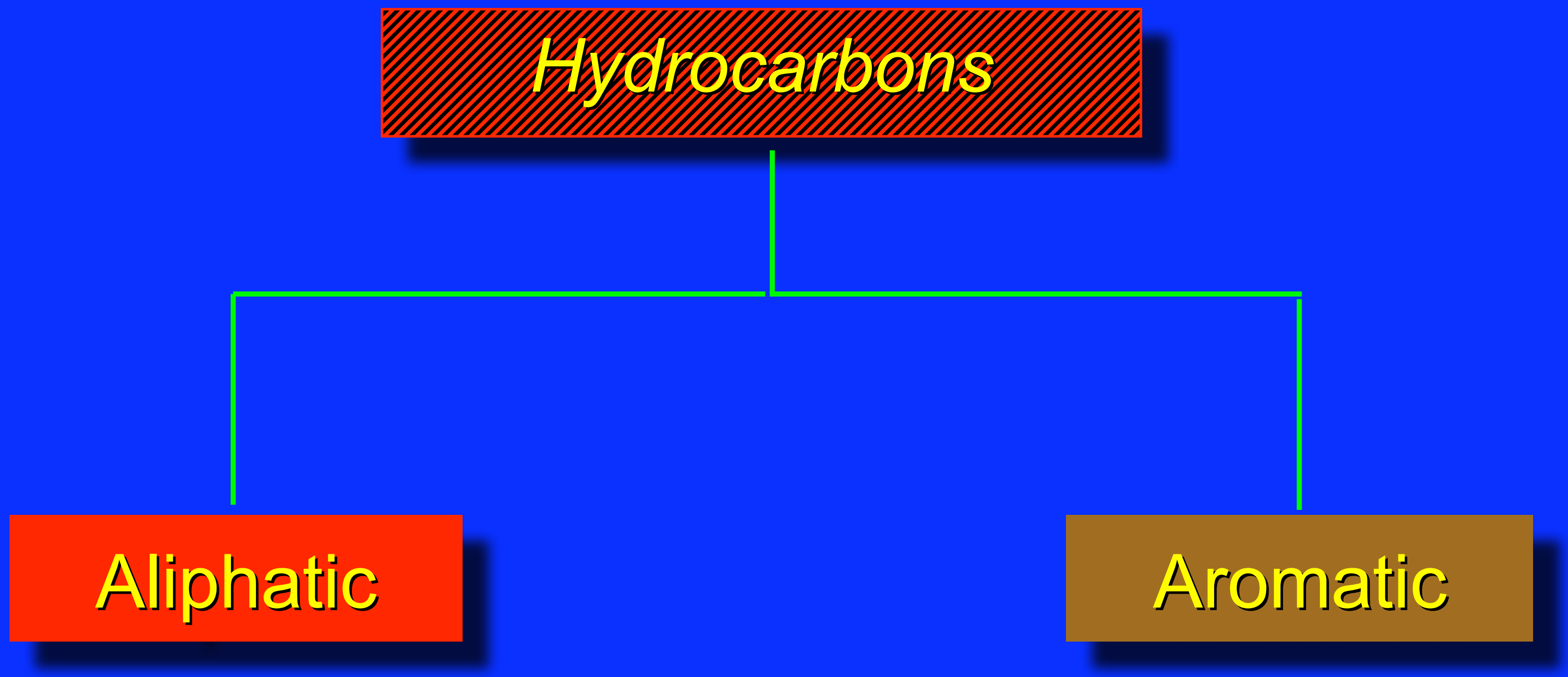
Chapter 24 From Petroleum to Pharmaceuticals

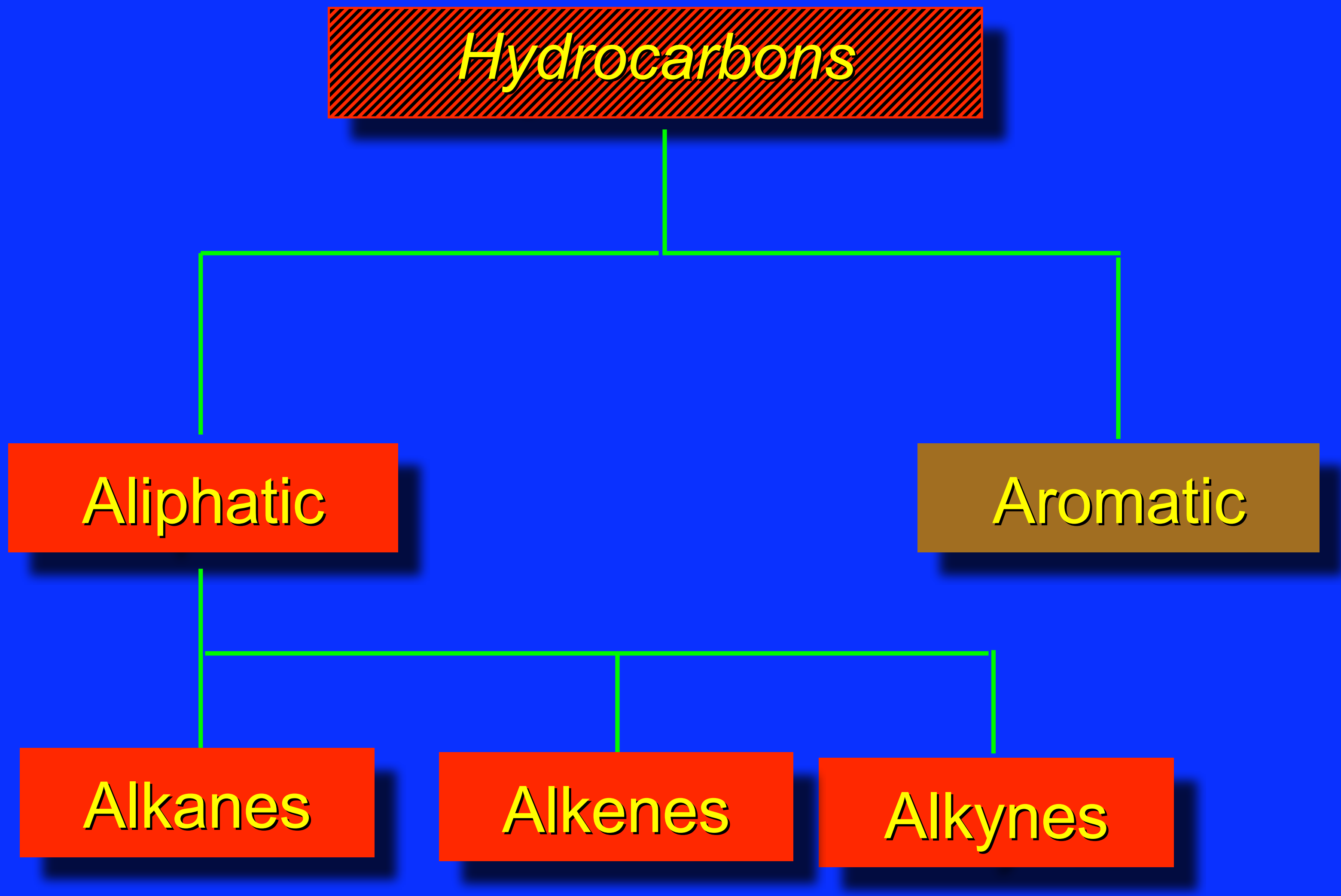
24.1 Petroleum Refining and the Hydrocarbons

24.2 Functional Groups and Organic Synthesis

24.3 Pesticides and Pharmaceuticals

IR Tutor and Infrared Spectroscopy


Hydrocarbons
Aliphatic
Aromatic

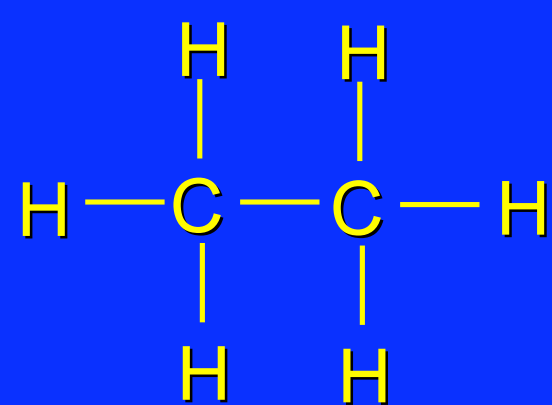

Hydrocarbons
Aliphatic
Aromatic
Alkanes
Alkenes
Alkynes

Hydrocarbons

Aliphatic

Alkanes

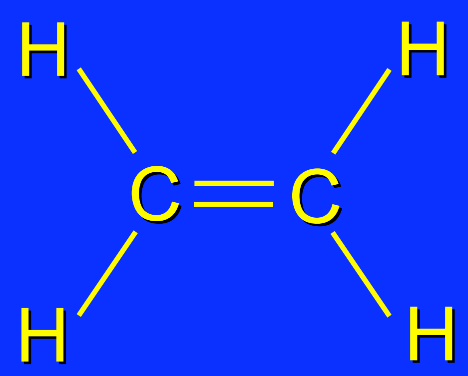
Alkanes are hydrocarbons in which all of the bonds are *single* bonds.



Hydrocarbons

- Aliphatic
  - Alkenes

Alkenes are hydrocarbons that contain at least one carbon-carbon *double* bond.



Hydrocarbons

Aliphatic

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

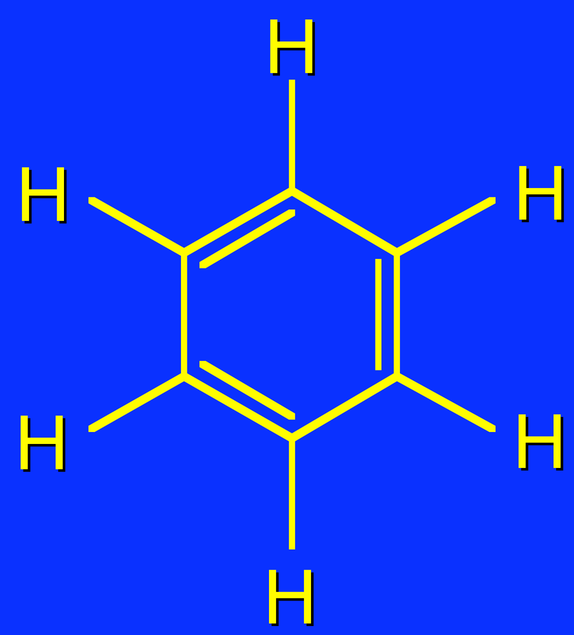
Alkynes

$HC \equiv CH$

Hydrocarbons

Aromatic

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



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

$$R{-}H \longrightarrow R{-}X$$

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

$$R{-}H \longrightarrow R{-}X$$

functional group is a hydrogen

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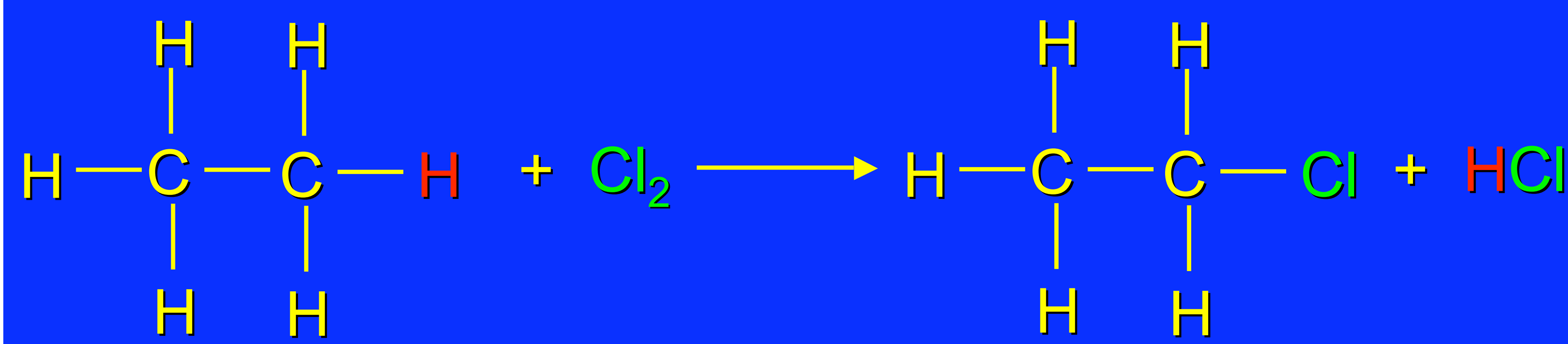
one of the hydrogens is substituted by some other atom or group

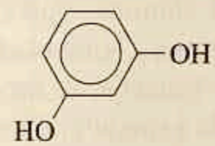


Functional Groups in Hydrocarbons

alkanes	RH
alkenes	RH, double bond
alkynes	RH, triple bond
aromatics	ArH, double bond

Some Key Functional Groups

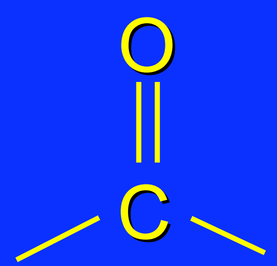
TABLE 24-2 Some Important Functional Groups in Organic Compounds

Functional Group	Type of Compound	Examples
—F, —Cl, —Br, —I	Alkyl or aryl halide	CH_3CH_2Br (bromoethane)
—OH	Alcohol	CH_3CH_2OH (ethanol)
	Phenol	 (1,3,-dihydroxybenzene, or resorcinol)
—O—	Ether	$CH_3—O—CH_3$ (dimethyl ether)
$—C(=O)H$	Aldehyde	$CH_3CH_2CH_2—C(=O)—H$ (butyraldehyde, or butanal)
$>C=O$	Ketone	$CH_3—C(=O)—CH_3$ (propanone, or acetone)
$—C(=O)OH$	Carboxylic acid	CH_3COOH (acetic acid, or ethanoic acid)
$—C(=O)O—$	Ester	$CH_3—C(=O)—O—CH_3$ (methyl acetate or methyl ethanoate)
$—N<$	Amine	CH_3NH_2 (methylamine)
$—C(=O)N<$	Amide	$CH_3—C(=O)NH_2$ (acetamide)

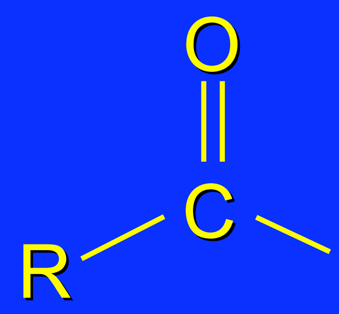
Families of organic compounds and their functional groups

Alcohols	ROH
Alkyl halides	RX (X = F, Cl, Br, I)
Amines	primary amine: RNH_2
	secondary amine: R_2NH
	tertiary amine: R_3N
Ethers	ROR

Many classes of organic compounds contain a carbonyl group

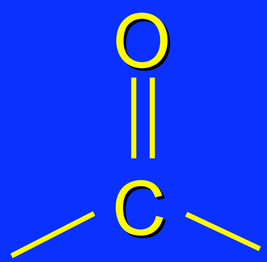


Carbonyl group

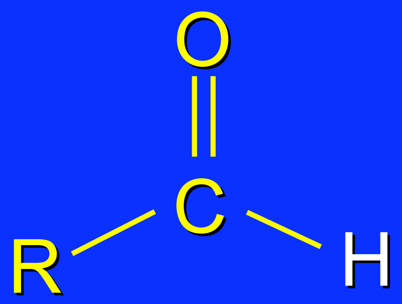


Acyl group

Many classes of organic compounds contain a carbonyl group

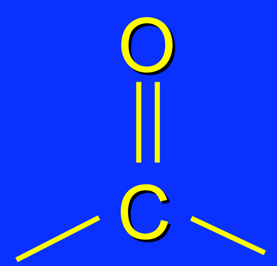


Carbonyl group

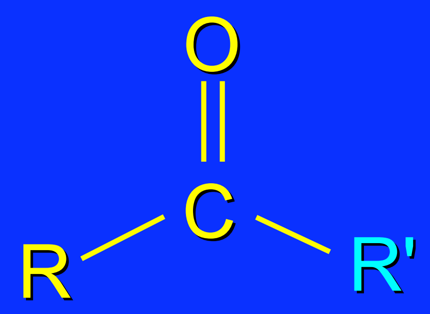


Aldehyde

Many classes of organic compounds contain a carbonyl group

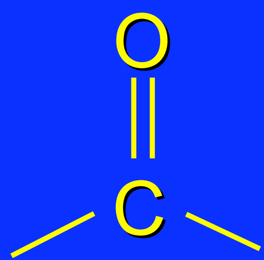


Carbonyl group

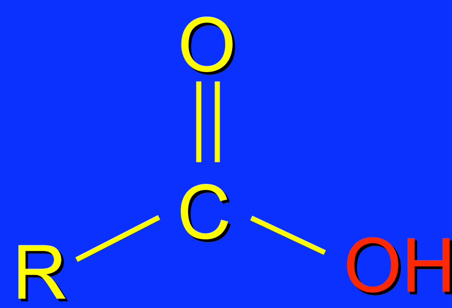


Ketone

Many classes of organic compounds contain a carbonyl group



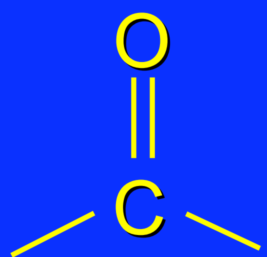
Carbonyl group



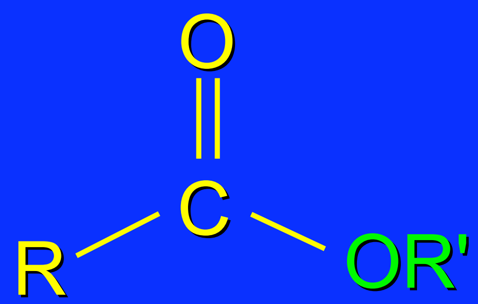
Carboxylic acid

Not a ketone-alcohol!

Many classes of organic compounds contain a carbonyl group



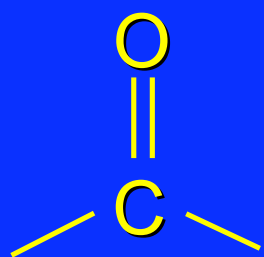
Carbonyl group



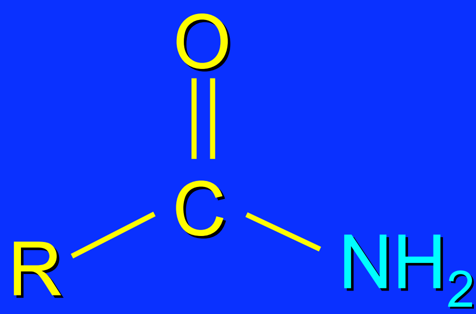
Ester

Not a ketone-ether!

Many classes of organic compounds contain a carbonyl group



Carbonyl group



Amide

Note a ketone-amine!

Alkanes

General formula for an alkane

C_nH_{2n+2}

Introduction to Alkanes:

Methane, CH_4

Ethane, C_2H_6

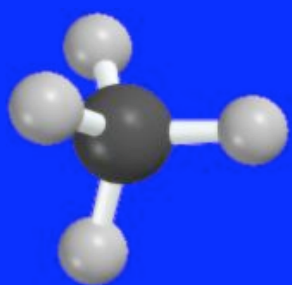
Propane, C_3H_8

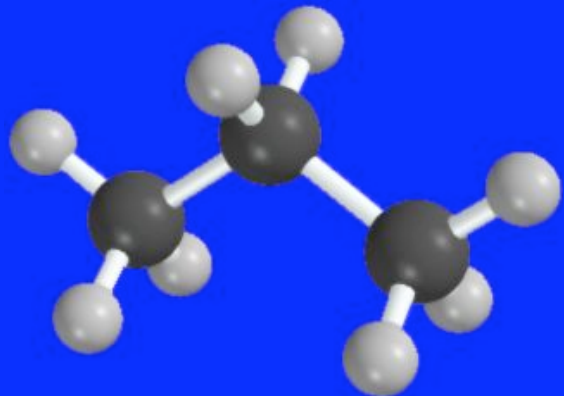
The simplest alkanes

Methane (CH_4) CH_4

Ethane (C_2H_6) CH_3CH_3

Propane (C_3H_8) $CH_3CH_2CH_3$





bp -160°C bp -89°C bp -42°C

No isomers possible for C1, C2, C_3 hydrocarbons

Isomeric Alkanes:
The Butanes

C_4H_{10}

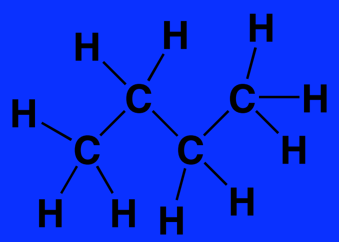
General formula for any butane

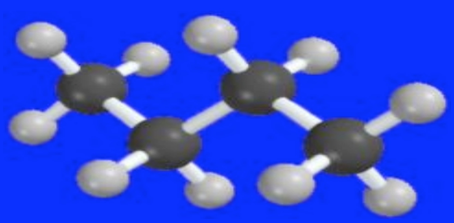
Isomers: same composition, different structures at the constitutional or stereochemical levels

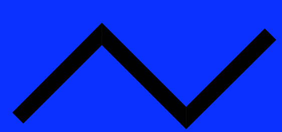
C_4H_{10}

n-Butane (bp -0.4°C)

$CH_3CH_2CH_2CH_3$

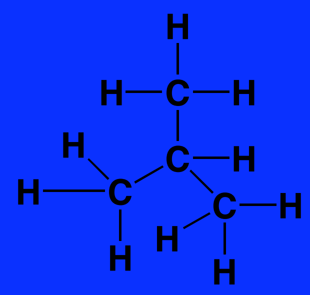


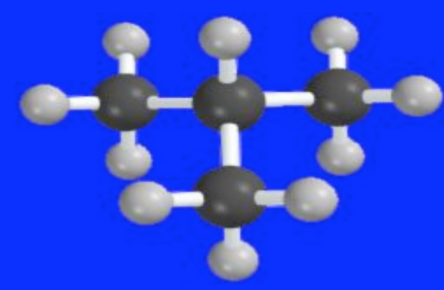


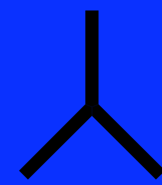


Isobutane (bp -10.2°C)

$(CH_3)_3CH$







Higher *n*-Alkanes
Pentane (C_5H_{12}) and Beyond

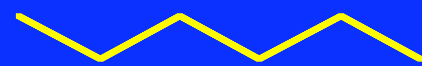
C_nH_{2n+2}
$n > 4$

$CH_3CH_2CH_2CH_2CH_3$

n-Pentane

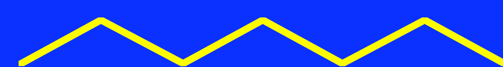
C_nH_{2n+2}

n > 4



$CH_3CH_2CH_2CH_2CH_2CH_3$

n-Hexane



$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$

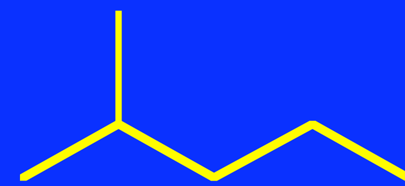
n-Heptane

The C_5H_{12} Isomers

C_5H_{12}

$CH_3CH_2CH_2CH_2CH_3$

n-Pentane



$(CH_3)_2CHCH_2CH_3$

Isopentane

$(CH_3)_4C$

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

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

Table 2.3
Number of Constitutionally Isomeric Alkanes

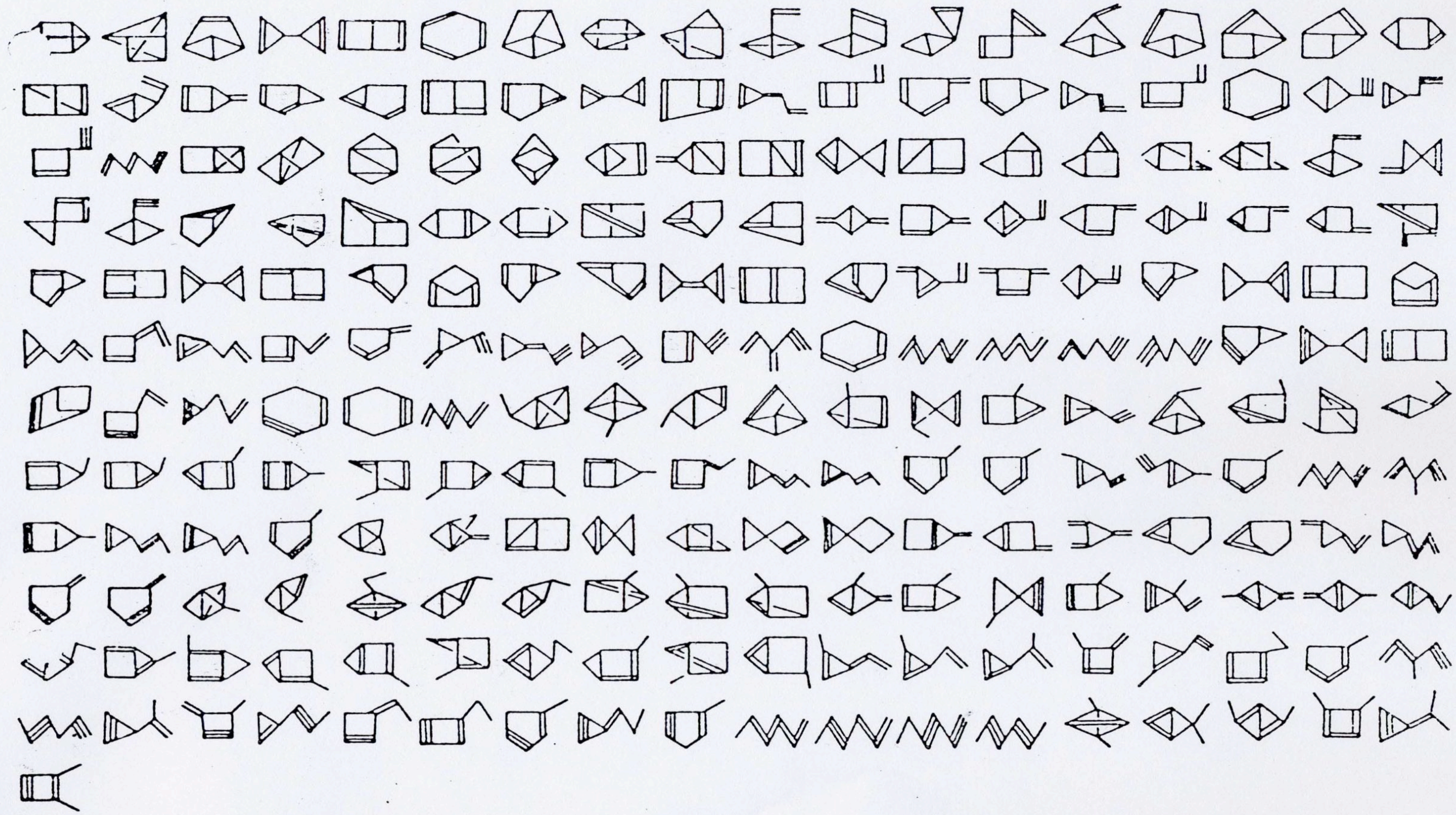
CH_4	1	C_8H_{18}	18
C_2H_6	1	C_9H_{20}	35
C_3H_8	1	$C_{10}H_{22}$	75
C_4H_{10}	2	$C_{15}H_{32}$	4,347
C_5H_{12}	3	$C_{20}H_{42}$	366,319
C_6H_{14}	5	$C_{40}H_{82}$	62,491,178,805,831
C_7H_{16}	9		

(~6 x 10^{13} isomers!)

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

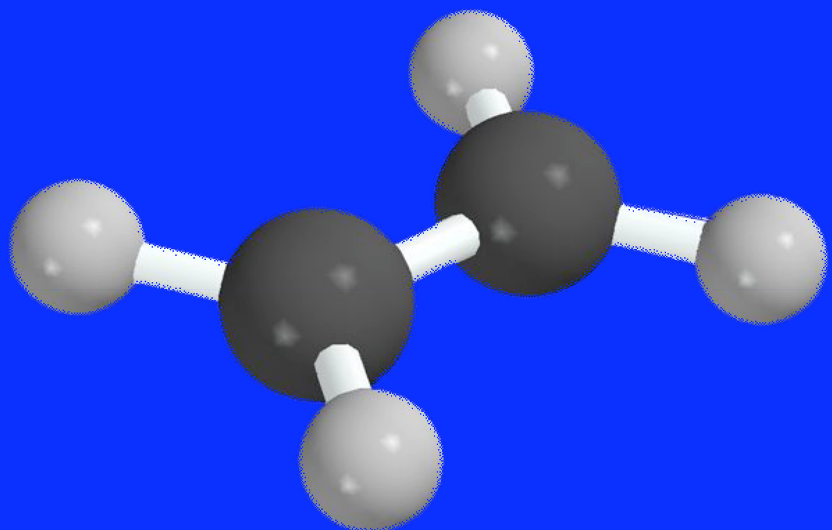
Structure of Ethylene

bond angles: H-C-H = 117°

H-C-C = 121°

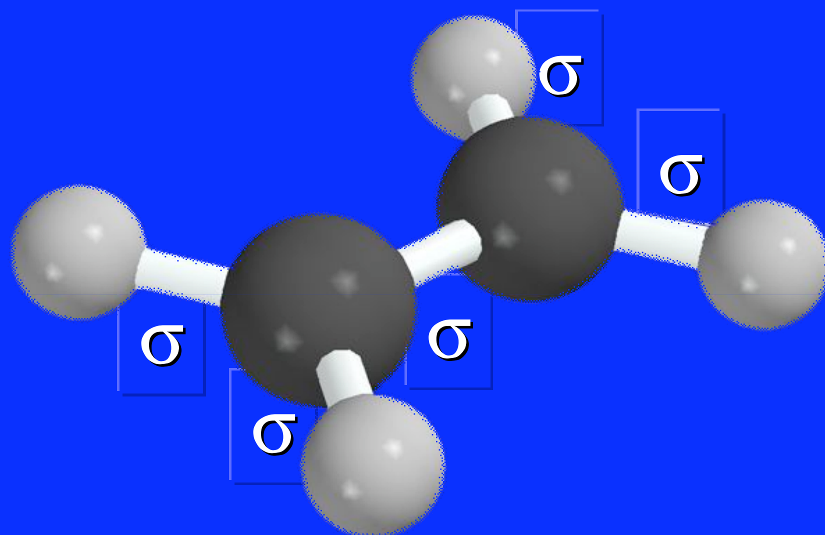
bond distances: C—H = 110 pm

C=C = 134 pm



planar

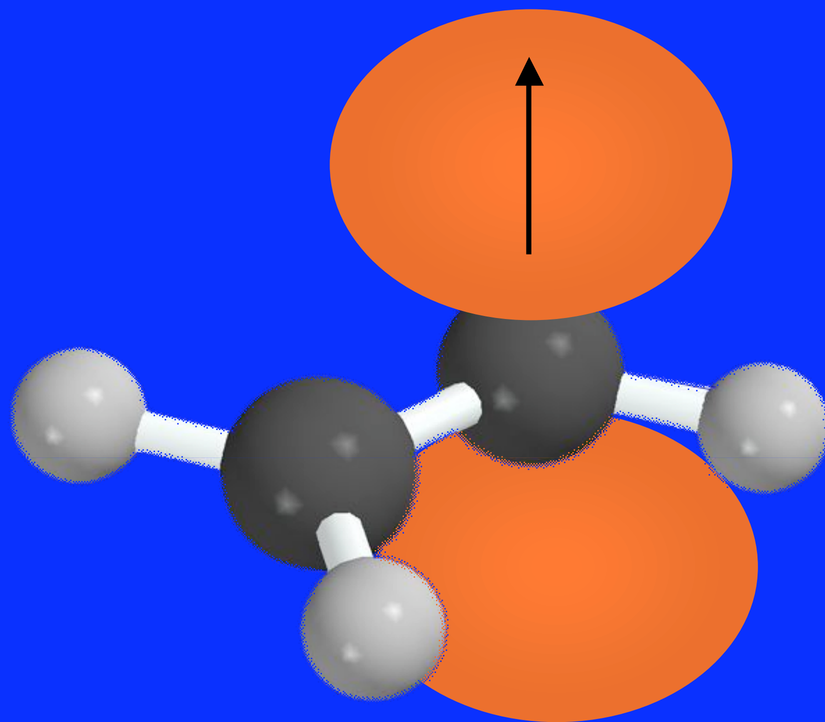
Bonding in Ethylene



Framework of σ bonds

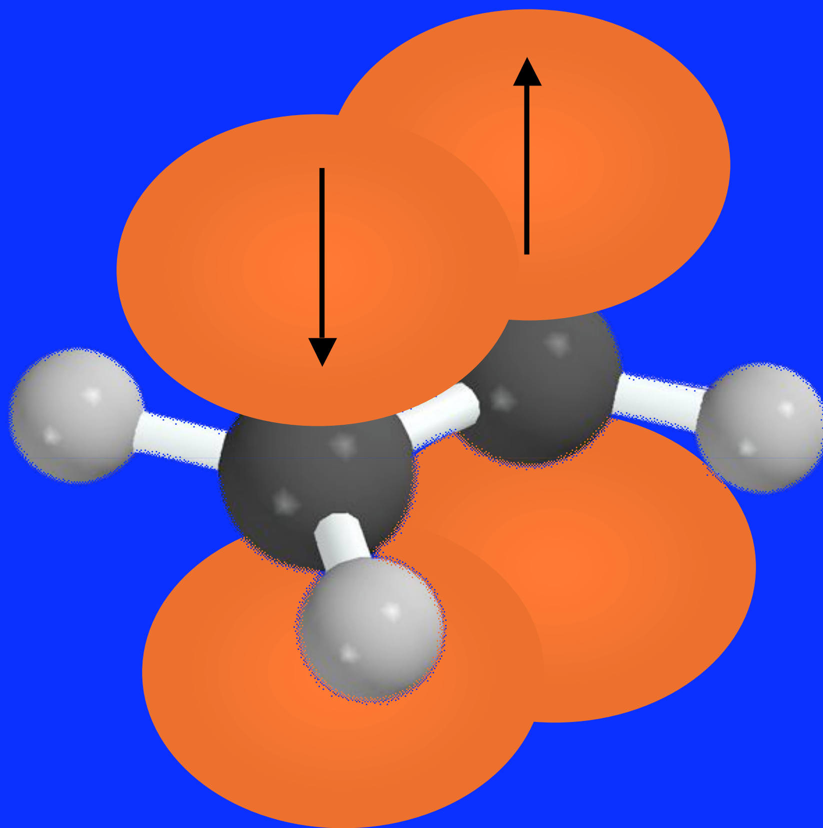
Each carbon is *sp*^{2} hybridized

Bonding in Ethylene



Each carbon has a half-filled *p* orbital

Bonding in Ethylene



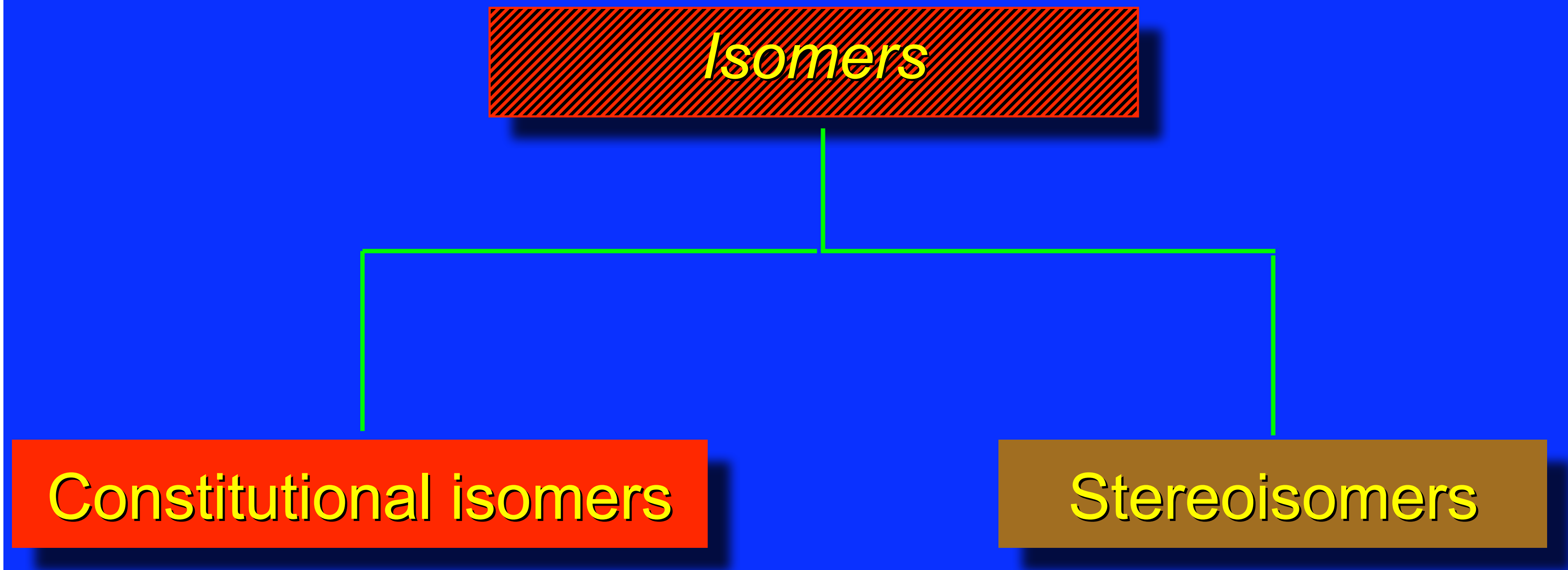
Side-by-side overlap of half-filled *p* orbitals gives a π bond which makes it ***very*** difficult to rotate about the C=C bond

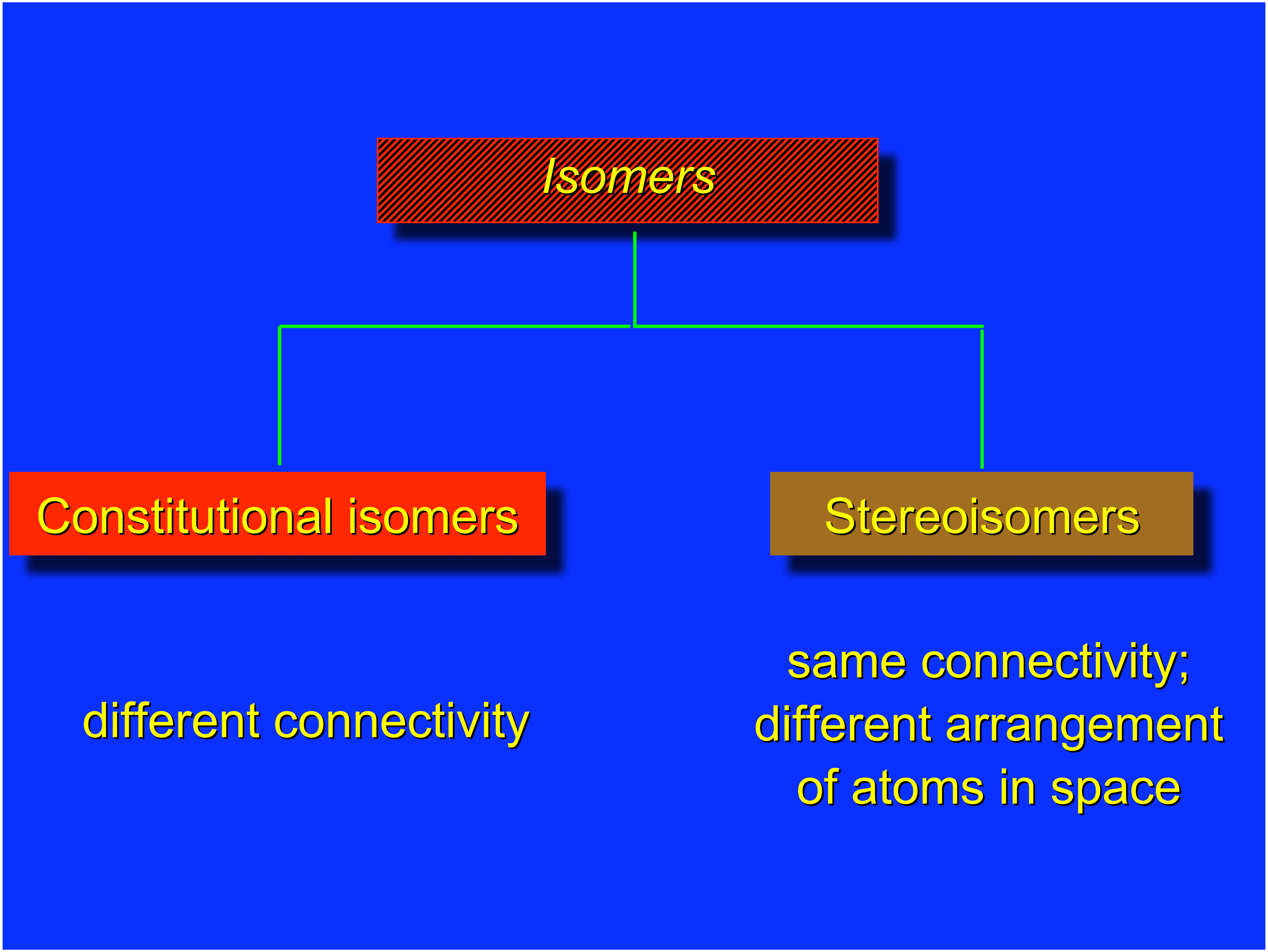
Isomerism in Alkenes

Isomers

Isomers are different compounds that have the same composition (numbers and kinds. of atoms).

Since the compounds are different, they must have different structures in the way the atoms are connected or arranged in space


Isomers
Constitutional isomers
Stereoisomers

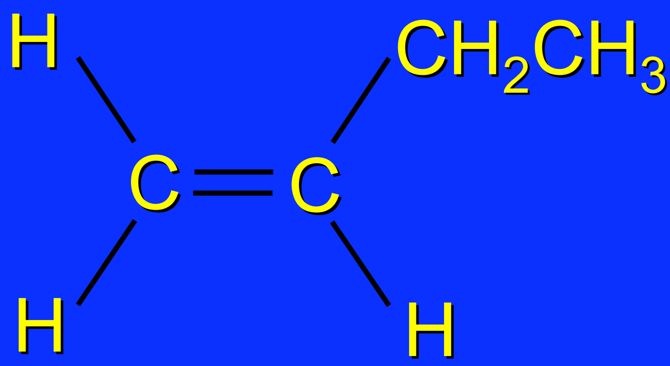

Isomers
Constitutional isomers
Stereoisomers
different connectivity
same connectivity;
different arrangement
of atoms in space

Isomers

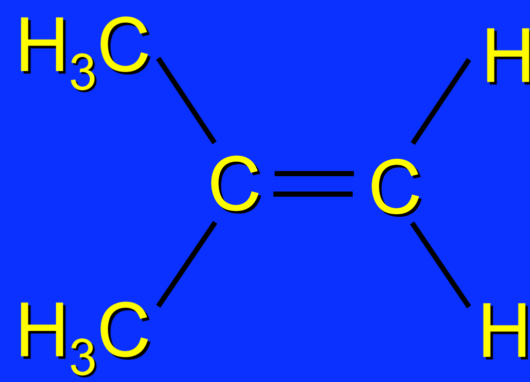
Constitutional isomers

Stereoisomers

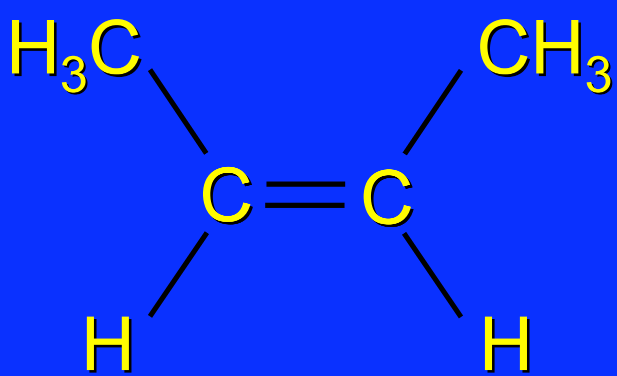
consider the isomeric alkenes of molecular formula C_4H_8



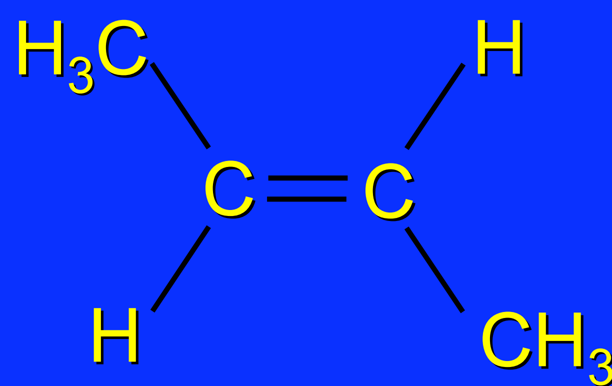
1-Butene



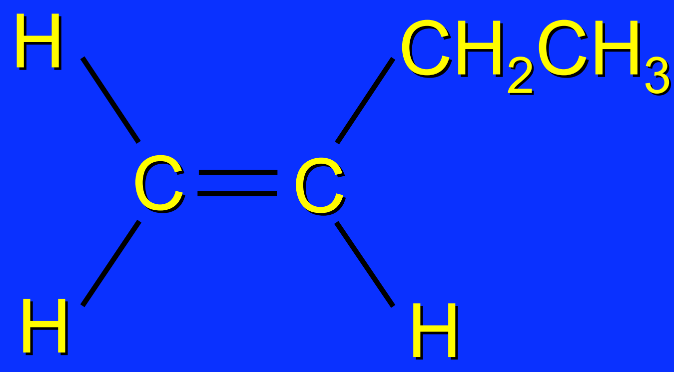
2-Methylpropene



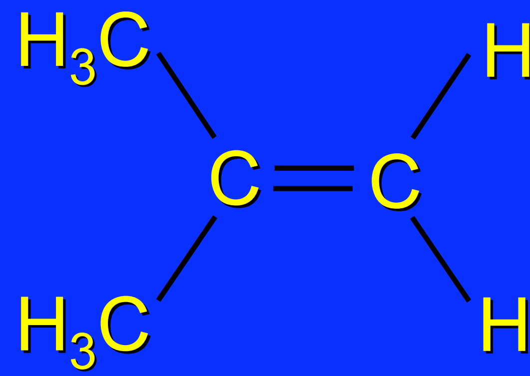
cis-2-Butene



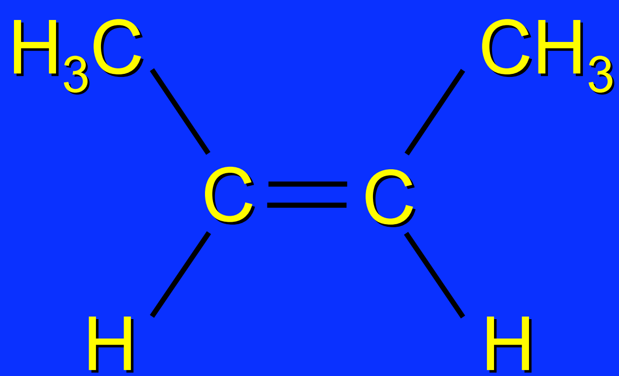
trans-2-Butene



1-Butene



2-Methylpropene

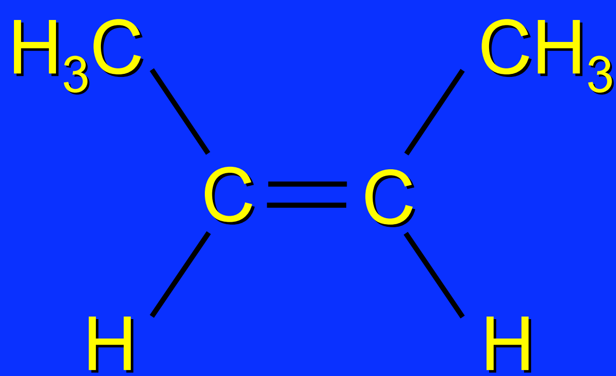


cis-2-Butene

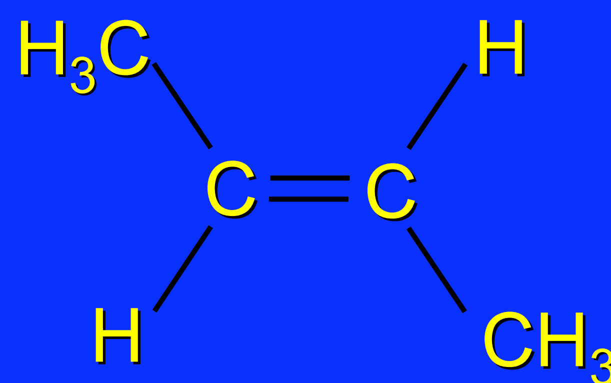
Constitutional isomers

Same connections, different atomic positions in space

Stereoisomers



cis-2-Butene

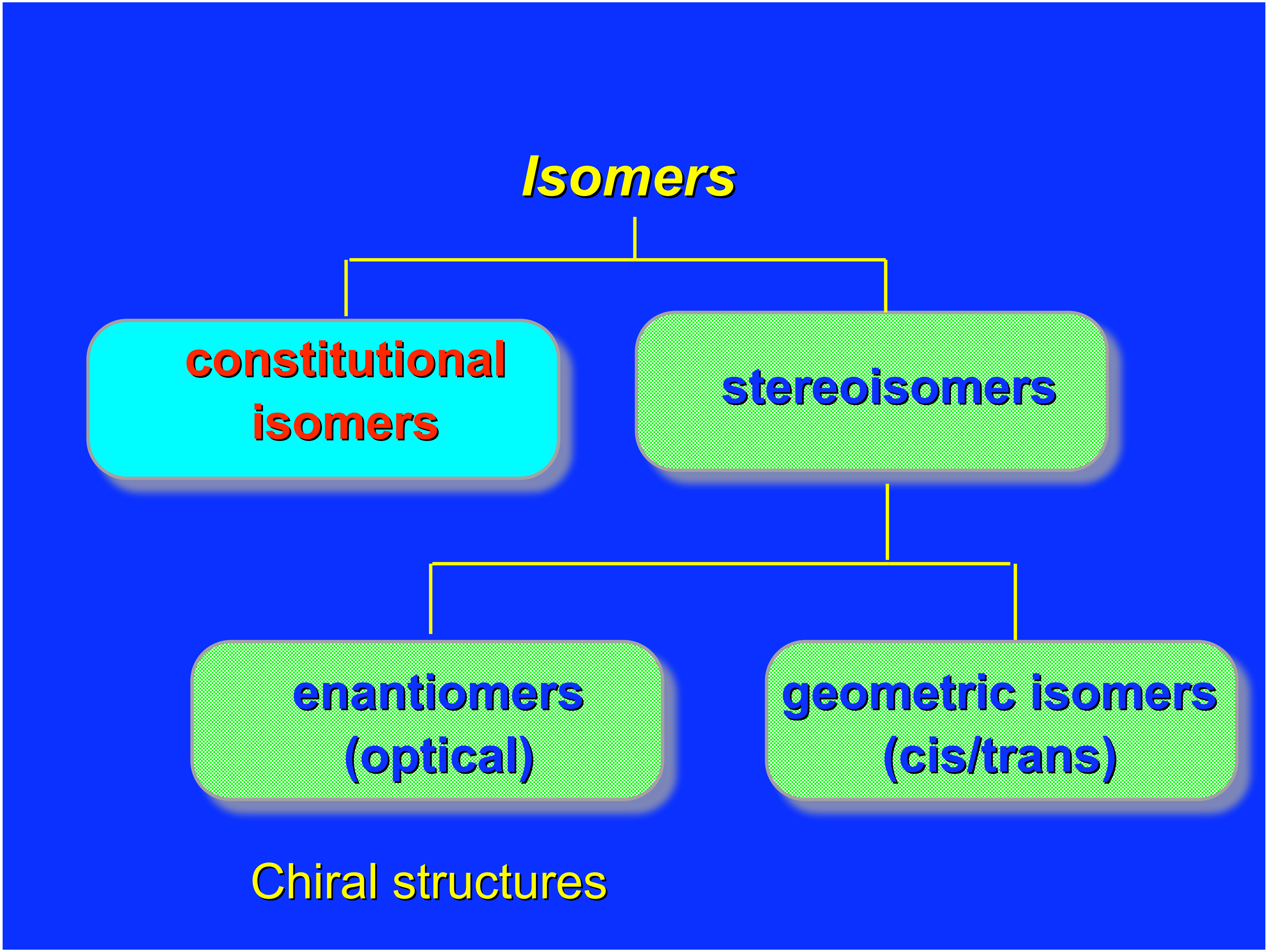


trans-2-Butene

Molecular Chirality:
Enantiomers

Isomers

- constitutional isomers
- stereoisomers

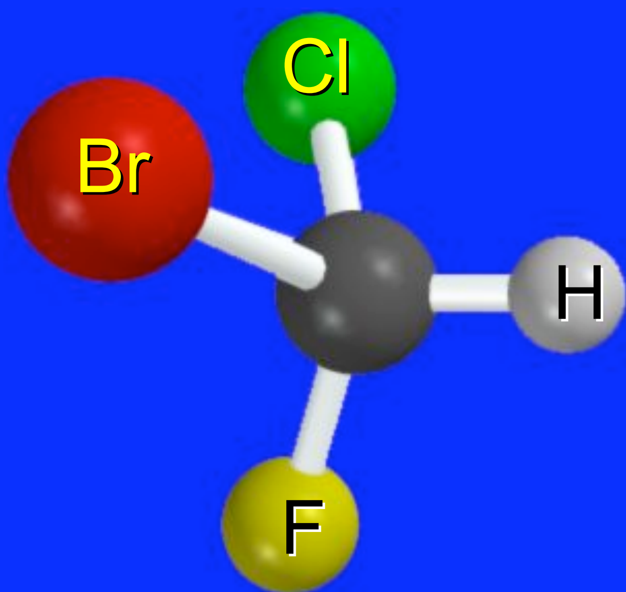

Isomers
constitutional isomers
stereoisomers
enantiomers (optical)
geometric isomers (cis/trans)
Chiral structures

Chirality

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

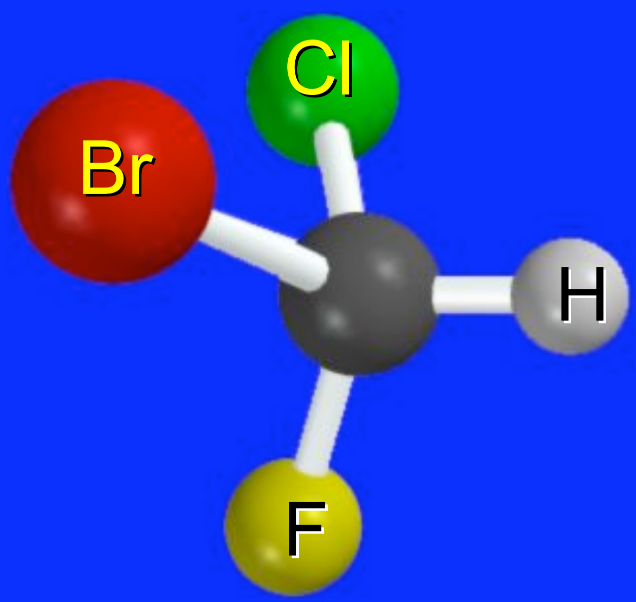
A molecule is *achiral* if its two mirror image forms are superposable.

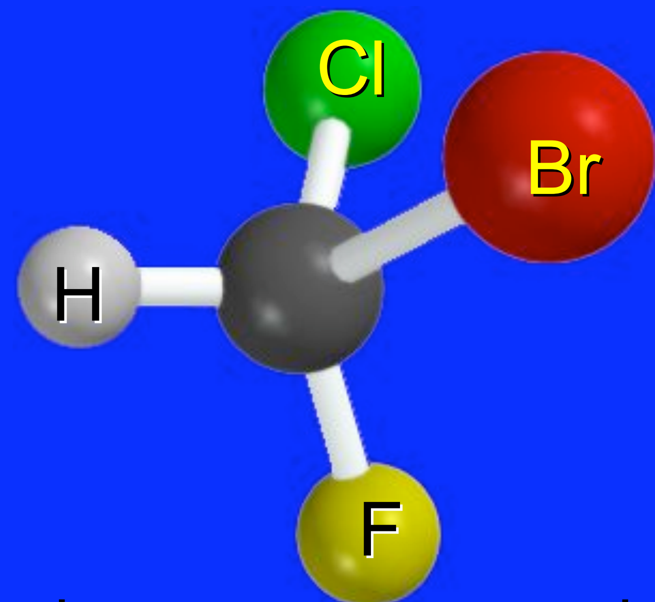
Bromochlorofluoromethane is chiral



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

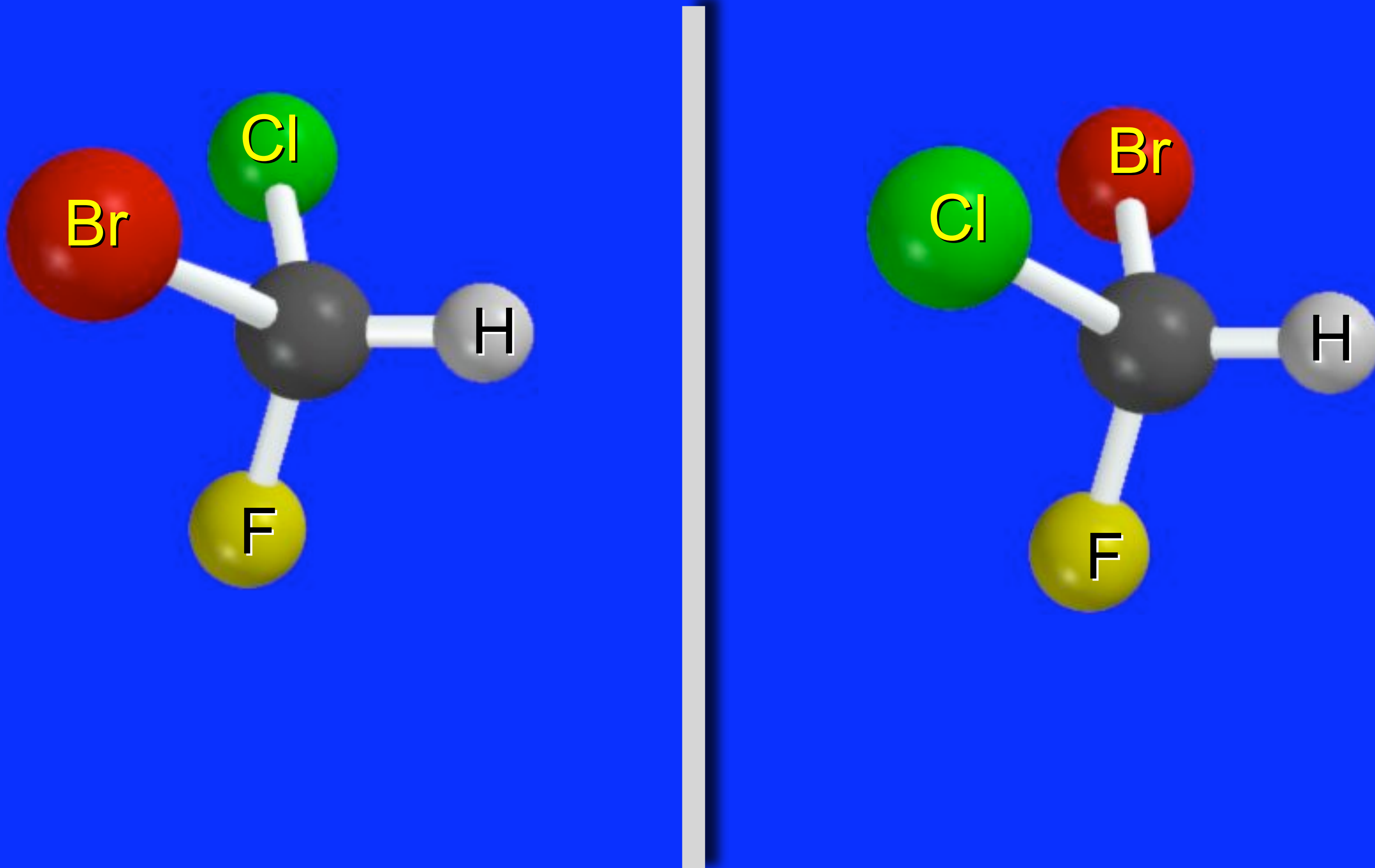
Bromochlorofluoromethane is chiral

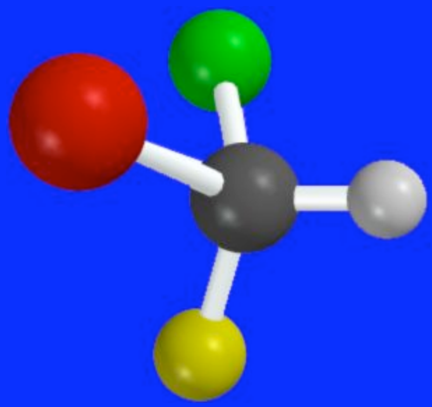




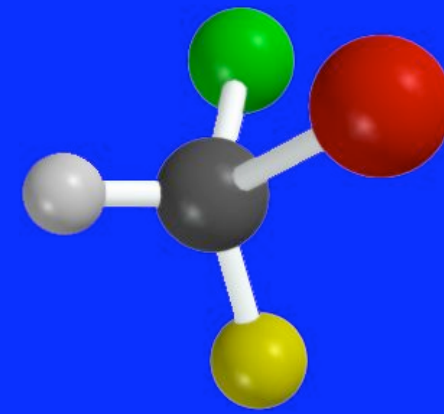
To show nonsuperposability, rotate this model 180° around a vertical axis.

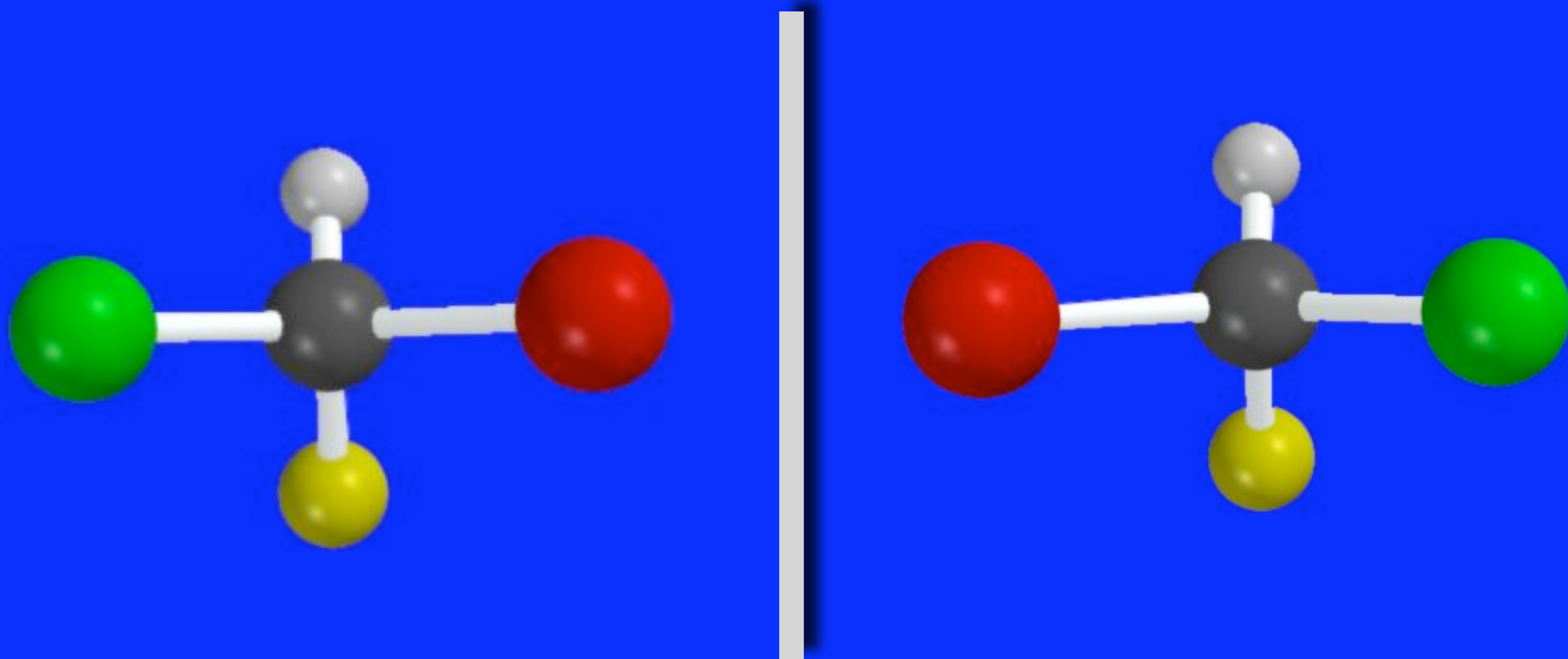
Bromochlorofluoromethane is chiral





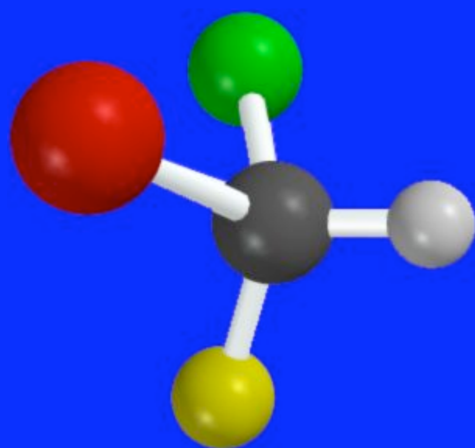
Another look



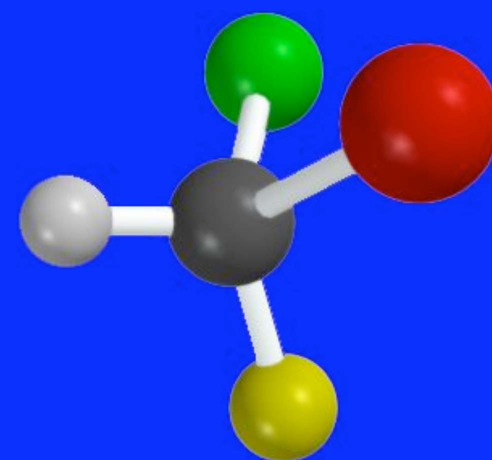


Enantiomers

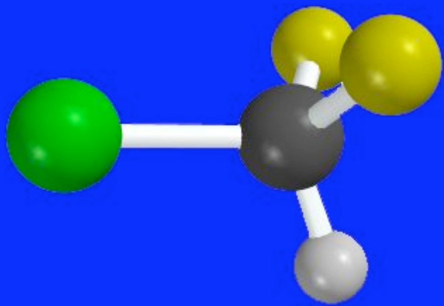
nonsuperposable mirror images are called enantiomers



and

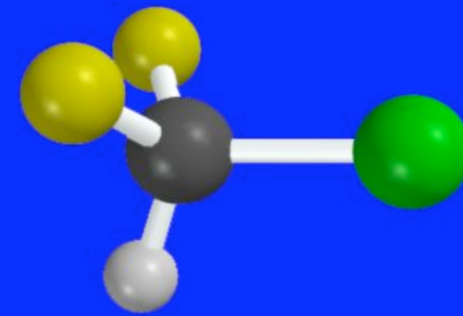


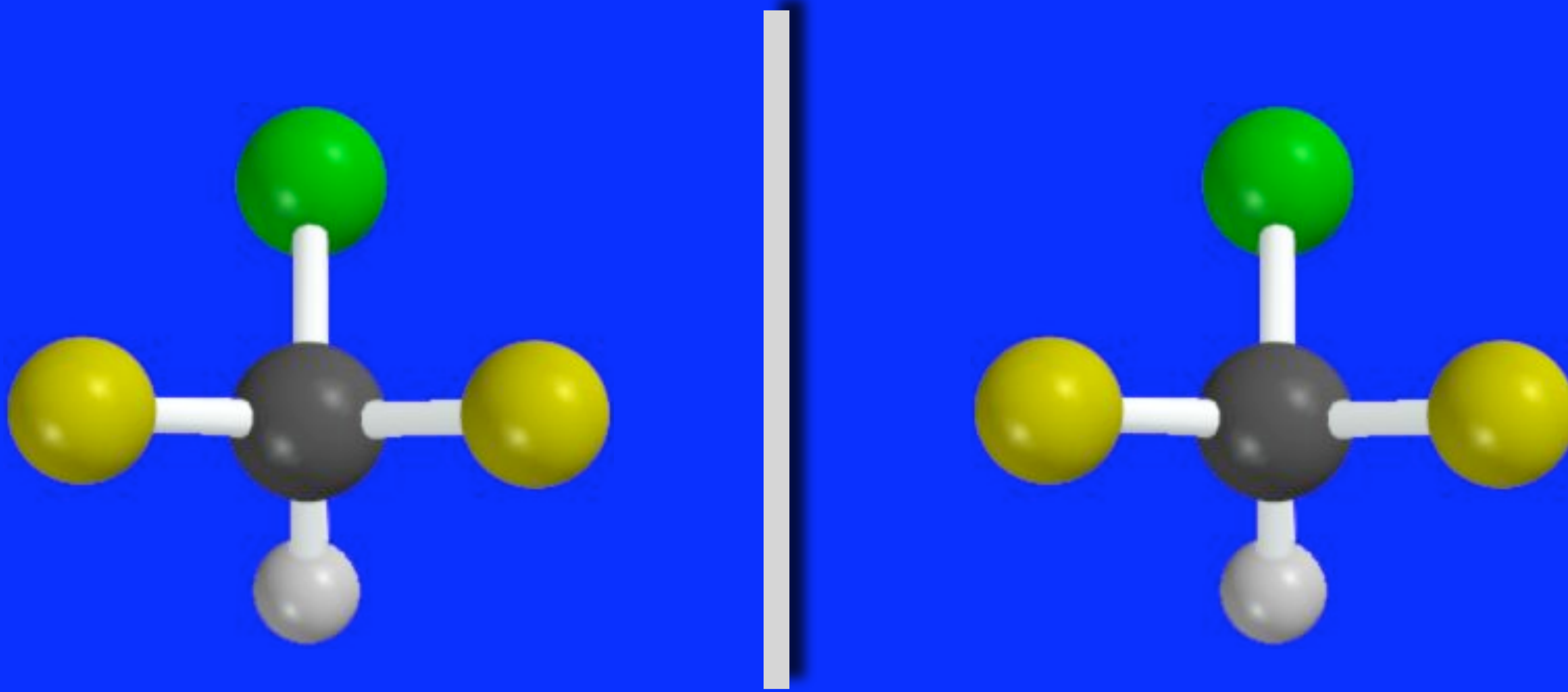
are enantiomers with respect to each other

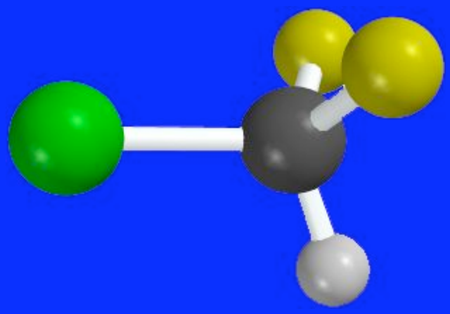


Chlorodifluoromethane

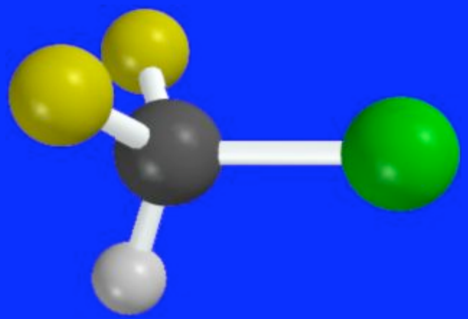
is achiral

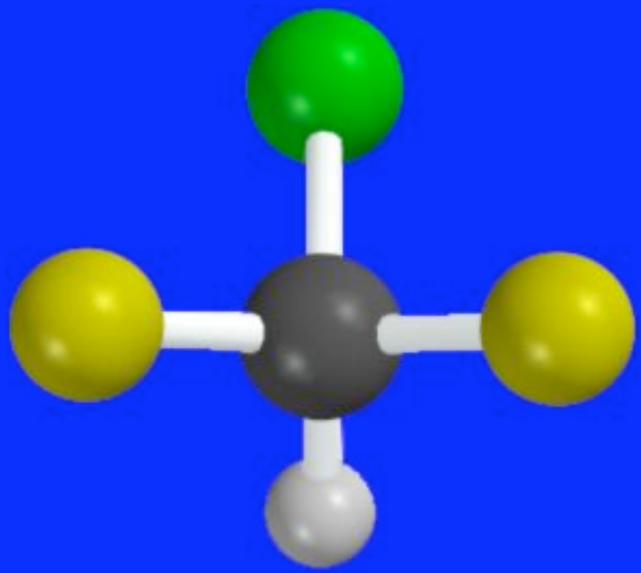






Chlorodifluoromethane is achiral





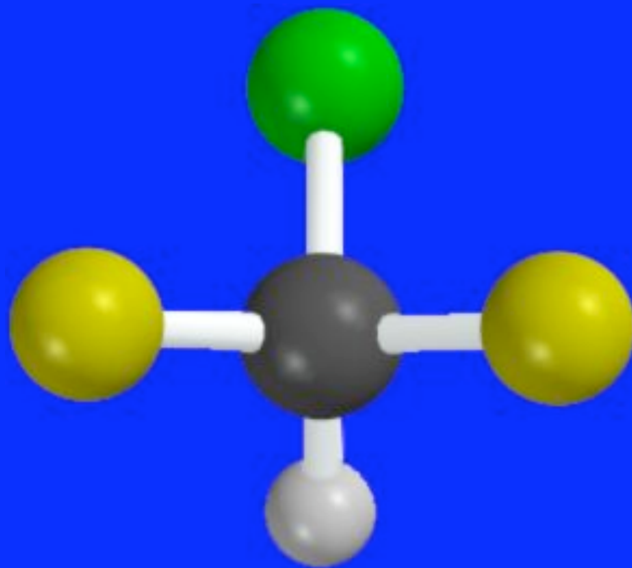
The two structures are mirror images, but are not enantiomers, because they can be superposed on each other.

Symmetry in Achiral Structures

Symmetry tests for achiral structures

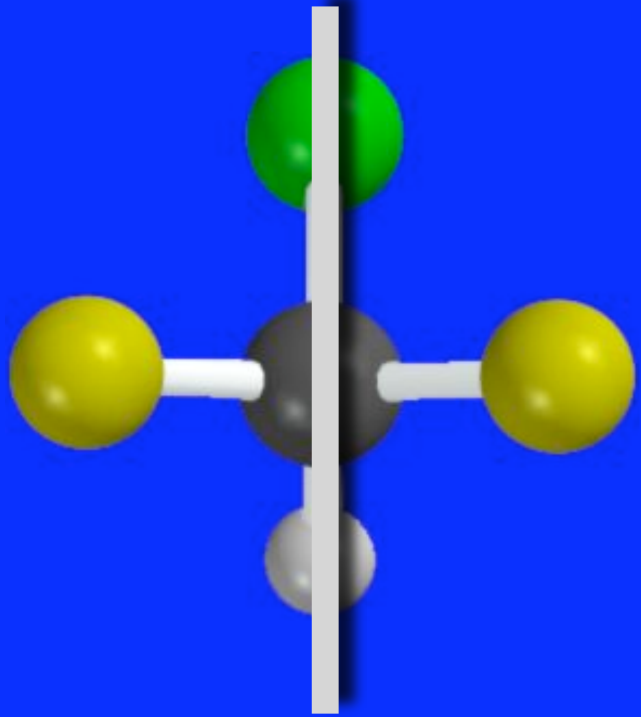
Any molecule with a plane of symmetry must be achiral.

Plane of symmetry



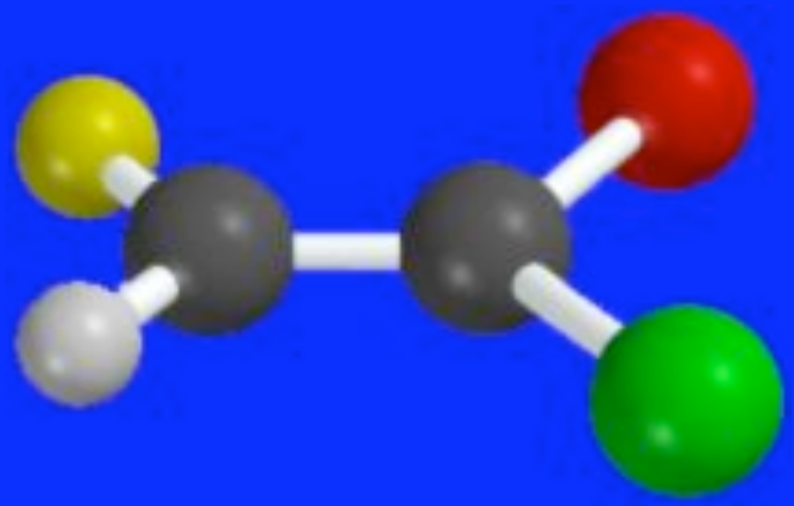
A plane of symmetry bisects a molecule into two mirror image halves. Chlorodifluoromethane has a plane of symmetry.

Plane of symmetry



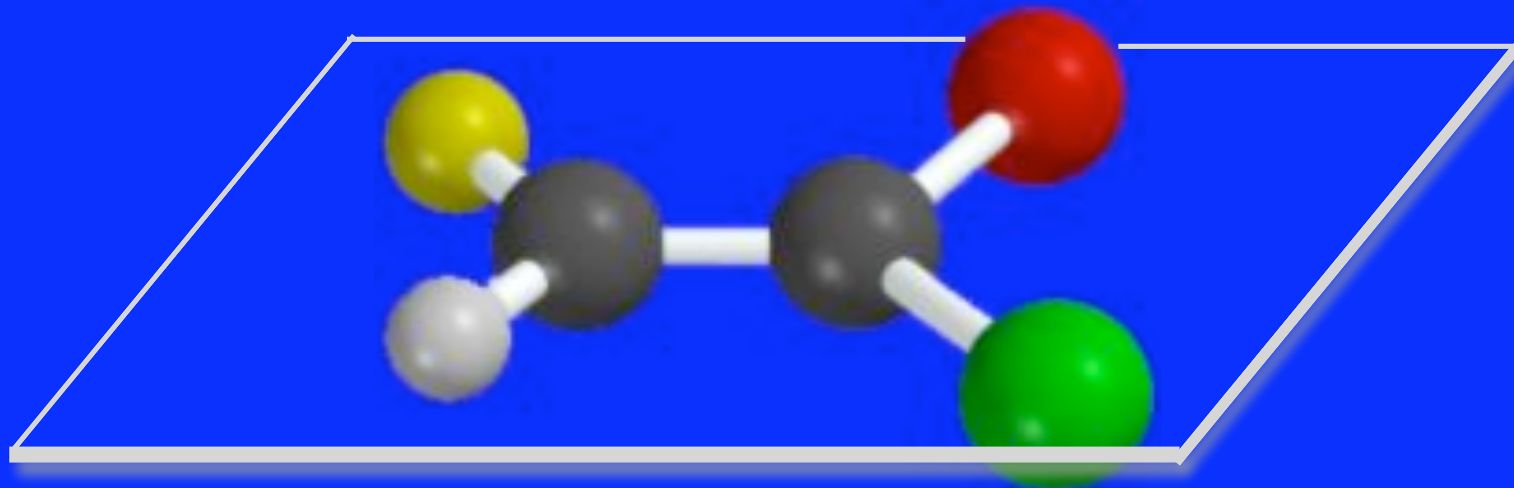
A plane of symmetry bisects a molecule into two mirror image halves. Chlorodifluoromethane has a plane of symmetry.

Plane of symmetry



A plane of symmetry bisects a molecule into two mirror image halves.
1-Bromo-1-chloro-2-fluoroethene has a plane of symmetry.

Plane of symmetry



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

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