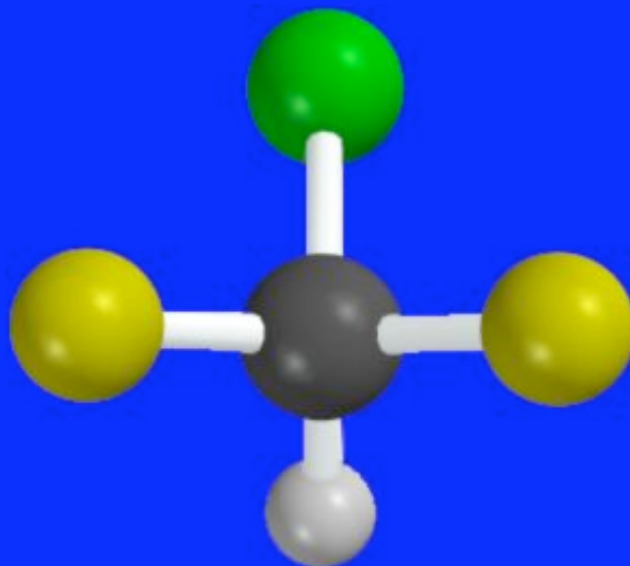
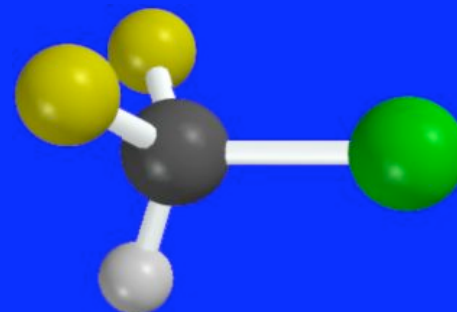


Chlorodifluoromethane  
is achiral





Chlorodifluoromethane  
is achiral



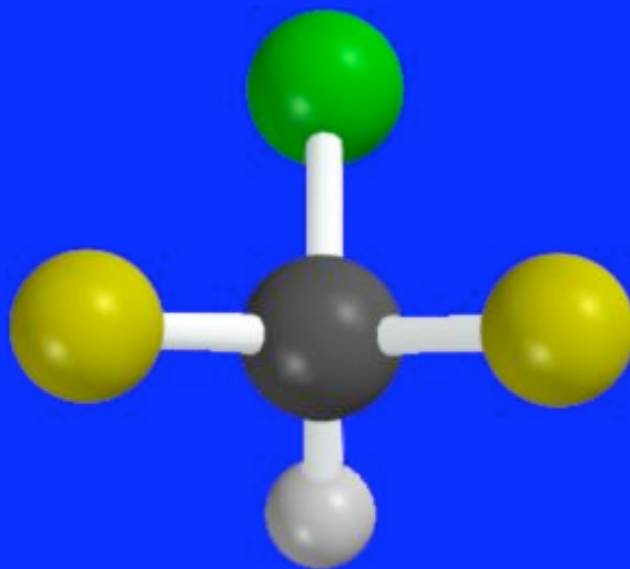
The two structures  
are mirror images,  
but are not  
enantiomers,  
because they can  
be superposed on  
each other.

# Symmetry in Achiral Structures

## Symmetry tests for achiral structures

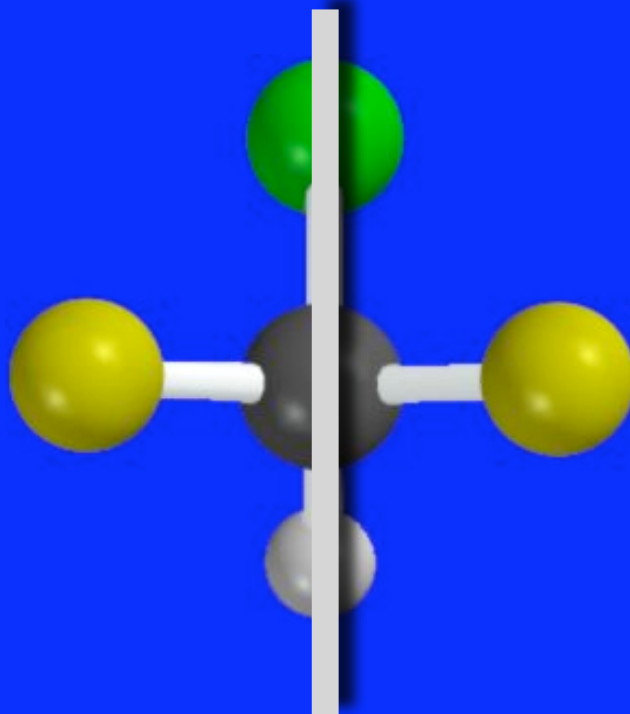
Any molecule with a plane of symmetry  
must be achiral.

## *Plane of symmetry*



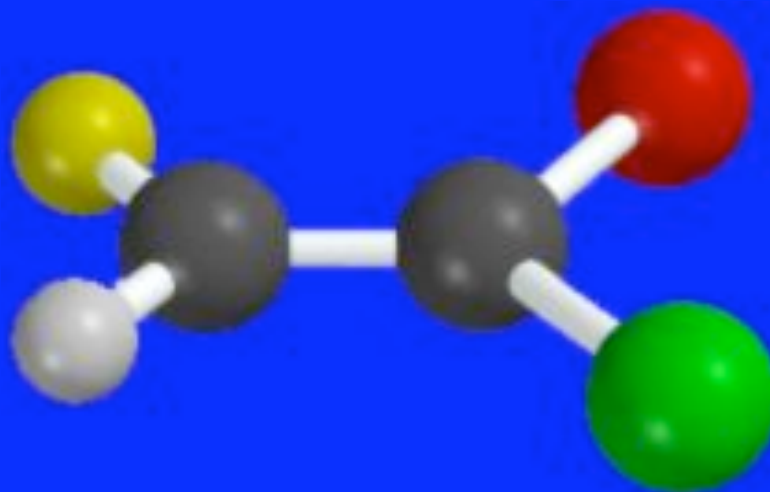
A plane of symmetry bisects a molecule into two mirror image halves. Chlorodifluoromethane has a plane of symmetry.

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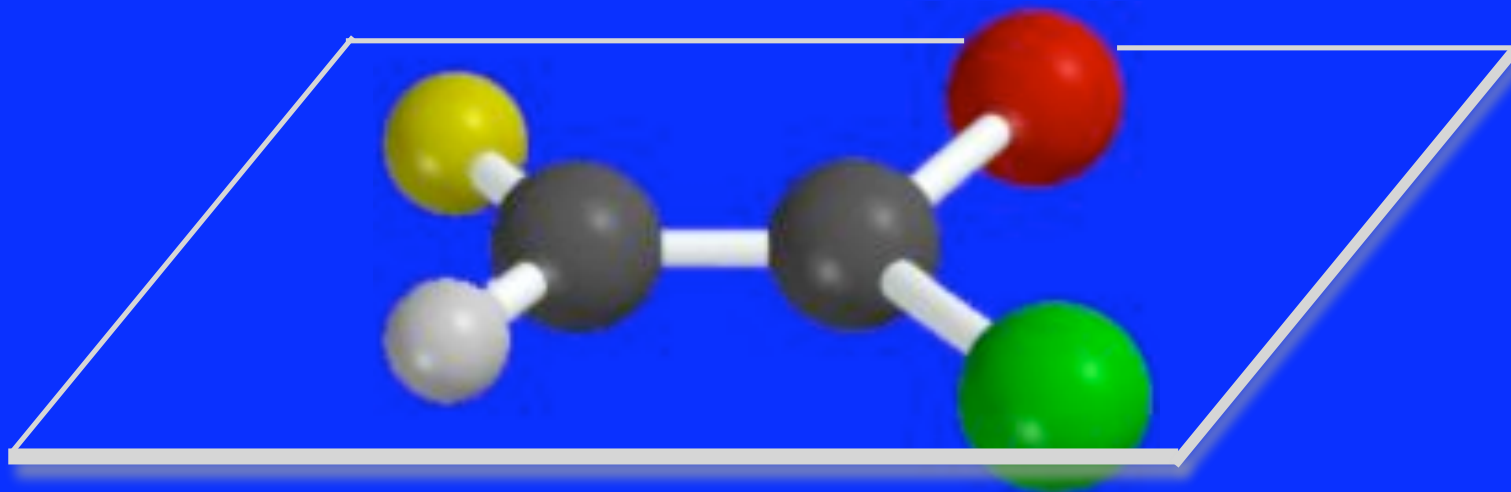
## *Plane of symmetry*



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1-Bromo-1-chloro-2-fluoroethene has a plane of symmetry.

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# Physical Properties of Alkanes and Cycloalkanes

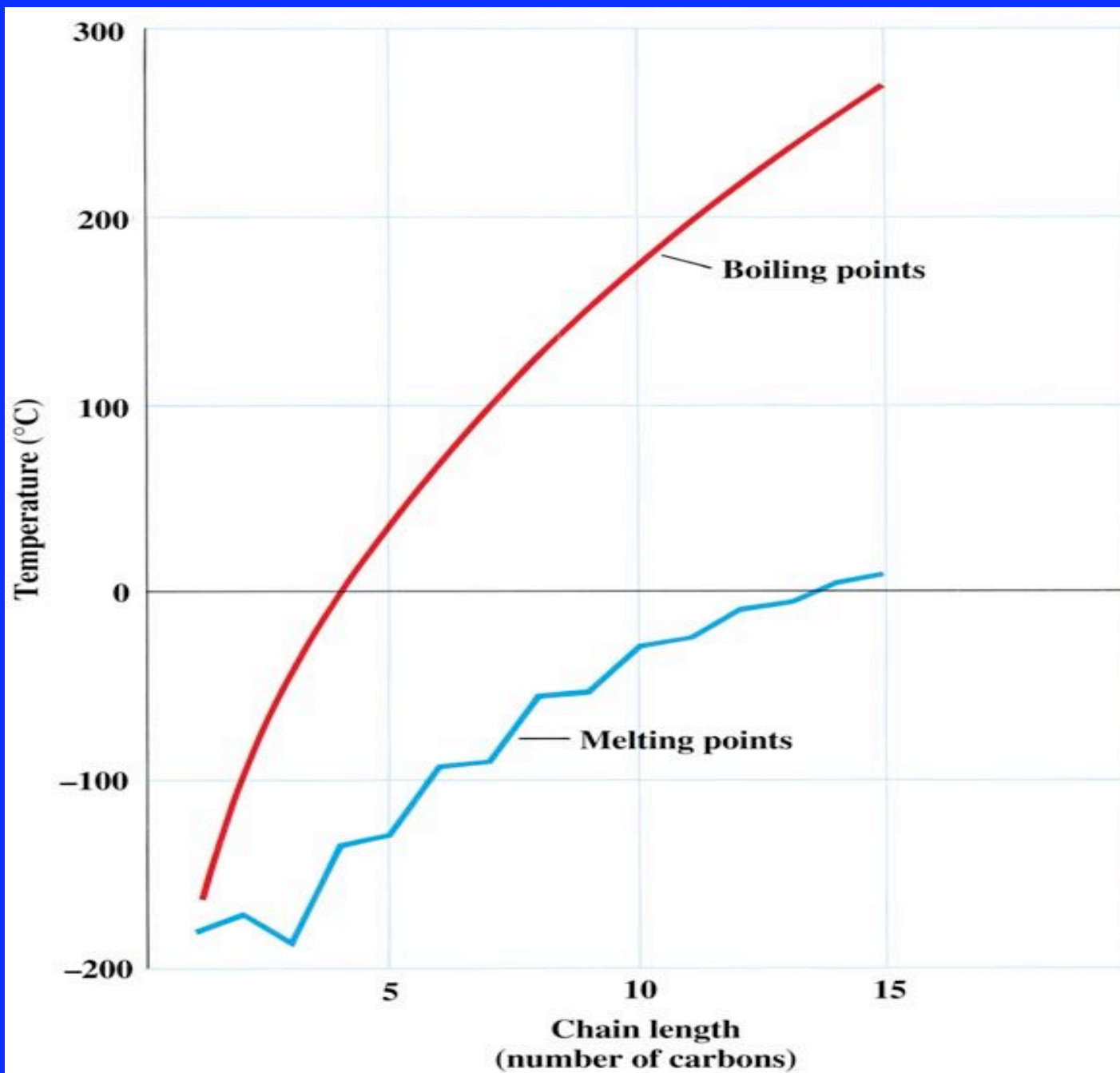
## *Boiling Points*

increase with increasing number of carbons

more atoms, more electrons, more opportunities for induced dipole-induced dipole forces

decrease with chain branching

branched molecules are more compact with smaller surface area—fewer points of contact with other molecules



## Boiling Points

increase with increasing number of carbons

more atoms, more electrons, more opportunities for induced dipole-induced dipole forces



Heptane  
bp 98°C



Octane  
bp 125°C



Nonane  
bp 150°C

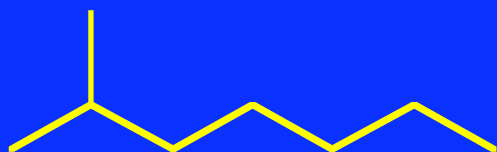
## Boiling Points

decrease with chain branching

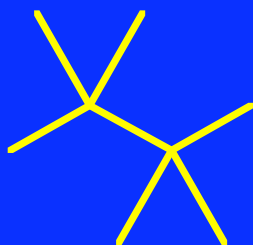
branched molecules are more compact with smaller surface area—fewer points of contact with other molecules



Octane: bp 125°C



2-Methylheptane: bp 118°C



2,2,3,3-Tetramethylbutane: bp 107°C

## *Boiling Points of Alkanes*

governed by strength of intermolecular attractive forces

alkanes are nonpolar, so dipole-dipole and dipole-induced dipole forces are absent

only forces of intermolecular attraction are induced dipole-induced dipole forces

## *Induced dipole-Induced dipole attractive forces*



two nonpolar molecules

center of positive charge and center of negative charge coincide in each

## *Induced dipole-Induced dipole attractive forces*



movement of electrons creates an  
instantaneous dipole in one molecule (left)

## *Induced dipole-Induced dipole attractive forces*



temporary dipole in one molecule (left) induces a complementary dipole in other molecule (right)

## *Induced dipole-Induced dipole attractive forces*



temporary dipole in one molecule (left) induces a complementary dipole in other molecule (right)

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the result is a small attractive force between the two molecules

## *Induced dipole-Induced dipole attractive forces*



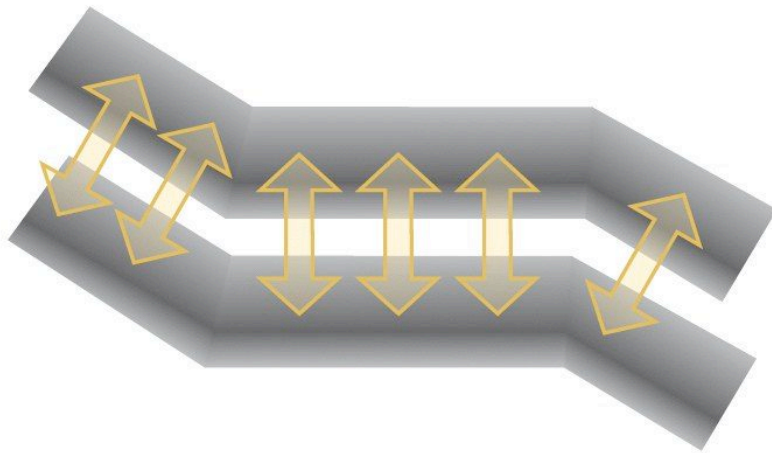
the result is a small attractive force between the two molecules

Straight chain hydrocarbon

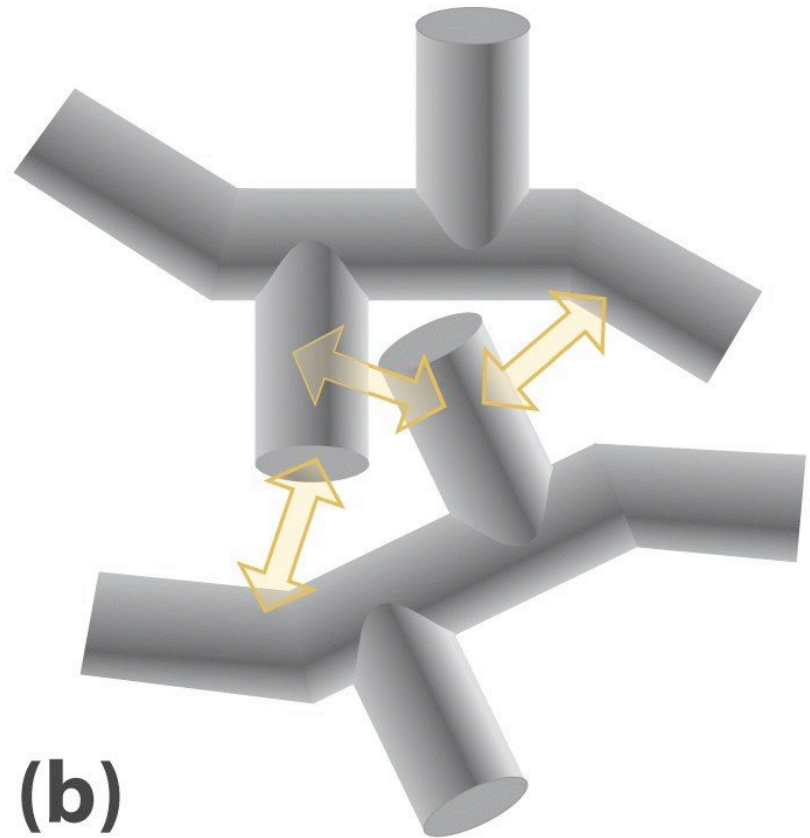
Branched hydrocarbon

Lots of intermolecular contacts

Fewer intermolecular contacts



**(a)**



**(b)**