Lecture
Organic Chemistry:

Chemistry of Living Things

- Living things and Your body is an incredibly complex chemical machine taking in chemicals & food, and causing countless reactions to occur every second.
- **Biochemistry** is the study of substances & processes occurring in all living organisms.

The most important element is…

Carbon

- If you take away the water, the rest of the human body is 53% **carbon**.
- It may not be the most abundant element in living things, but it certainly is the most important. At one time, scientists thought that the chemical reactions that took place inside of living things could not occur outside of them.
- The carbon molecules were so complex, scientists thought they must have been made in some unknown way. They called these carbon compounds **organic** compounds

The most important element is…

- The word "organic" has lots of meanings. Eventually, scientists realized that the reactions occurring inside the body could occur outside it as well.
- They also learned how important carbon is in all living things, because of its ability to **<u>bond</u>** with other atoms.

The most important element is...

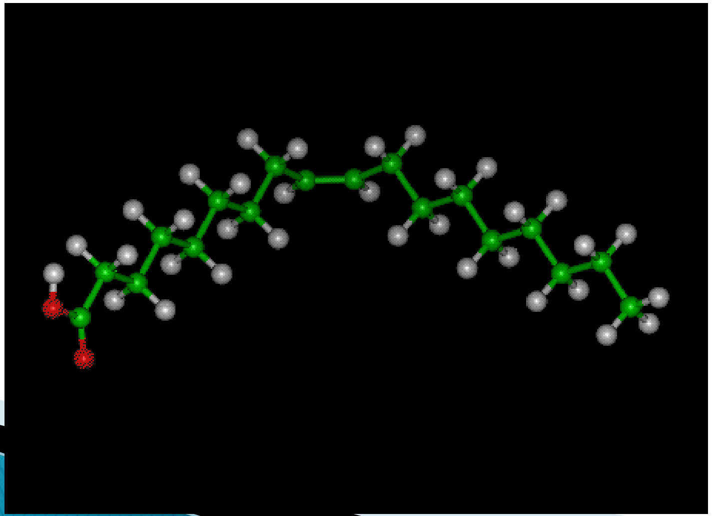
- Not all substances made of carbon are living. Diamonds & graphite are pure forms of carbon.
- Non-organic carbon compounds, and compounds without carbon, are called **inorganic** compounds.

What is organic chemistry?

- We used to describe organic chemistry as the chemistry of living things.
- Since the chemistry of living things is based on carbon, the chemistry of carbon compounds has come to be known as **organic chemistry**.
- It now includes the study of carbon compounds which are not found in living things and so is an incredibly large branch of modern chemistry.

Why is life based on the element carbon?

- There are two important properties of carbon that make it a suitable element to form the compounds in living things:
- Firstly, **carbon atoms can *link together*** to form stable chains of great length.



Why is life based on the element carbon?

- Carbon atoms bind strongly to each other and form very large molecules which are built around this carbon **'backbone'.**
- The **covalent bond** between two carbon atoms is strong so that the backbones **are stable**. In all of these compounds simple sub-units called monomers are linked together by condensation reactions.

- Elemental combustion analysis
- Identify and quantify elemental composition
- Provides empirical formulae

Lactic acid from milk (i.e. ‘organic’)

$$\text{Lactic acid} \xrightarrow{\text{Combustion}} CO_2 \quad H_2O \quad O_2$$

		CO_2	H_2O	O_2
1.00 g		1.47 g	0.60 g	0.51 g
	Mol. Wt.	44	18	32
	No. of Moles	0.033	0.033	0.016
		1 C	2H	1O

•Lactic acid composed of Carbon, Hydrogen and Oxygen
•Fixed proportion: 1C:2H:1O
•Empirical formula: CH_2O

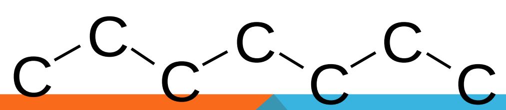
•Majority of ‘organic’ substances and many ‘inorganic’ composed of Carbon, Hydrogen and maybe other elements

•Mid 19th Century: re-define organic substances
•Those composed of Carbon, Hydrogen (usually) and other elements (maybe)

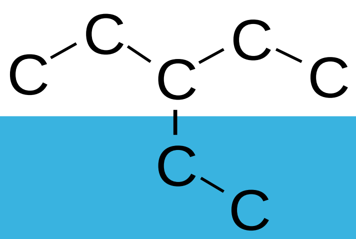
•1850-1860: Concept of *Molecules*
•Atoms of Carbon and other elements connected by covalent bonds
•Hence, fixed proportions of elements

	C-C	N-N	O-O
Bond Dissociation Energy (kJ mol^{-1})	348	163	157

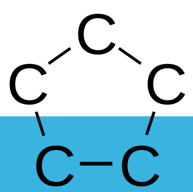
- Carbon-Carbon bonds: especially strong covalent bonds
- Carbon: unique in its ability to *catenate*
- [can form chains of atoms]
- Forms molecules composed of C-C bonds



Linear molecules



Branched molecules



Cyclic molecules

•Organic molecules = Carbon-based molecules

•Organic chemistry = Chemistry of carbon-based molecules

Some properties of organic molecules

- *Stability*: composed of stable C-C covalent bonds
- *Defined molecular structures*
- *Defined three-dimensional shapes*

ORGANIC CHEMICALS MAKE UP

Foods and foodstuff

Flavours and fragrances

Medicines

Materials, polymers, plastics

Plant, animal and microbial matter; natural products

A vast range of manufactured goods

[pharmaceuticals, foods, dyestuffs, adhesives, coatings, packaging, lubricants, cosmetics, films & fibres, etc. etc.]

ASPECTS OF ORGANIC MOLECULES

Structure & bonding

•Atom to atom connectivity

•3D shape (*Stereochemistry*)

•Naming (*Nomenclature*)

Physical properties

•Interaction with physical world

Chemical properties

•Transformation of molecular structure (*Reactions*)

•How reactions occur (*Mechanism*)

Need to expand the system of **nomenclature** to allow naming of individual structural isomers

- Compounds without branches are called ‘straight chain’
- Branched compounds are named as ***alkyl*** derivatives of the longest straight chain in the molecule
- The length of the longest chain provides the parent name
- The straight chain is numbered to allow indication of the point of branching
- The branching *alkyl* groups (or ***substituents***) are named from the corresponding alkane

Using elemental (combustion) analysis: a worked example

Galactose: a sugar obtained from milk

Molecular weight = 180.156 g mol^{-1}

What is the Molecular Formula?

Carry out elemental analysis

$$\underset{0.1000\text{ g}}{\textbf{Galactose}} \xrightarrow{\textbf{Combustion}} \underset{0.1450\text{ g}}{CO_2} + \underset{0.0590\text{ g}}{H_2O} + \underset{0.0540\text{ g}}{O_2}$$

	CO_2	H_2O	O_2
Mol. Wt. / g mol^{-1}	**44**	**18**	**32**
No. of moles	**0.0033**	**0.0033**	**0.0017**
	1C	**2H**	**1O**

Empirical Formula = $\mathbf{CH_2O}$

Molecular Formula = $\mathbf{(CH_2O)_n}$

Mol. Wt. "CH_2O" = 30.026 g mol^{-1}

Mol. Wt. galactose = 180.156 g mol^{-1} $\Rightarrow$ n = 6

i.e. Molecular Formula = $\mathbf{C_6H_{12}O_6}$

Atomic Wts. C: 12.011; H: 1.008; O: 15.999

$$\%C = \frac{6 \times 12.011}{180.156} \times 100 = \mathit{40.00\%}$$

Likewise:

$$\%H = \frac{12 \times 1.008}{180.156} \times 100 = \mathit{6.71\%} \qquad \%O = \frac{6 \times 15.999}{180.156} \times 100 = \mathit{53.28\%}$$

Galactose C: 40.00%
H: 6.71%
O: 53.28%

Elemental analysis data presented in this way

Can use as an experimental measure of purity

A pure material should return elemental analysis data which is within ±0.30% for each element

E.g. given two samples of galactose

Sample 1	*Sample 2*
C: 39.32%	C: 40.11%
H: 7.18%	H: 6.70%
O: 53.50%	O: 53.19%
Sample impure	Sample pure

Electronic configuration of Carbon $C \ 1s^2 \ 2s^2 \ 2p^2$

- *Covalent bonds*: sharing of electrons between atoms
- Carbon: can accept 4 electrons from other atoms
- i.e. **Carbon is tetravalent (valency = 4)**

Ethane: a gas (b.p. ~ -100^{o}C)

Empircal formula (elemental combustion analysis): CH_3

i.e. an organic chemical

Measure molecular weight (e.g. by mass spectrometry):

30.070 g mol^{-1}, i.e $(CH_3)_n$ $n = 2$

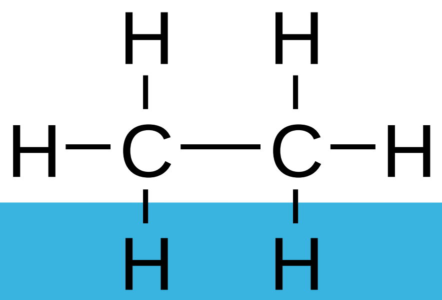
Implies **molecular formula** = C_2H_6

Molecular formula: gives the identity and number of different atoms comprising a molecule

Ethane: molecular formula = C_2H_6

Valency:	Carbon	4
	Hydrogen	1

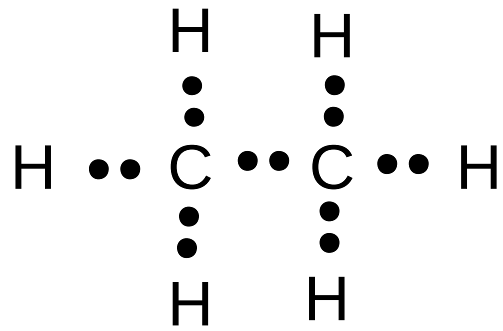
Combining this information, can propose



i.e. a ***structural formula*** for ethane

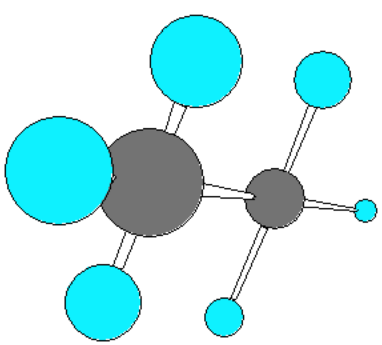
•Each line represents a single covalent bond

•i.e. one shared pair of electrons



•Structural formulae present information on atom-to-atom connectivity

•However, is an inadequate represention of some aspects of the molecule



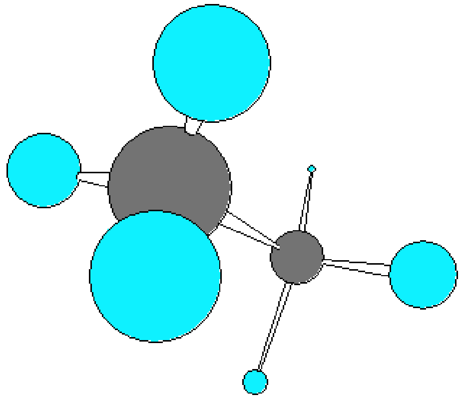
•Suggests molecule is planar

•Suggests different types of hydrogen

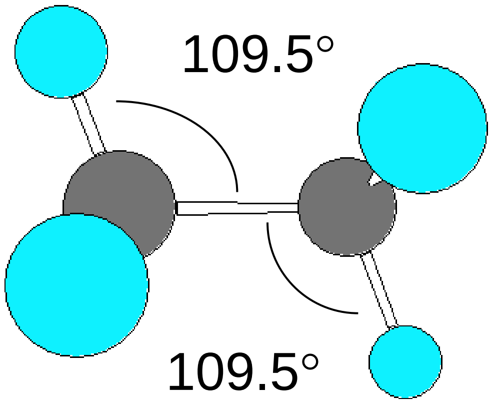
Experimental evidence shows:

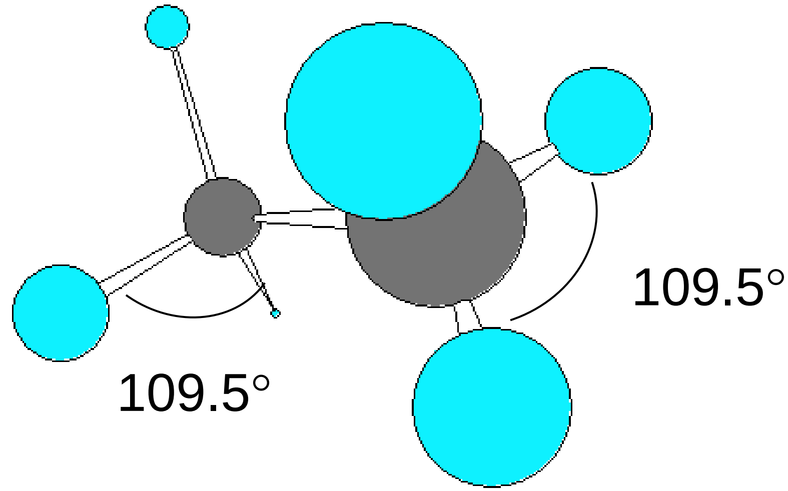
- Ethane molecules not planar
- All the hydrogens are equivalent

3 Dimensional shape of the molecule has *tetrahedral* carbons

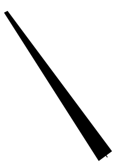


- Angle formed by any two bonds to any atom = ~ 109.5°



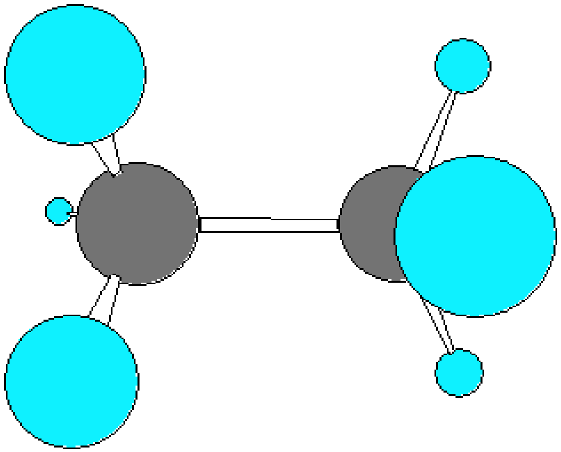


Need to be able to represent 3D molecular structure in 2D

 $\Longrightarrow$ Bond coming out of plane of screen

 $\Longrightarrow$ Bond going into plane of screen

e.g.



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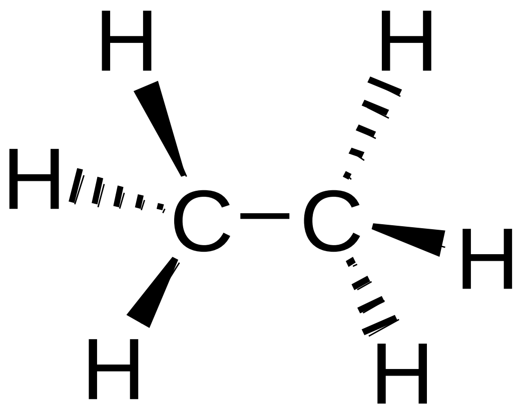
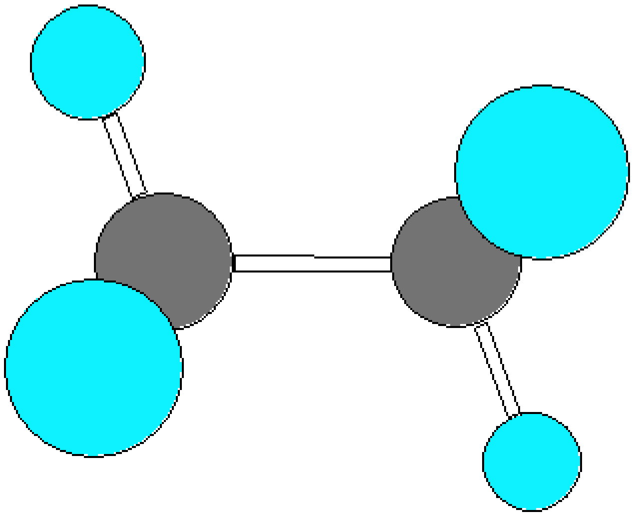


Or



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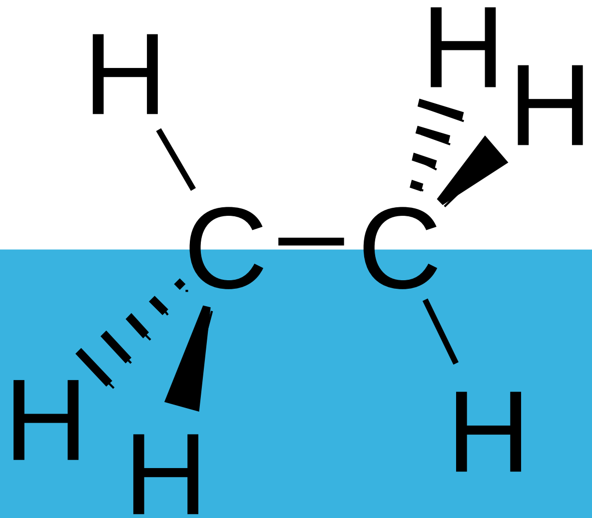
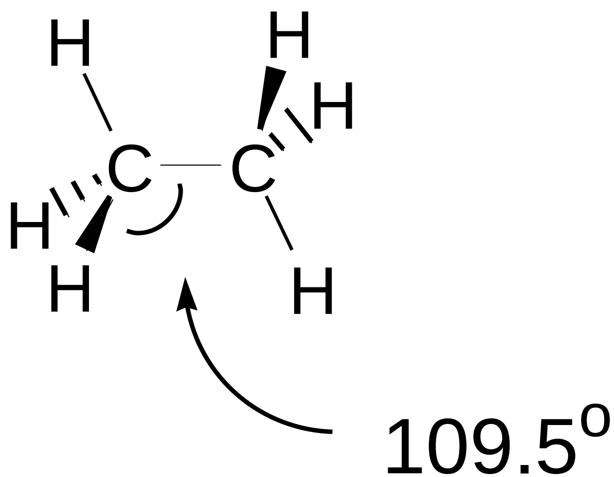
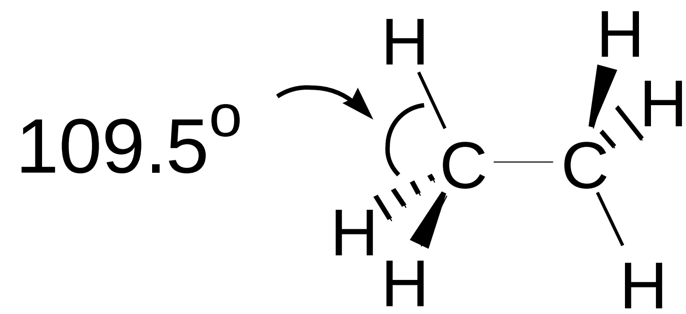


Angle between any two bonds at a Carbon atom = 109.5°





Ethane: a gas b.p. ~ -100^{o}C

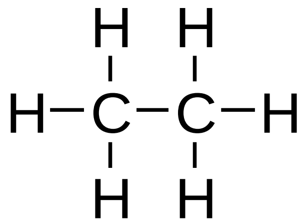
Empirical formula: CH_3

- An organic chemical
- Substance composed of organic molecules

Molecular formula C_2H_6

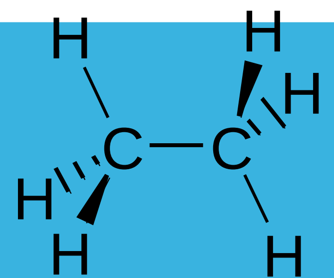
- Identity and number of atoms comprising each molecule

Structural formula



- Atom-to-atom connectivity

Structural formula showing stereochemistry



- 3D shape

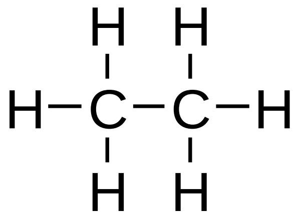
- Ethane: a substance composed of molecules of formula C_2H_6
- 30.070 g of ethane (1 mole) contains 6.022×10^{23} molecules (Avogadro's number)

- Can use the structural formula to show behaviour of molecules
- Assume all molecules of a sample behave the same

- Sometimes need to consider behaviour of a population of molecules

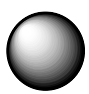
Electronic configuration of Carbon C $1s^2\ 2s^2\ 2p^2$

Hydrogen H $1s^1$



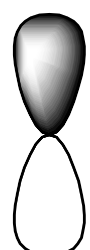
Ethane

Orbitals available for covalent bonding?



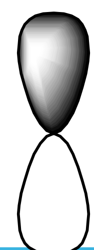
H 1s

(1 $e^{\ominus}$)



C $2p_y$

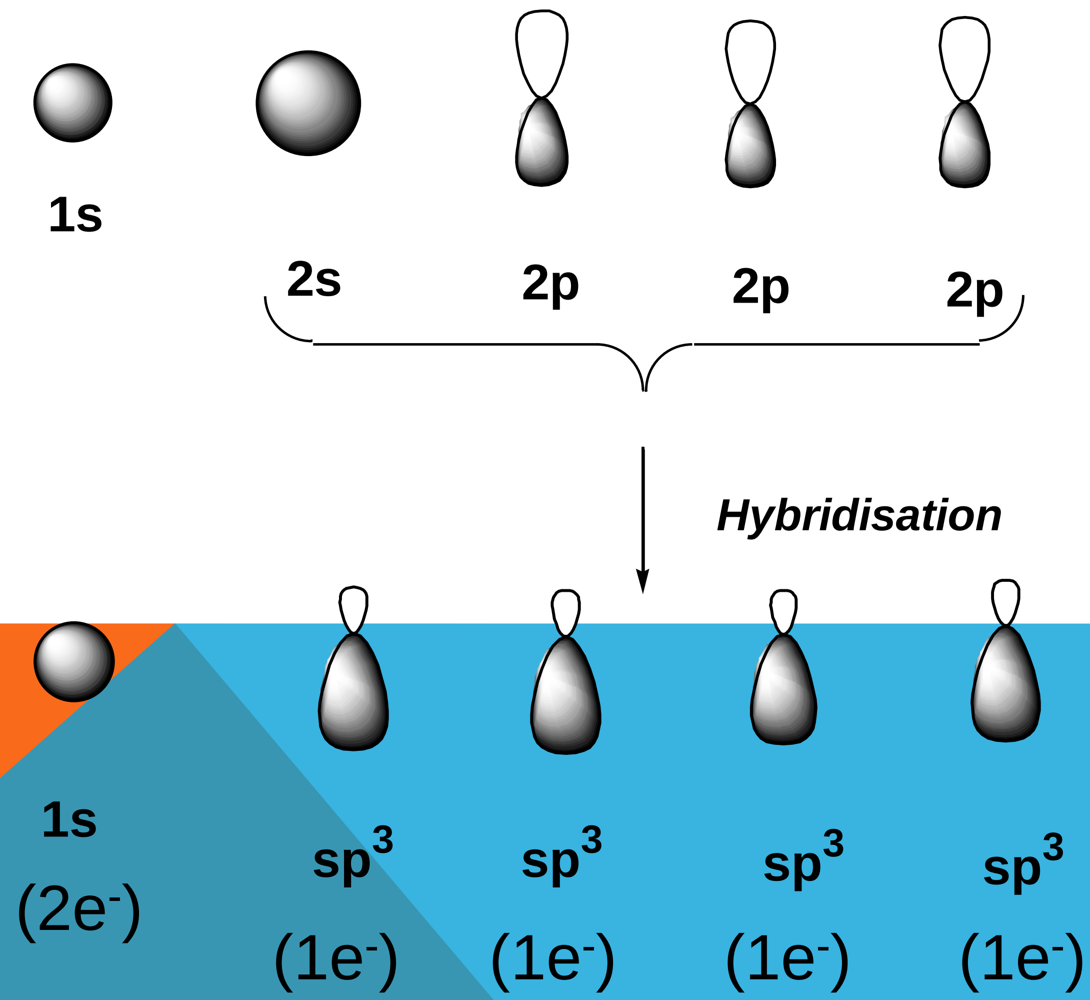
(vacant)



C $2p_z$

(vacant)

- However, know that the geometry of the Carbons in ethane is tetrahedral
- Cannot array p_y and p_z orbitals to give tetrahedral geometry
- Need a modified set of atomic orbitals - *hybridisation*



Bonding in ethane

Atomic orbitals available:

2 Carbons, both contributing 4 **sp^3** hybridised orbitals

6 Hydrogens, each contributing an **s** orbital

Total atomic orbitals = 14

Combine to give 14 molecular orbitals

7 Bonding molecular orbitals; 7 anti-bonding molecular orbitals

Electrons available to occupy molecular orbitals

One for each **sp^3** orbital on Carbon;
one for each **s** orbital on Hydrogen = 14

Just enough to fully occupy the bonding molecular orbitals

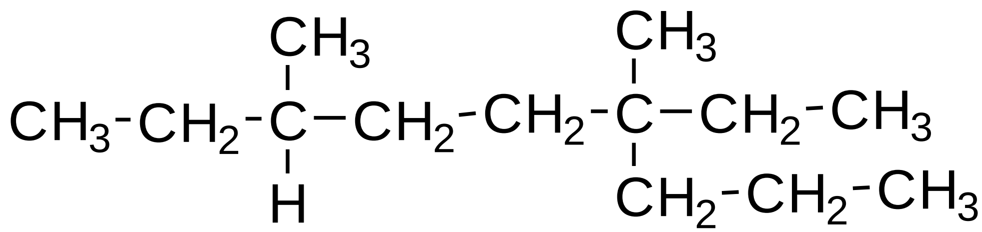
Anti-bonding molecular orbitals not occupied

Alkane	Alkyl group
Methane	Methyl (CH_3-)
Ethane	Ethyl (CH_3CH_2-)
Propane	Propyl ($CH_3CH_2CH_2$-)
Butane	Butyl ($CH_3CH_2CH_2CH_2$-)
Etc.	

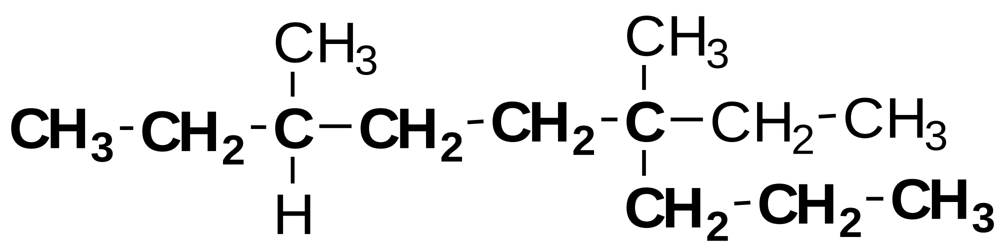
$$\begin{array}{cccc} & & CH_3 & \\ & & | & \\ CH_3 - & CH_2 - & CH - & CH_3 \\ 4 & 3 & 2 & 1 \end{array}$$

2-Methylbutane

[Straight chain numbered so as to give the lower branch number]

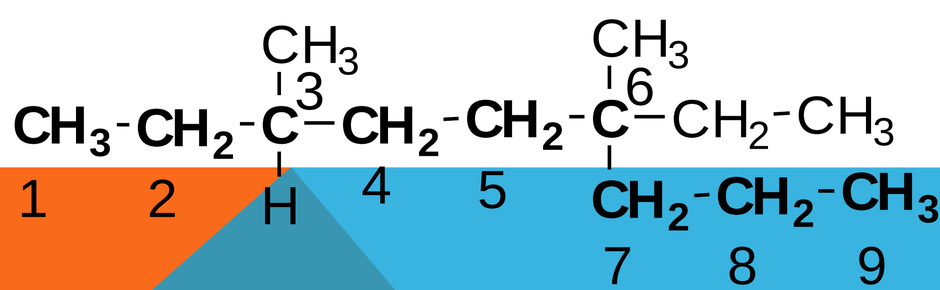


First, identify longest straight chain



‘…nonane’

Number so as to give lower numbers for branch points



Branches at C3 and C6

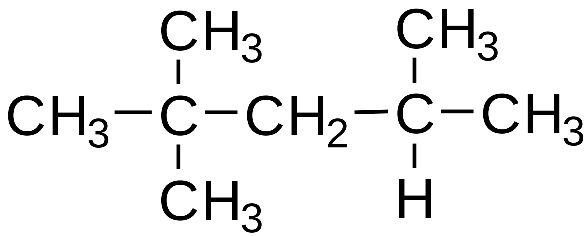
Not at C4 and C7

3,6-Dimethyl-6-ethylnonane

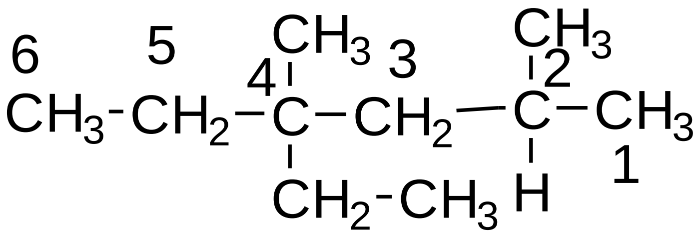
Identical substituents grouped together with a prefix

- ‘di…’ for two identical
- ‘tri…’ for three
- ‘tetra…’ for four

Substituents named in alphabetical order

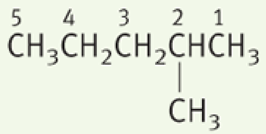
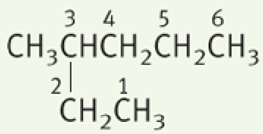
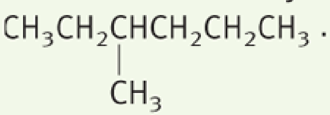
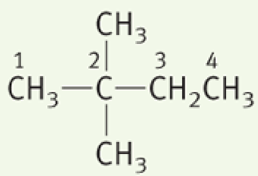
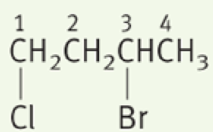


2,2,4-Trimethylpentane

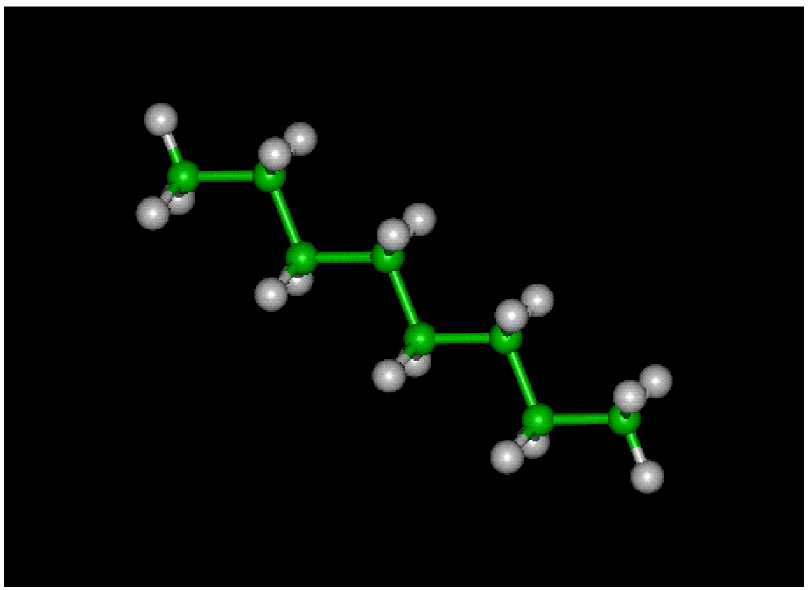


2,4-dimethyl-4-ethylhexane

TABLE 2.2 EXAMPLES OF USE OF THE IUPAC RULES

 2-methylpentane (*not* 4-methylpentane)	The ending *-ane* tells us that all the carbon–carbon bonds are single; *pent-* indicates five carbons in the longest chain. We number them from right to left, starting closest to the branch point.
 3-methylhexane (*not* 2-ethylpentane or 4-methylhexane)	This is a six-carbon saturated chain with a methyl group on the third carbon. We would usually write the structure as  .
 2,2-dimethylbutane (*not* 2,2-methylbutane or 2-dimethylbutane)	There must be a number for each substituent, and the prefix *di-* says that there are two methyl substituents.
 3-bromo-1-chlorobutane (*not* 1-chloro-3-bromobutane or 2-bromo-4-chlorobutane)	First, we number the butane chain from the end closest to the first substituent. Then we name the substituents in alphabetical order, regardless of position number.

Carbon atoms form organic molecule

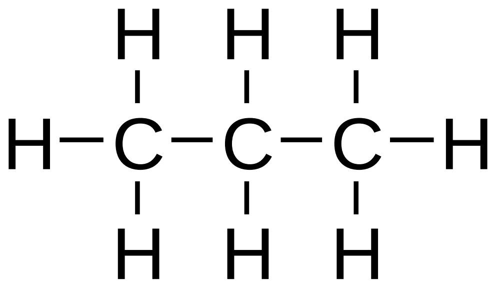


Ethane C_2H_6

- Contains Carbon and Hydrogen only (is a *hydrocarbon*)
- Contains σ bonds only (C-C and C-H single bonds only)
- Contains only sp^3 hybridised Carbon

Do other molecules exist which have these properties?

Yes, e.g. propane C_3H_8



How many such compounds could exist?

In principle, an infinite number

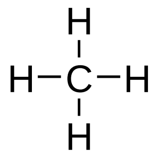
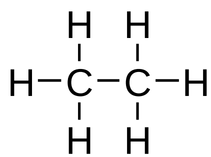
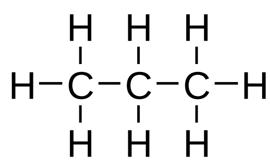
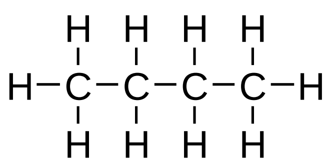
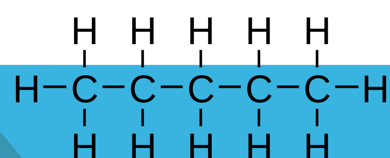
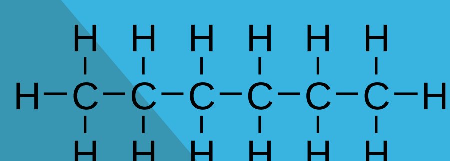
In reality, a vast unknown number

There exists a vast (and potentially infinite) number of compounds consisting of molecules which:

- Contain only C and H
- Contain only σ bonds
- Contain only **sp^3** hybridised C

These are known as ***alkanes***

C_2H_6 ethane	C_3H_8 propane	C_nH_{2n+2} General formula for alkanes

n	Molecular Formula	Structural formula	Name	Condensed structural formula
1	CH_4		methane	CH_4
2	C_2H_6		ethane	CH_3CH_3
3	C_3H_8		propane	$CH_3CH_2CH_3$
4	C_4H_{10}		butane	$CH_3CH_2CH_2CH_3$
5	C_5H_{12}		pentane	$CH_3CH_2CH_2CH_2CH_3$
6	C_6H_{14}		hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$

Further members of the series

Heptane	$CH_3CH_2CH_2CH_2CH_2CH_3$
Octane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
Nonane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
Decane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
Undecane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
Dodecane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Etc., etc.

Some points concerning this series of alkanes

1. Series is generated by repeatedly adding 'CH_2' to the previous member of the series

A series generated in this manner is known as an ***homologous series***

2. **Nomenclature** (naming)

Names all share a common suffix, i.e.' …ane'

The suffix '…ane' indicates that the compound is an alkane

The prefix indicates the *number of carbons in the compound*

‘Meth…’ = 1 Carbon

‘Eth…’ = 2 Carbons

‘Prop…’ = 3 Carbons

‘But…’ = 4 Carbons

‘Pent…’ = 5 Carbons

‘Hex…’ = 6 Carbons

‘Hept…’ = 7 Carbons

‘Oct…’ = 8 Carbons

‘Non…’ = 9 Carbons

‘Dec…’ = 10 Carbons

‘Undec…’ = 11 Carbons

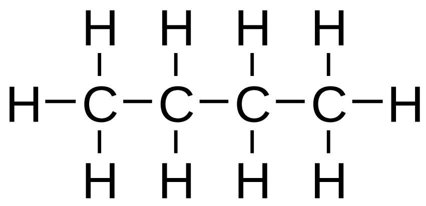
‘Dodec…’ = 12 Carbons

Heptane $\mathbf{CH_3CH_2CH_2CH_2CH_2CH_2CH_3}$

‘Hept…’ implies 7 Carbons

‘…ane’ implies compound is an alkane

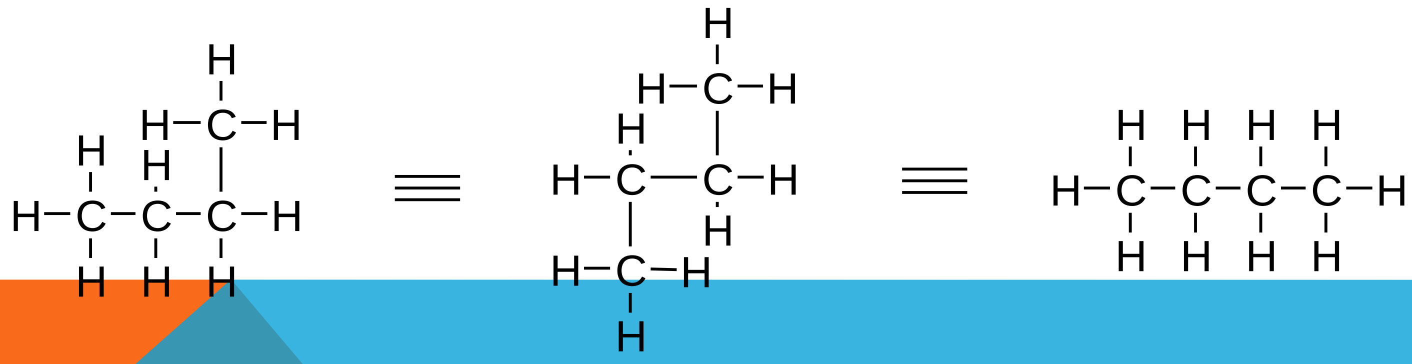
3. Representation and conformation



Butane
(full structural formula)

•Structural formulae: give information on *atom-to-atom connectivity*

•Do not give information on stereochemistry



Same structural formula

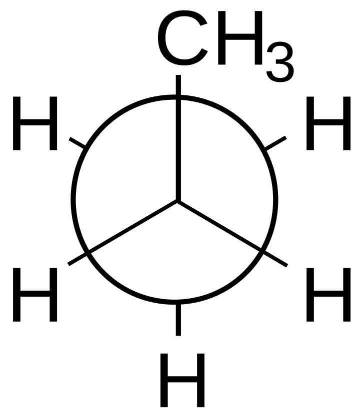
Have the same information content

Propane $CH_3\text{-}CH_2\text{-}CH_3$

Both C-C bonds identical

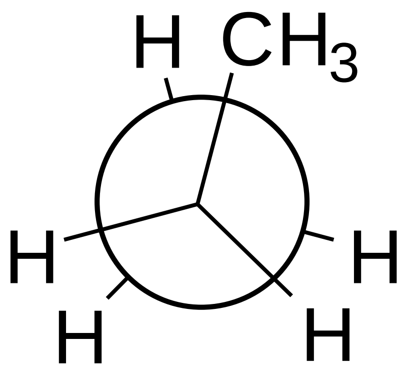
Consider the different conformations that can arise during one full rotation about C-C

Energy maxima and minima:



Staggered conformation
(energy minimum)

6 kJ mol^{-1}



4 kJ mol^{-1} 4 kJ mol^{-1}

Eclipsed conformation
(energy maxmium)

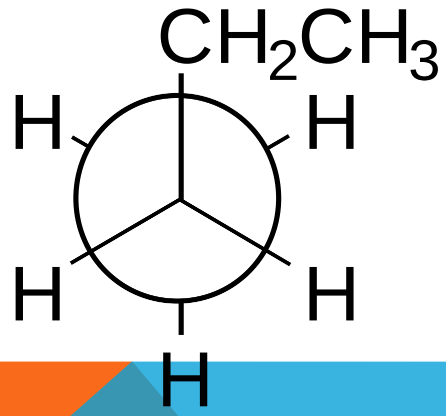
Eclipsed conformation of propane possesses 14 kJ mol^{-1} of torsional strain energy relative to the staggered conformation

Butane $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$

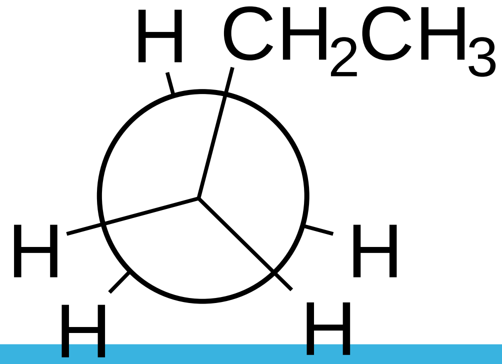
Two equivalent terminal C-C bonds;

one unique central C-C bond

Conformations arising due to rotation about the terminal C-C bonds similar to those for propane



Staggered conformation

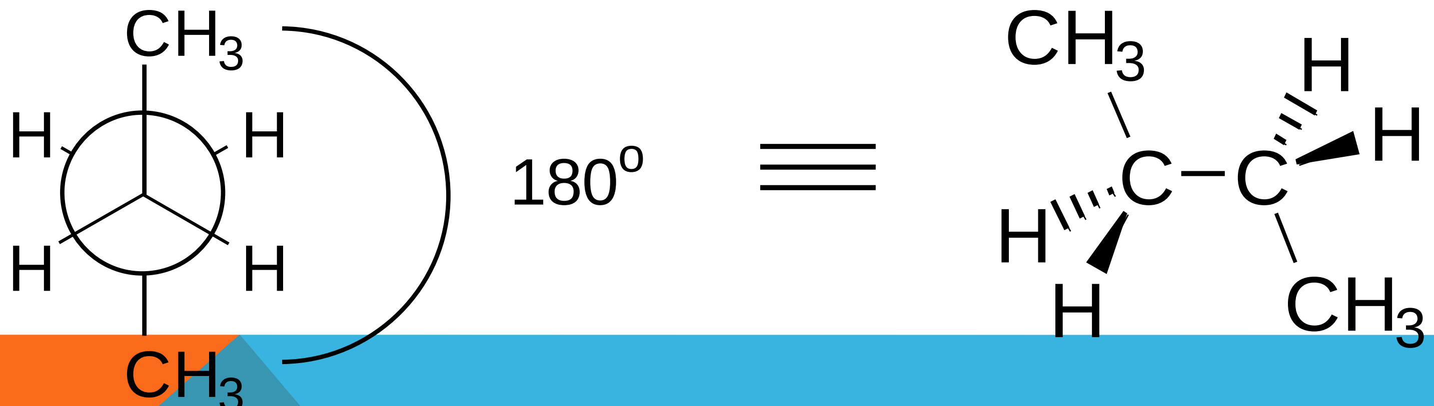


Eclipsed conformation

More complex for central C-C bond

Define torsional angle φ as angle formed by terminal C-C bonds

e.g.



$\boldsymbol{\varphi}$ **= 180°**

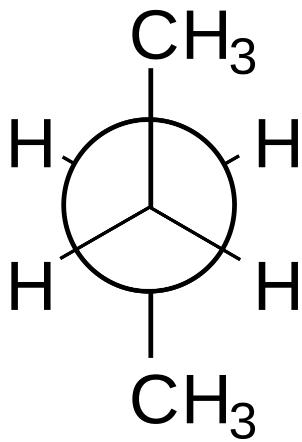
One full 360° rotation about the central C-C of butane

Pass through three staggered and three eclipsed conformations

No longer equivalent

Staggered conformations

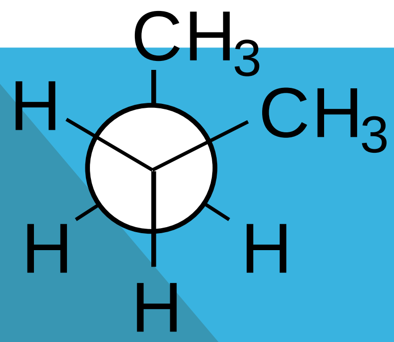
$\varphi = 180°$



Unique conformation

Anti-periplanar conformation (ap)

$\varphi = 60°$
[& $\varphi = 300°$]



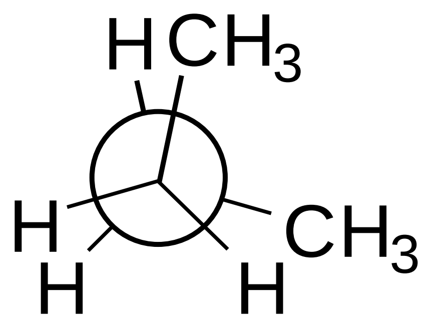
Two equivalent conformations

Gauche or *synclinal conformations (sc)*

3.8 kJ mol^{-1} steric strain energy

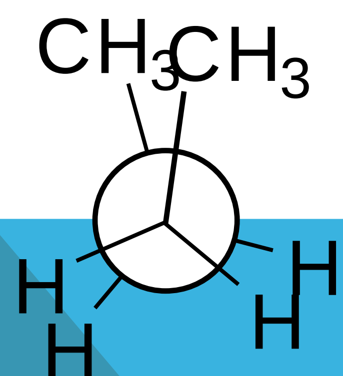
Eclipsed conformations

$\varphi = 120°$
[& $\varphi = 240°$]



Two equivalent conformations
Anticlinal conformations (ac)
Strain energy = 16 kJ mol^{-1}

$\varphi = 0°$



Unique conformation
Syn-periplanar conformation (sp)
Strain energy = 19 kJ mol^{-1}

Syn-periplanar conformation: global energy maximum

Anti-periplanar conformation: global energy minimum

Synclinal and *anticlinal* conformations: local energy minima and maxima respectively

Energy barrier to rotation = 19 kJ mol^{-1}

Too low to prevent free rotation at room temperature

Sample of butane at 25°C (gas)

At any instant in time:

- ~ 75% of the molecules in the sample will exist in the *anti-periplanar* conformation

- ~ 25% of the molecules in the sample will exist in the *synclinal* conformation

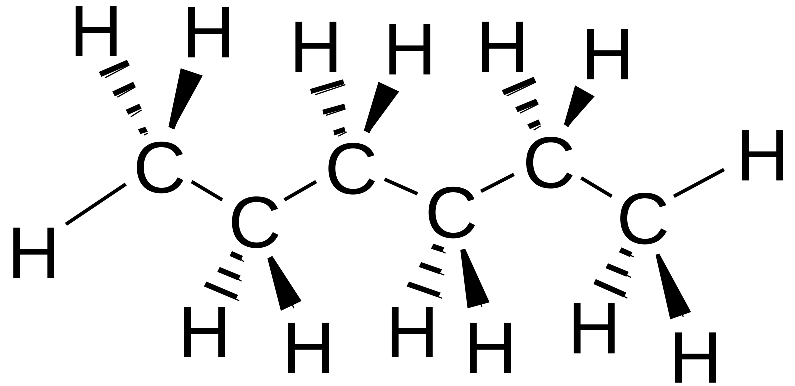
< 1% will exist in all other conformations

Simple alkanes have conformational freedom at room temperature

i.e. have rotation about C-C bonds

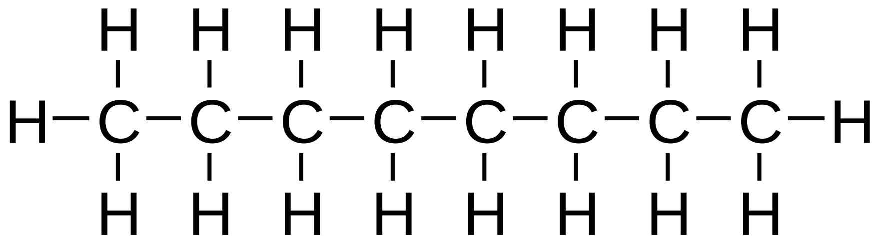
the most stable (lowest energy) conformation for these is the all staggered ‘straight chain’

e.g. for hexane



4. Representing larger molecules

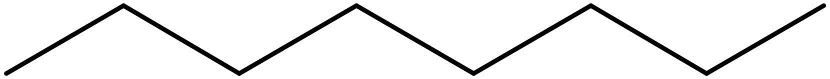
Full structural formula for, e.g. octane



Condensed structural formula

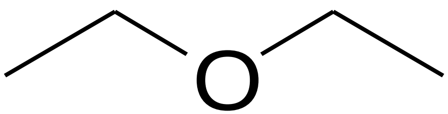
$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

Line segment structural formula



Line segment structural formula for octane

- Each line represents a covalent bond between atoms
- Unless indicated otherwise, assume bonds are between Carbons
- C-H bonds not shown, assume they are present
- [so as make up valency of Carbon to 4]



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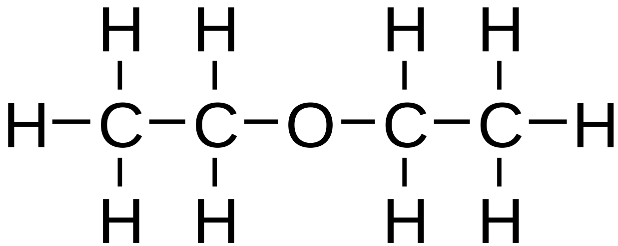

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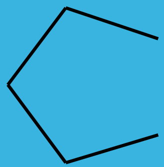
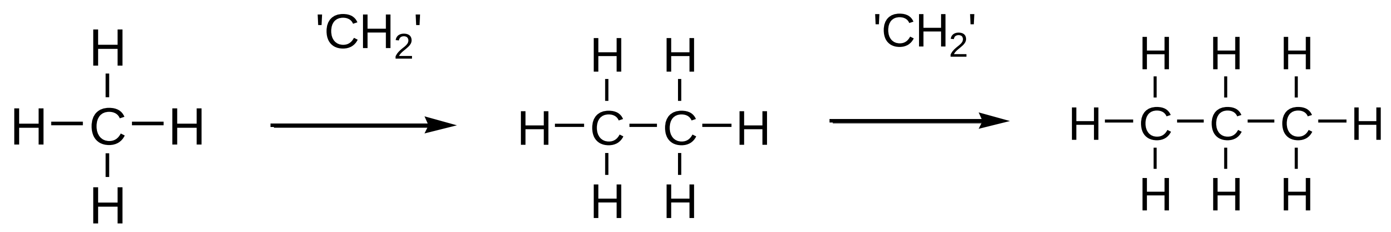
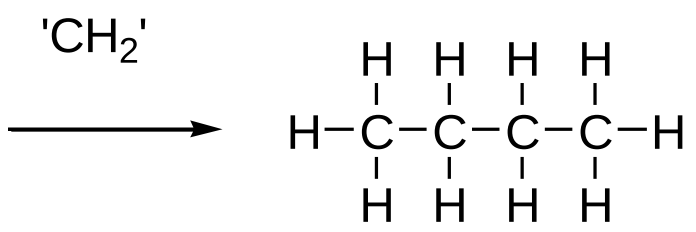


etc. = pentane

Generating the series of alkanes by incrementally adding ‘CH_2’

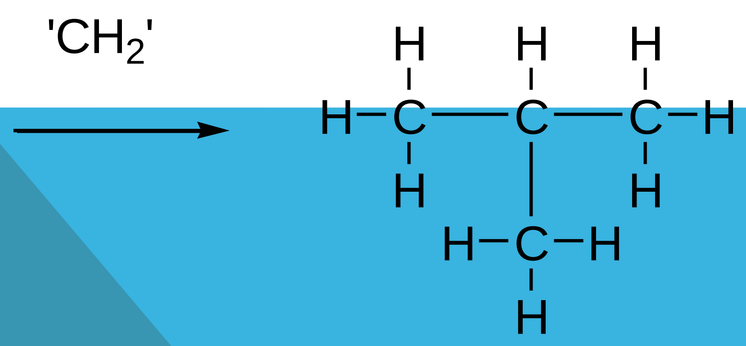


Methane Ethane Propane

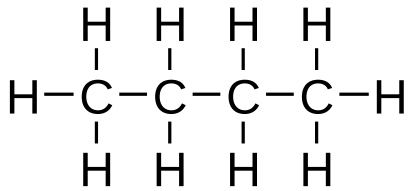


Butane

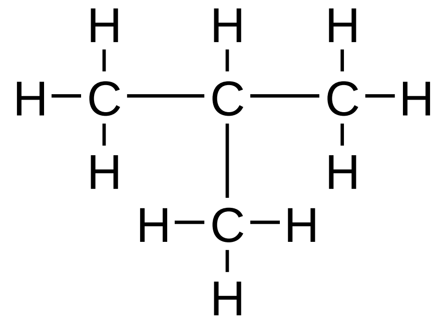
However, the last increment could also give



Isobutane



Butane (C_4H_{10})



Isobutane (C_4H_{10})

Structural isomers

‘Isomer’, from Greek *isos* (equal) and *meros* (in part)

- Structural isomers: same molecular formulae
- Different structural formulae

(different atom-to-atom connectivity)

- Structural isomers: different physical properties

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$

n-butane

b.p. - 0.5^{o}C

$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ CH_3 & - & CH & - & CH_3 \end{array}$$

isobutane

b.p. - 12.0^{o}C

- Are different chemical entities

Extent of structural isomerism in alkanes

Alkane	No. of structural isomers	
Methane	1	All known
Ethane	1	
Propane	1	
Butane	2	
Pentane	3	
Hexane	5	
Decane	75	
Pentadecane	4347	
Eicosane	366,319	
Triacontane ($C_{30}H_{62}$)	44 x 10^9	

Pentane C_5H_{12} 3 structural isomers

$$CH_3-CH_2-CH_2-CH_2-CH_3$$

$$\begin{array}{cccc} & & CH_3 & \\ & & | & \\ CH_3- & CH_2- & CH & -CH_3 \end{array}$$

$$\begin{array}{ccc} & CH_3 & \\ & | & \\ CH_3- & C & -CH_3 \\ & | & \\ & CH_3 & \end{array}$$

- All of these based on tetrahedral (**sp³** hybridised) Carbon
- No other arrangements of C_5H_{12} possible

Note

$$\begin{array}{cccc} & & CH_3 & \\ & & | & \\ CH_3- & CH_2- & CH & -CH_3 \end{array} = \begin{array}{cccc} CH_3- & CH & -CH_2- & CH_3 \\ & | & & \\ & CH_3 & & \end{array} = \begin{array}{ccc} & & CH_3 \\ & & | \\ CH_3- & CH_2- & CH \\ & & | \\ & & CH_3 \end{array}$$

etc.

Need to expand the system of **nomenclature** to allow naming of individual structural isomers

•Compounds without branches are called ‘straight chain’

•Branched compounds are named as ***alkyl*** derivatives of the longest straight chain in the molecule

•The length of the longest chain provides the parent name

•The straight chain is numbered to allow indication of the point of branching

•The branching *alkyl* groups (or ***substituents***) are named from the corresponding alkane

Using elemental (combustion) analysis: a worked example

Galactose: a sugar obtained from milk

Molecular weight = 180.156 g mol^{-1}

What is the Molecular Formula?

Carry out elemental analysis

		CO_2	+	H_2O	+	O_2
Galactose 0.1000 g	**Combustion** $\longrightarrow$	**0.1450 g**		**0.0590 g**		**0.0540 g**
	Mol. Wt. / g mol^{-1}	**44**		**18**		**32**
	No. of moles	**0.0033**		**0.0033**		**0.0017**
		1C		**2H**		**1O**

Empirical Formula = $\mathbf{CH_2O}$

Molecular Formula = $\mathbf{(CH_2O)_n}$

Mol. Wt. "CH_2O" = 30.026 g mol^{-1}

Mol. Wt. galactose = 180.156 g mol^{-1} $\Longrightarrow$ n = 6

i.e. Molecular Formula = $\mathbf{C_6H_{12}O_6}$

Atomic Wts. C: 12.011; H: 1.008; O: 15.999

$$\%C = \frac{6 \times 12.011}{180.156} \times 100 = \mathit{40.00\%}$$

Likewise:

$$\%H = \frac{12 \times 1.008}{180.156} \times 100 = \mathit{6.71\%}$$

$$\%O = \frac{6 \times 15.999}{180.156} \times 100 = \mathit{53.28\%}$$

Galactose C: 40.00%
H: 6.71%
O: 53.28%

Elemental analysis data presented in this way

Can use as an experimental measure of purity

A pure material should return elemental analysis data which is within ±0.30% for each element

E.g. given two samples of galactose

Sample 1

C: 39.32%

H: 7.18%

O: 53.50%

Sample impure

Sample 2

C: 40.11%

H: 6.70%

O: 53.19%

Sample pure

Electronic configuration of Carbon $C\ 1s^2\ 2s^2\ 2p^2$

- *Covalent bonds*: sharing of electrons between atoms
- Carbon: can accept 4 electrons from other atoms
- i.e. **Carbon is tetravalent (valency = 4)**

Ethane: a gas (b.p. ~ -100°C)

Empircal formula (elemental combustion analysis): CH_3

i.e. an organic chemical

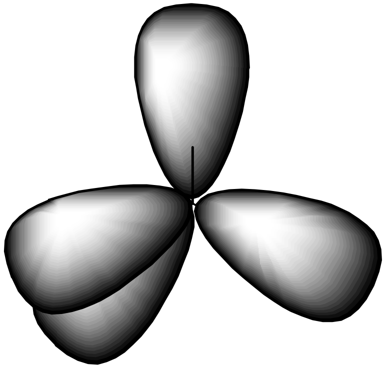
Measure molecular weight (e.g. by mass spectrometry):

$30.070\ g\ mol^{-1}$, i.e $(CH_3)_n$ $n = 2$

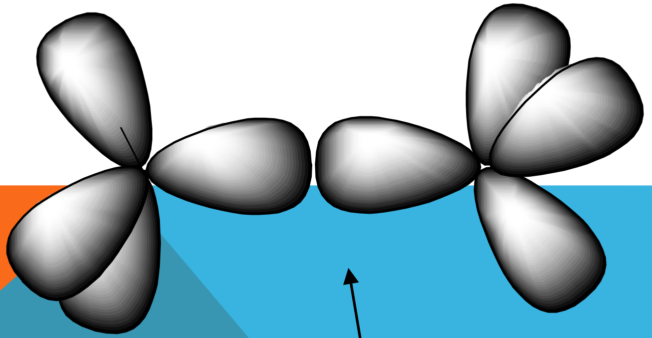
Implies **molecular formula** = C_2H_6

Visualising the molecular orbitals in ethane

Four sp^3 hybridised orbitals can be arrayed to give tetrahedral geometry



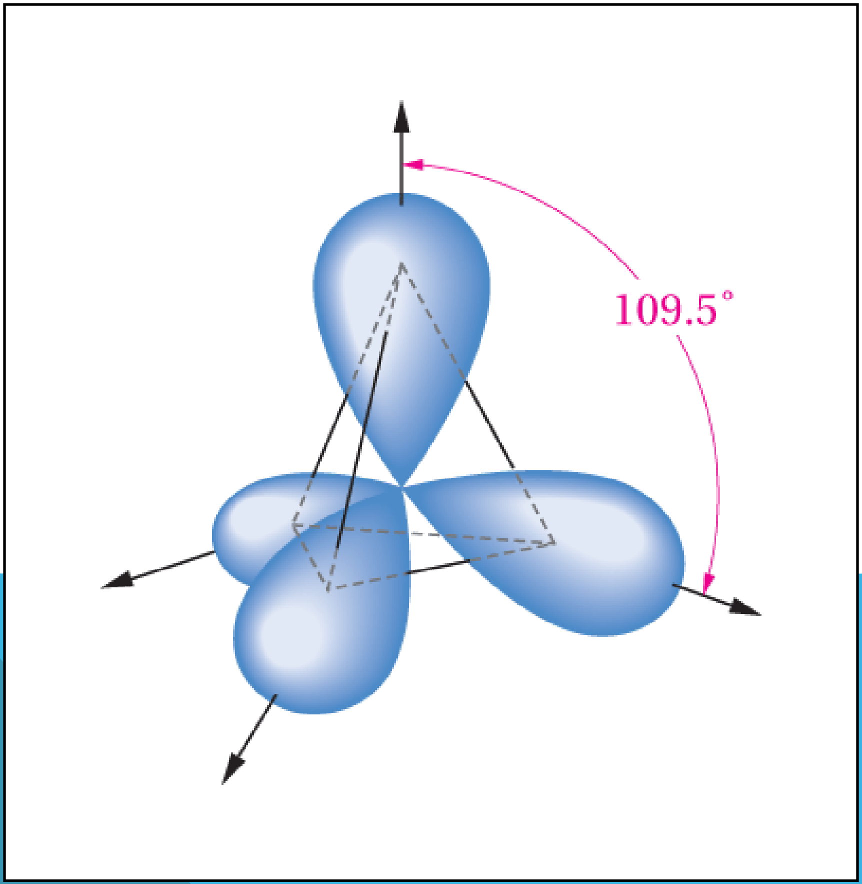
sp^3 hybridised orbitals from two Carbon atoms can overlap to form a Carbon-Carbon σ bond



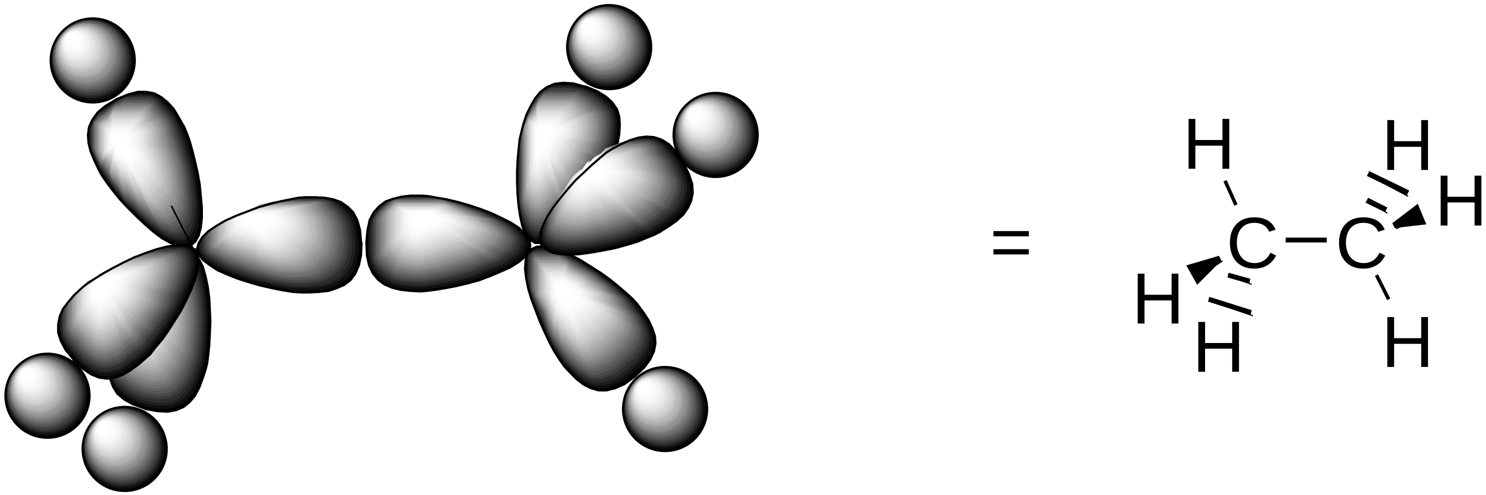
C-C σ bond

Each sp^3 orbital contributes one electron to form C-C [C⠅C]

AN SP^3 ORBITAL EXTENDS MAINLY IN ONE DIRECTION FROM THE NUCLEUS AND FORMS BONDS WITH OTHER ATOMS IN THAT DIRECTION.



Carbon sp^3 orbitals can overlap with Hydrogen 1s orbitals to form Carbon-Hydrogen σ bonds



Each sp^3 orbital contributes one electron; each s orbital contributes one electron to form C-H [C··H]

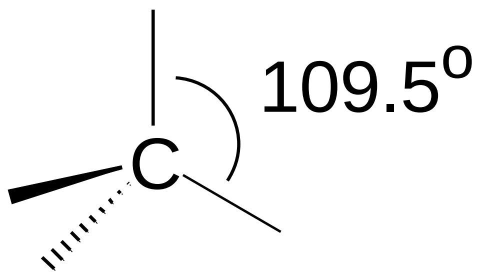
[Anti-bonding orbitals also formed; not occupied by electrons]

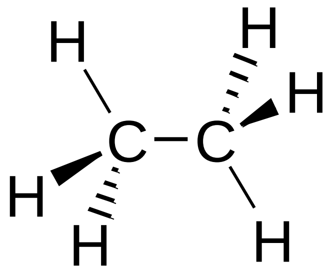
σ bonds: symmetrical about the bond axis

Geometry of Carbon in ethane is tetrahedral and is based upon sp^3 hybridisation

sp^3 hybridised Carbon = tetrahedral Carbon

Tetrahedral angle ≈ 109.5°

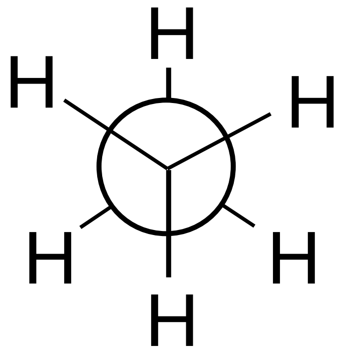




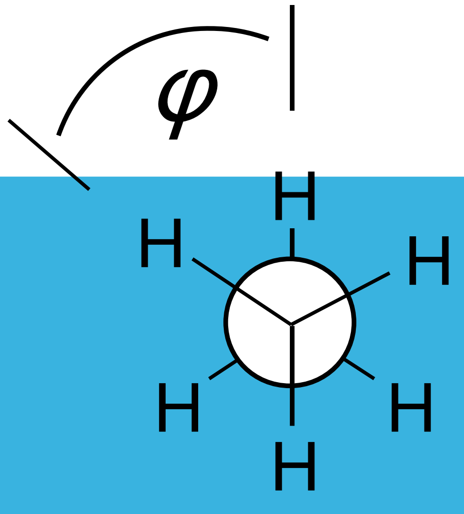
Ethane

This represents a particular orientation of the C-H bonds on adjacent Carbons

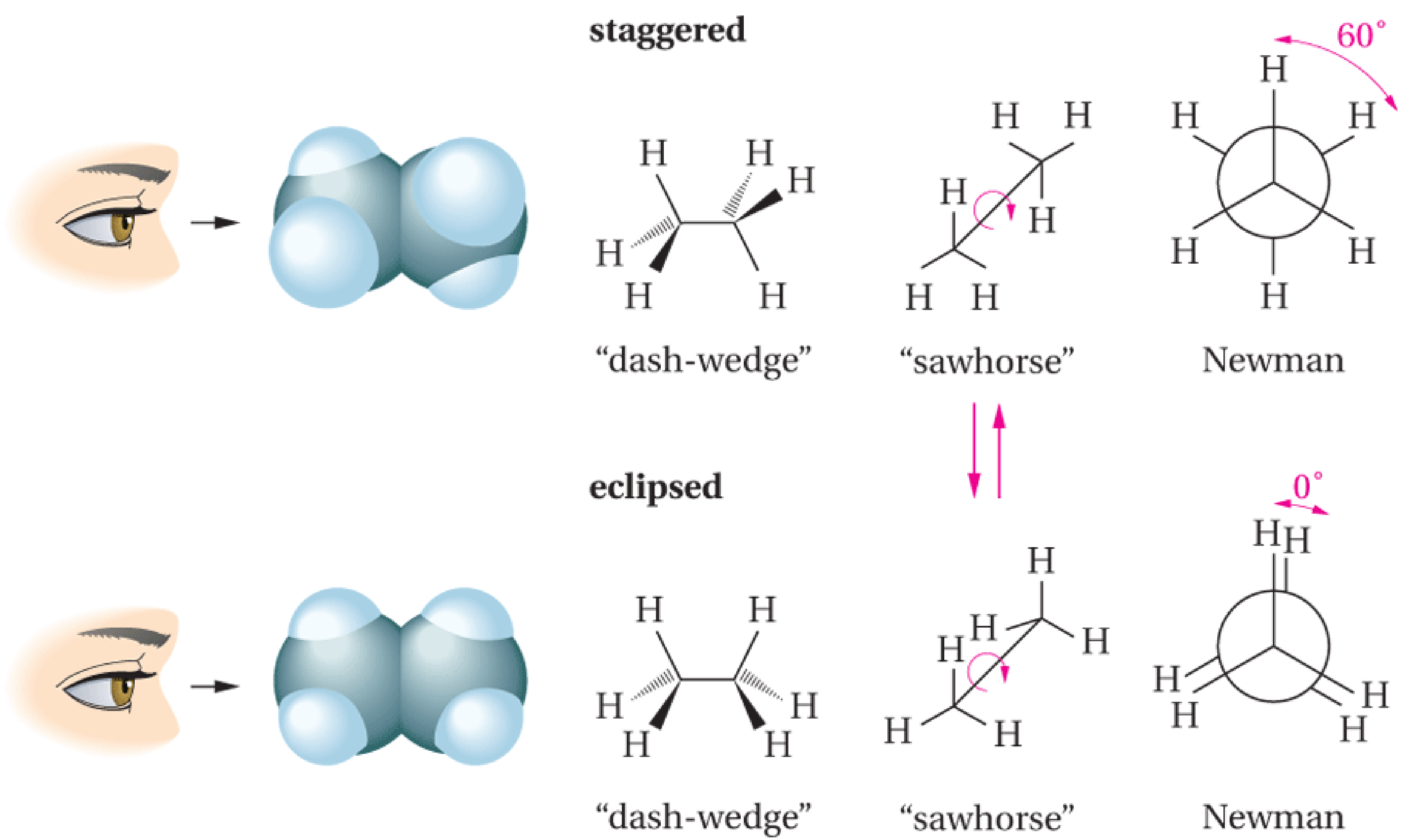
View along C-C bond:



Newman projection

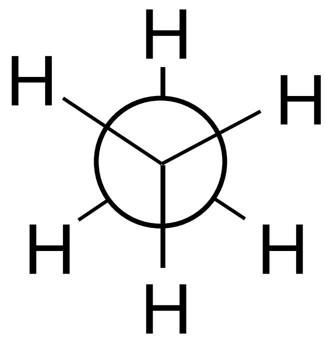


Can select one C-H bond on either carbon and define a ***dihedral angle*** or ***torsional angle (φ)***



staggered
60°
“dash-wedge”
“sawhorse”
Newman
eclipsed
0°
“dash-wedge”
“sawhorse”
Newman

$\varphi = 60^o$



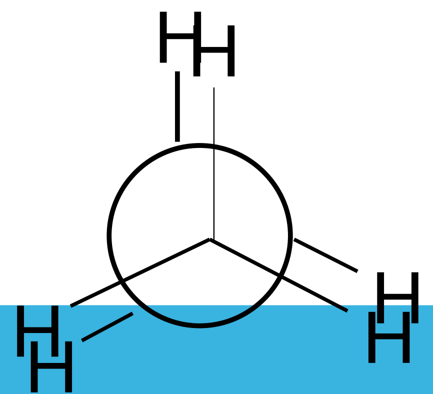
Staggered conformation

Minimum energy conformation (least crowded possible conformation)

C-C σ bonds: symmetrical about the bond axes.

In principle, no barrier to rotation about C-C bond

Could have $\varphi = 0^o$



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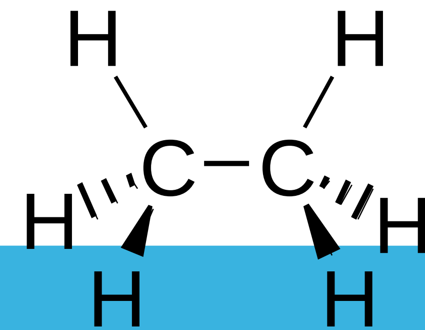


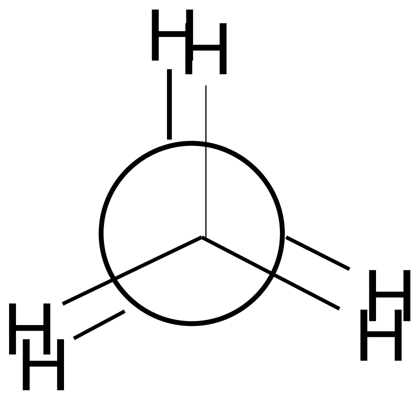
Eclipsed conformation

Maximum energy conformation

(most crowded possible conformation)

•Eclipsed conformation experiences ***steric hindrance***

•Unfavourable interaction between groups which are close together in space



Steric hindrance exists between the eclipsing C-H bonds in this conformation

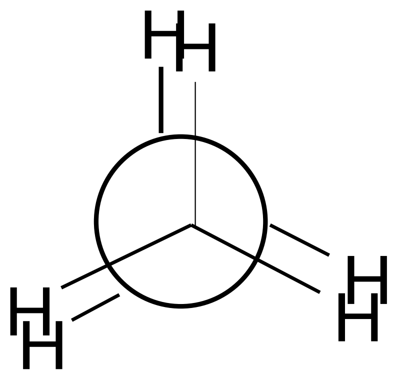
•These unfavourable interactions absent in the staggered conformation

•Hence, the staggered conformation is lower in energy

•Energy difference between eclipsed and staggered conformations of ethane = 12 kJ mol^{-1}

•Each C-H eclipsing interaction contributes 4 kJ mol^{-1} of torsional strain energy

4 kJ mol^{-1}



4 kJ mol^{-1}

4 kJ mol^{-1}

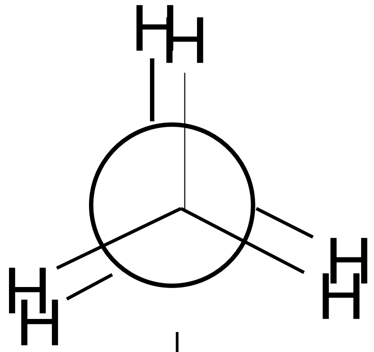
Total: 12 kJ mol^{-1} torsional strain

Conformations: different orientations of molecules arising from rotations about C-C σ bonds

Consider one full rotation about the C-C bond in ethane

Start at $\varphi = 0°$ (eclipsed conformation)

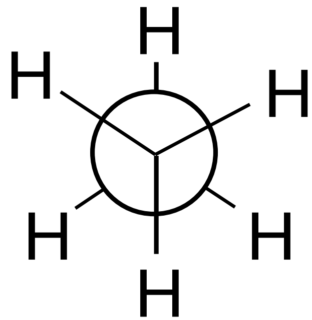
$\varphi = 0°$



Eclipsed conformation
strain energy 12 kJ mol^{-1}

Rotate 60°

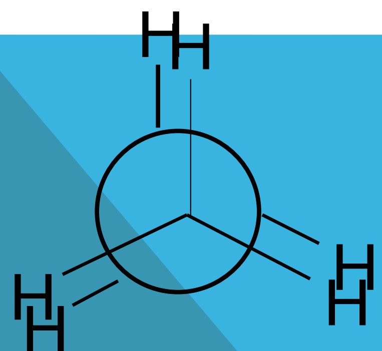
$\varphi = 60°$



Staggered conformation
strain energy 0 kJ mol^{-1}

Rotate 60°

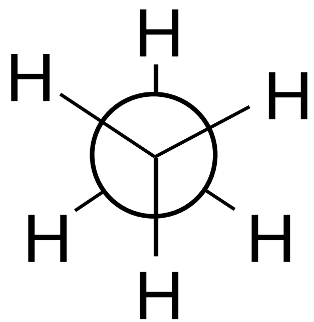
$\varphi = 120°$



Eclipsed conformation
strain energy 12 kJ mol^{-1}

Rotate 60°

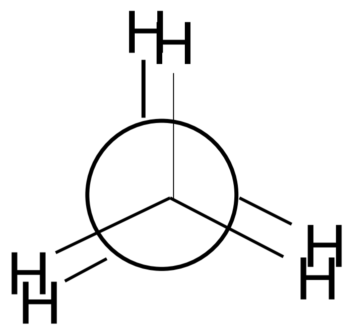
$\varphi = 180°$



Staggered conformation
strain energy 0 kJ mol^{-1}

Rotate 60°

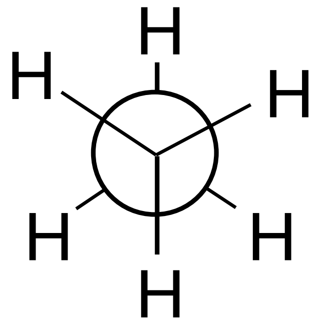
$\varphi = 240°$



Eclipsed conformation
strain energy 12 kJ mol^{-1}

Rotate 60°

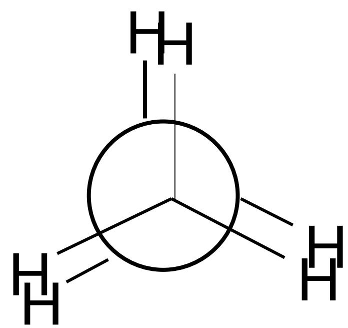
$\varphi = 300°$



Staggered conformation
strain energy 0 kJ mol^{-1}

Rotate 60°

$\varphi = 360°$
Full rotation
Return to starting position



Eclipsed conformation
strain energy 12 kJ mol^{-1}
Identical to that at $\varphi = 0°$

Hence, in one full rotation about the C-C bond

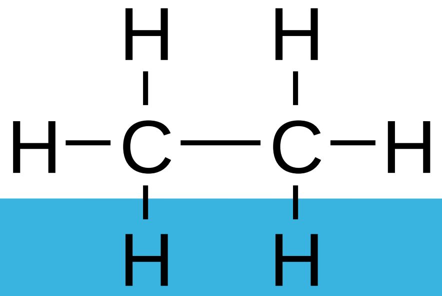
- Pass through three equivalent eclipsed conformations (energy maxima)
- Pass through three equivalent staggered conformations (energy minima)
- Pass through an infinite number of other conformations

Molecular formula: gives the identity and number of different atoms comprising a molecule

Ethane: molecular formula = C_2H_6

Valency:	Carbon	4
	Hydrogen	1

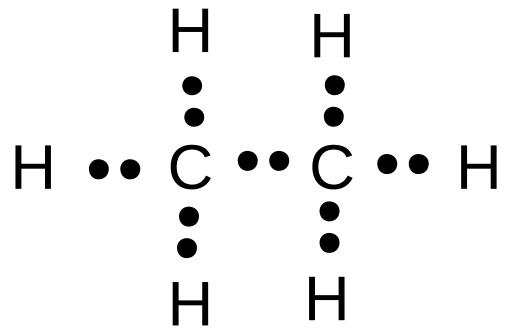
Combining this information, can propose



i.e. a ***structural formula*** for ethane

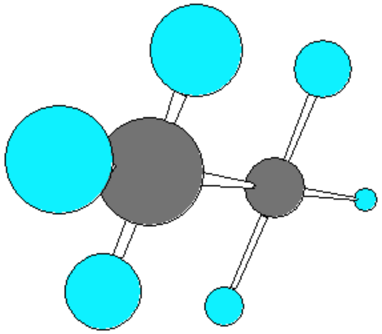
•Each line represents a single covalent bond

•i.e. one shared pair of electrons



•Structural formulae present information on atom-to-atom connectivity

•However, is an inadequate represention of some aspects of the molecule



•Suggests molecule is planar

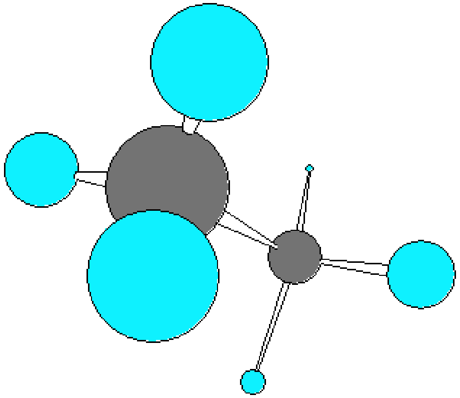
•Suggests different types of hydrogen

Experimental evidence shows:

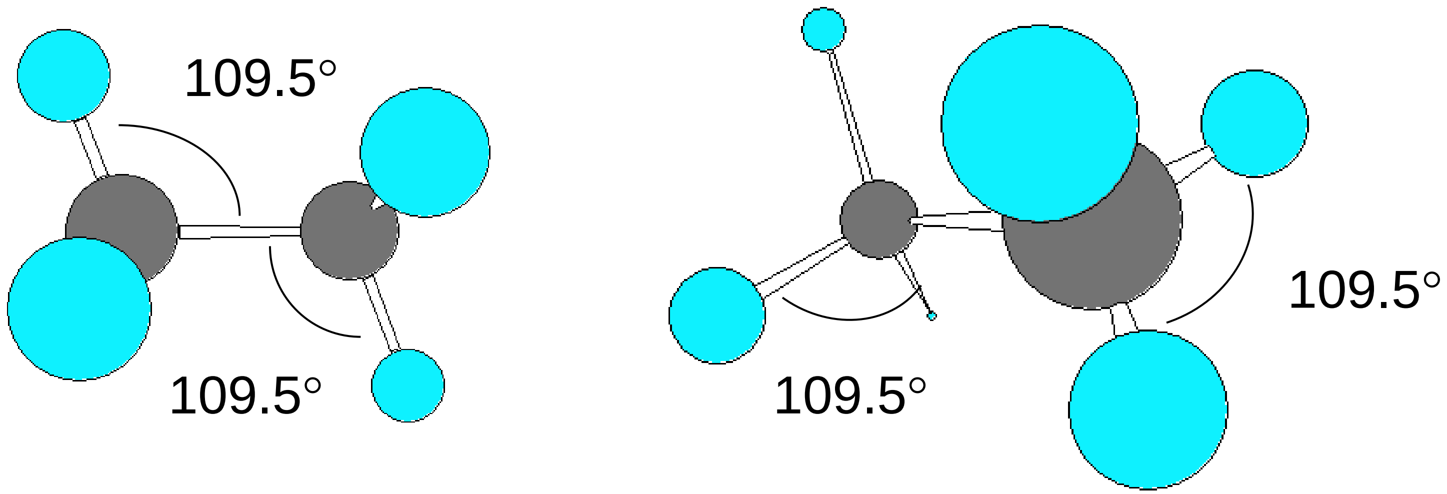
•Ethane molecules not planar

•All the hydrogens are equivalent

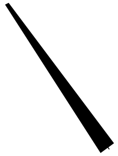
3 Dimensional shape of the molecule has *tetrahedral* carbons



•Angle formed by any two bonds to any atom = ~ 109.5^{o}

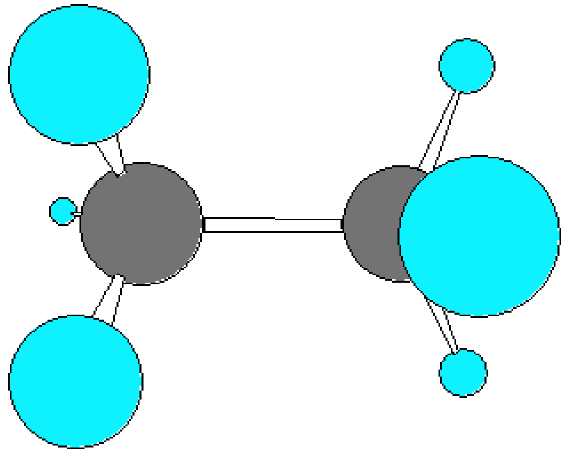


Need to be able to represent 3D molecular structure in 2D



$\Longrightarrow$ Bond coming out of plane of screen

$\Longrightarrow$ Bond going into plane of screen e.g.



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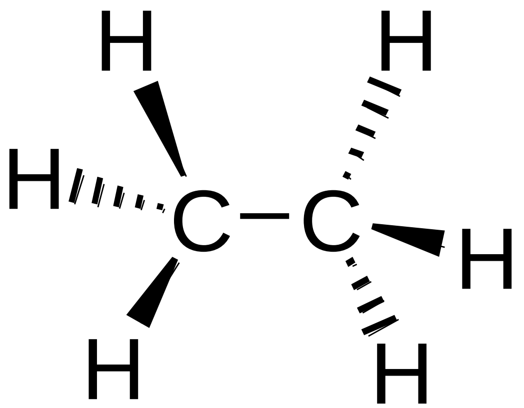
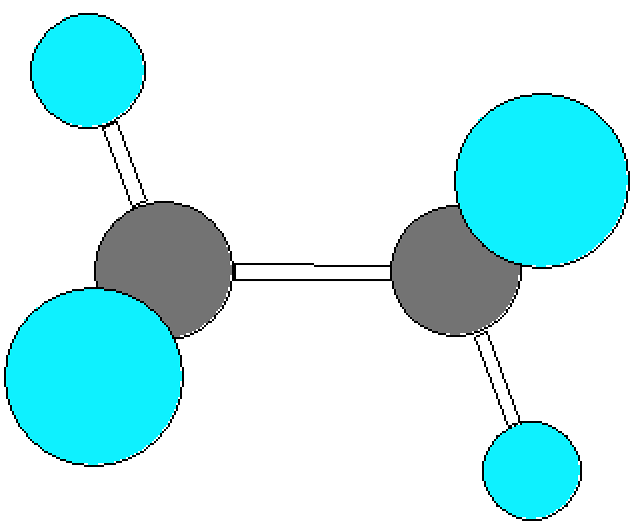


Or



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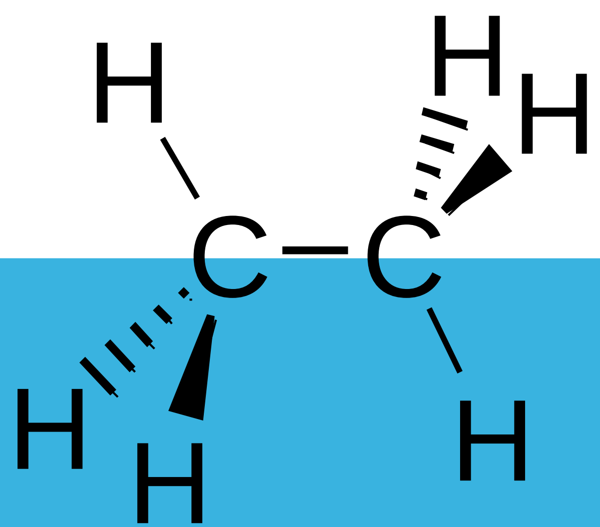
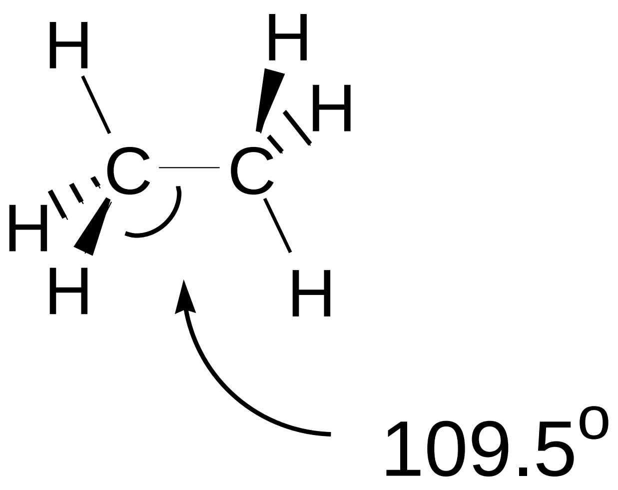
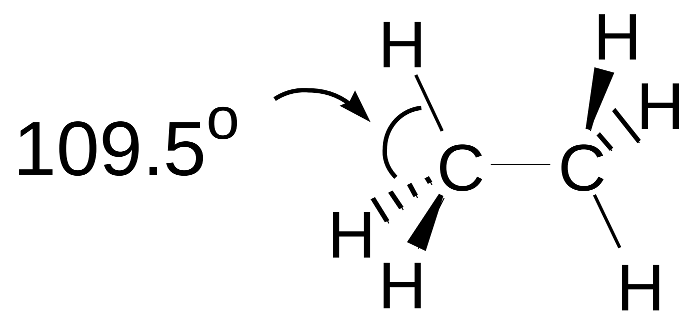


Angle between any two bonds at a Carbon atom = 109.5^o





Ethane: a gas b.p. ~ -100^{o}C

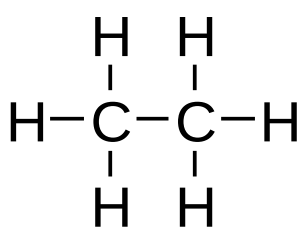
Empirical formula: CH_3

- An organic chemical
- Substance composed of organic molecules

Molecular formula C_2H_6

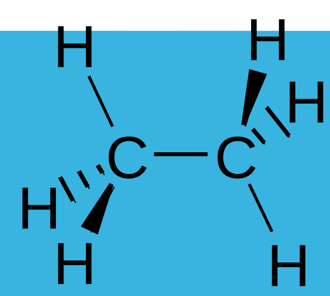
- Identity and number of atoms comprising each molecule

Structural formula



- Atom-to-atom connectivity

Structural formula showing stereochemistry



- 3D shape

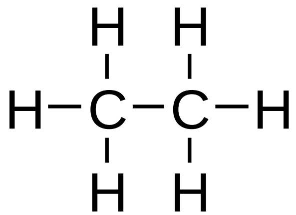
- Ethane: a substance composed of molecules of formula C_2H_6
- 30.070 g of ethane (1 mole) contains 6.022×10^{23} molecules (Avogadro's number)

- Can use the structural formula to show behaviour of molecules
- Assume all molecules of a sample behave the same

- Sometimes need to consider behaviour of a population of molecules

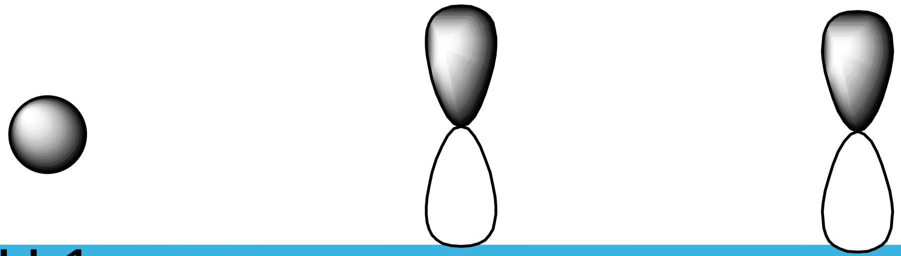
Electronic configuration of Carbon   C $1s^2\ 2s^2\ 2p^2$

Hydrogen   H $1s^1$



Ethane

Orbitals available for covalent bonding?



H 1s
(1 $e^{\ominus}$)

C $2p_y$

(vacant)

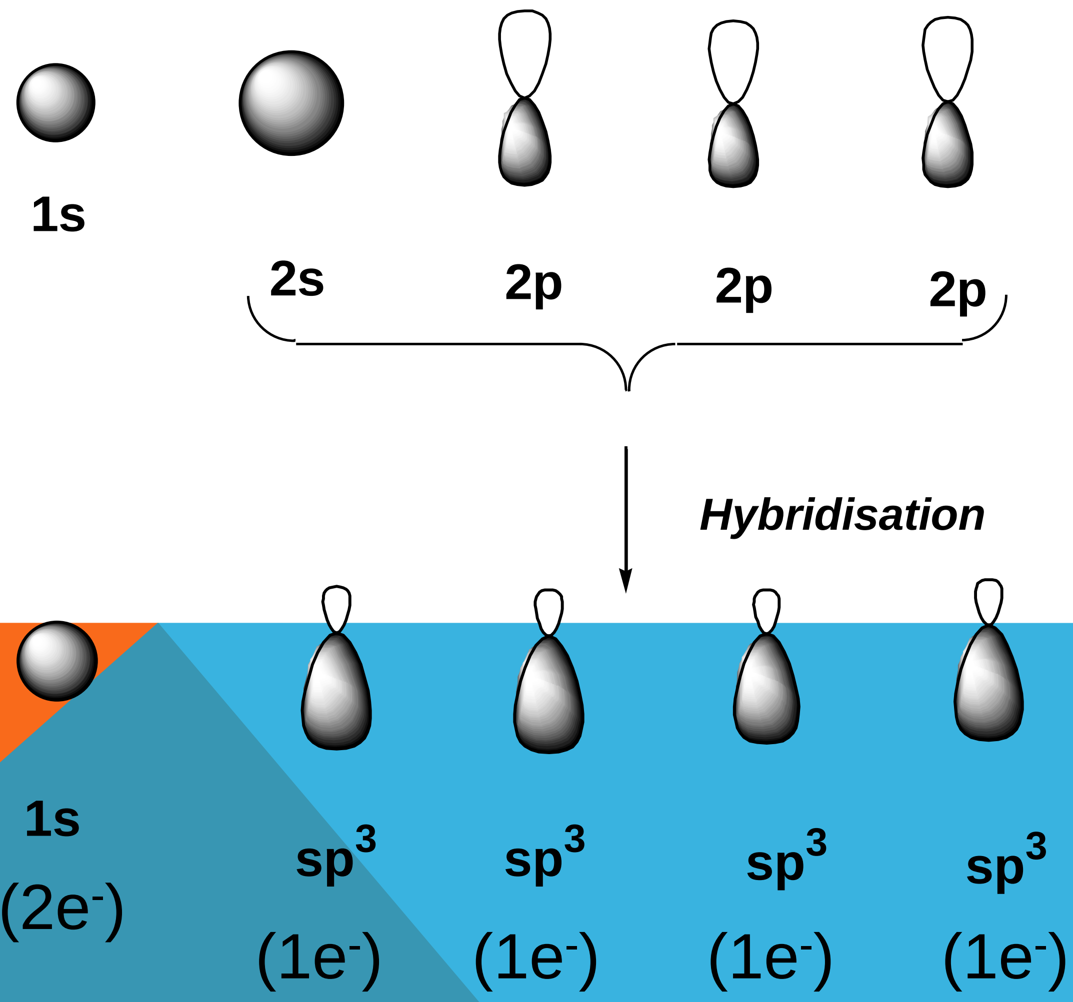
C $2p_z$

(vacant)

•However, know that the geometry of the Carbons in ethane is tetrahedral

•Cannot array p_y and p_z orbitals to give tetrahedral geometry

•Need a modified set of atomic orbitals - *hybridisation*



Bonding in ethane

Atomic orbitals available:

2 Carbons, both contributing 4 **sp^3** hybridised orbitals

6 Hydrogens, each contributing an **s** orbital

Total atomic orbitals = 14

Combine to give 14 molecular orbitals

7 Bonding molecular orbitals; 7 anti-bonding molecular orbitals

Electrons available to occupy molecular orbitals

One for each **sp^3** orbital on Carbon;
one for each **s** orbital on Hydrogen = 14

Just enough to fully occupy the bonding molecular orbitals

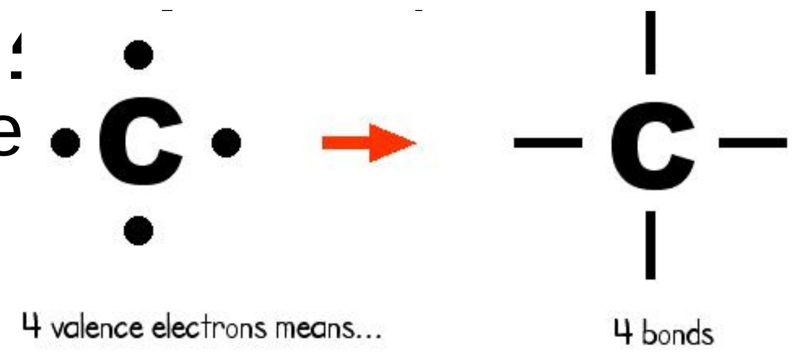
Anti-bonding molecular orbitals not occupied

What makes carbon so special?

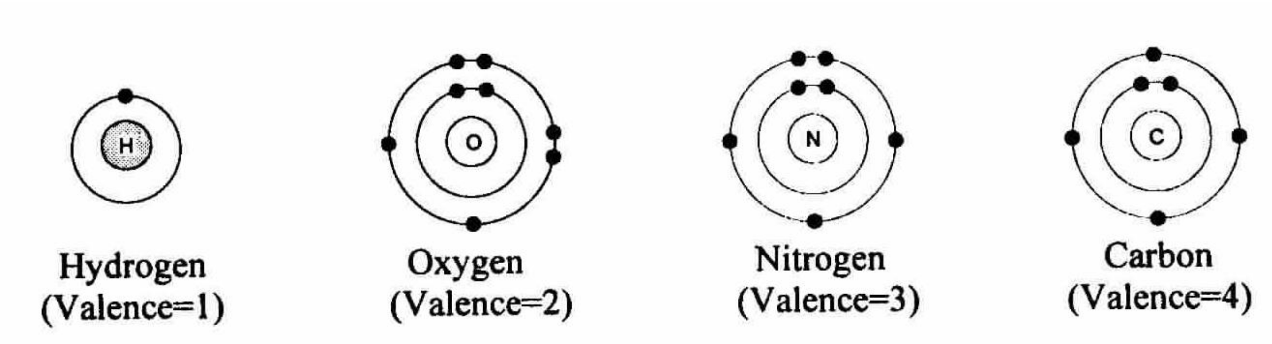
- It has a "central" role in all living organisms.

It has

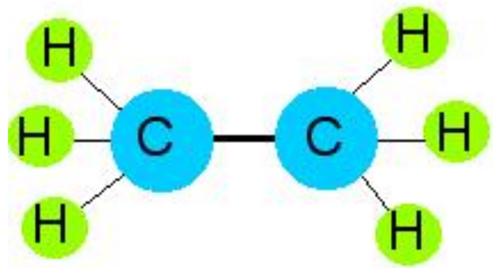
It make



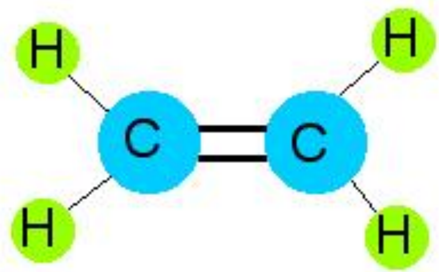
- but really loves to bond with other carbon atoms and make long chains



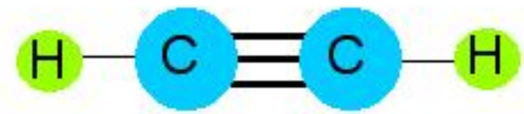
3 Types of Carbon Bonds



Single Bond

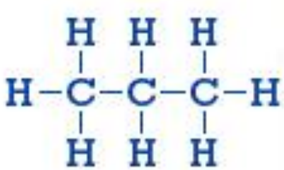


Double Bond



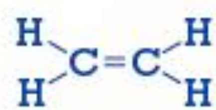
Triple Bond

Single Bond



The **propane** in this camping stove contains only single bonds.

Double Bond



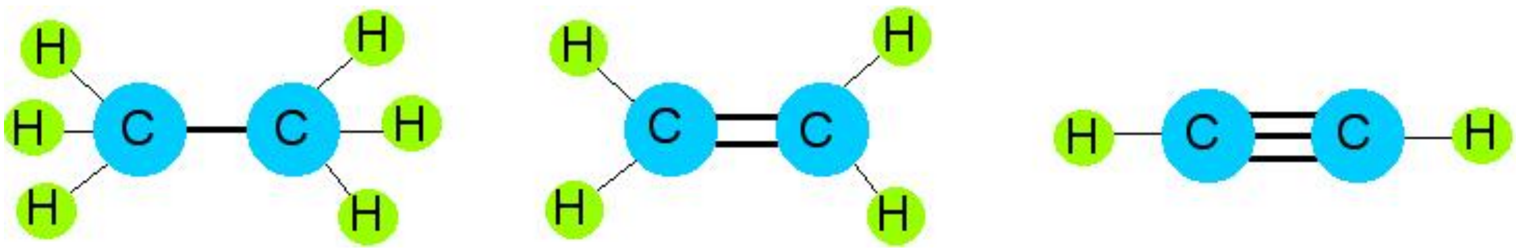
Fruits make **ethene,** which is a compound that helps ripen the fruit.

Triple Bond

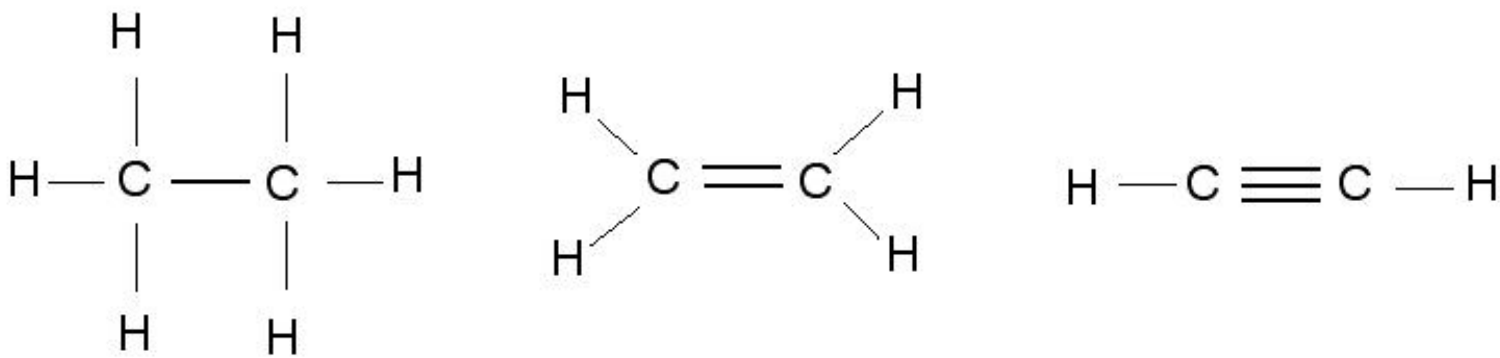
$H-C\equiv C-H$

Ethyne is better known as *acetylene*. It is burned in this miner's lamp and in welding torches.

Lots of ways to draw this…



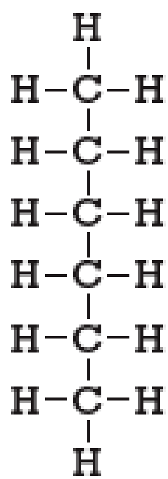
Full Structural Formulas



Simplified Structural Formulas

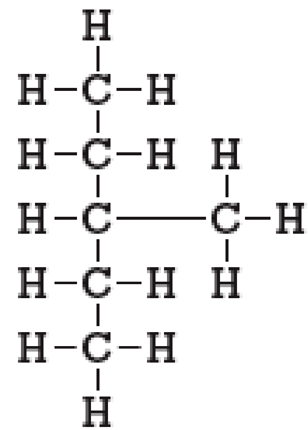
CH_3-CH_3 $CH_2=CH_2$ $CH\equiv CH$

3 Types of Carbon Backbones



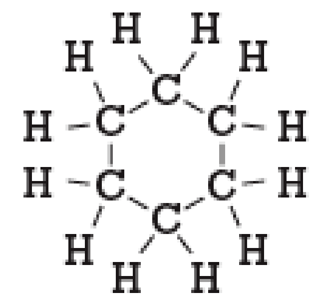
Straight chain

Carbon atoms are connected one after another.



Branched chain

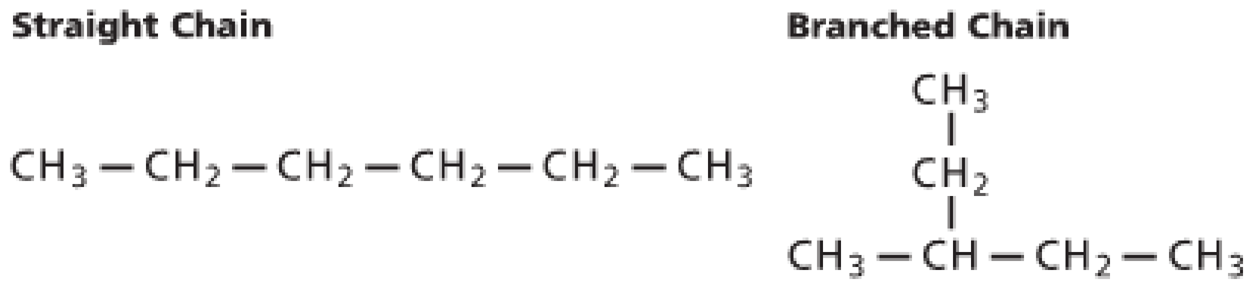
The chain of carbon atoms branches when a carbon atom bonds to more than two other carbon atoms.



Ring

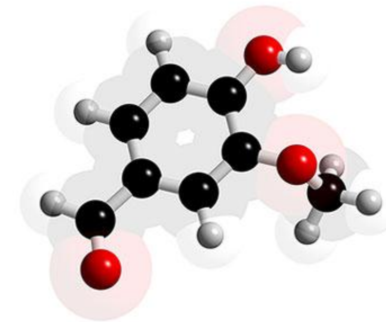
The chain of carbon atoms forms a ring.

Carbon forms <u>long chains</u>

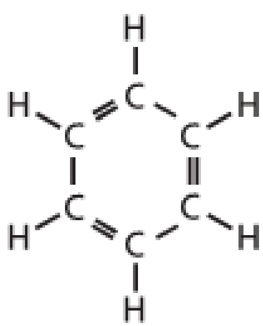


- One carbon chain may contain hundreds of carbon atoms.
- Unlike other elements, carbon atoms can bond to each other to form very long chains.
- One carbon chain may contain hundreds of carbon atoms. Notice how the CH_2 units repeat.
- A very large carbon-based molecule made of repeating units is called a **<u>polymer</u>**. Each unit of a polymer is called a **<u>monomer</u>**.
- Polymers can be *thousands* of atoms long

Carbon forms Rings

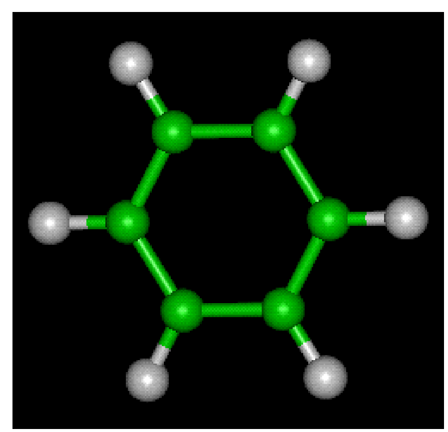


- Carbon-based molecules also can be shaped like rings. Most carbon rings contain **5** or **6** carbon atoms.
- One of the most important carbon rings is **benzene**.
- It has 6 carbons & 6 hydrogens , with alternating double bonds.

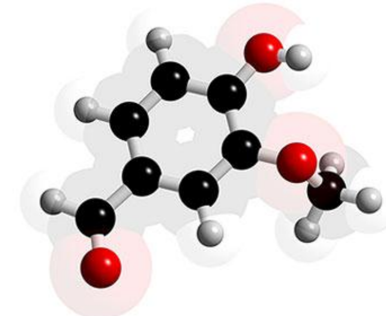


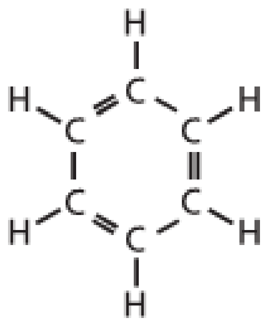
Benzene Ring

Simplified Benzene Ring

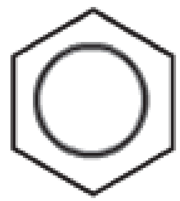


Carbon forms **Rings**

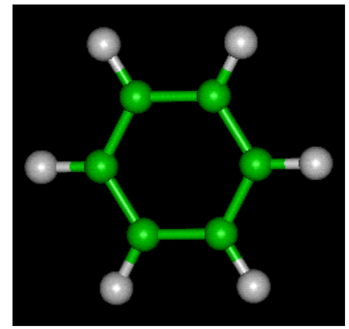




Benzene Ring



Simplified Benzene Ring



- Many compounds are based on Benzene.
- They often have very strong smells or aromas, so they are called **aromatic** compounds.
- An example of one aromatic compound is a molecule called vanillin.
- Guess what that smells like! (vanilla)

Silicon is similar to carbon. Why are there no life forms based on silicon?

Silicon is unsuitable because, although it is a valence IV element like carbon (4 electrons to share),

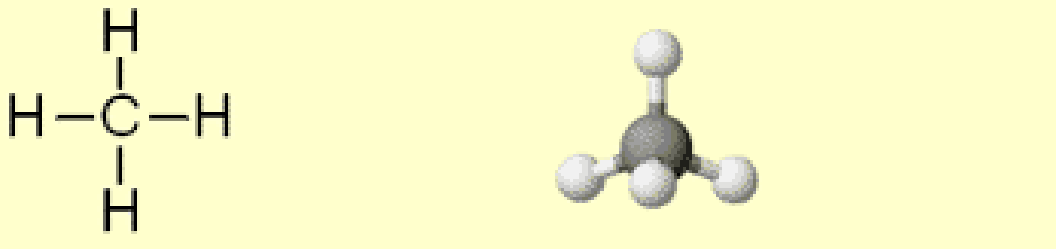
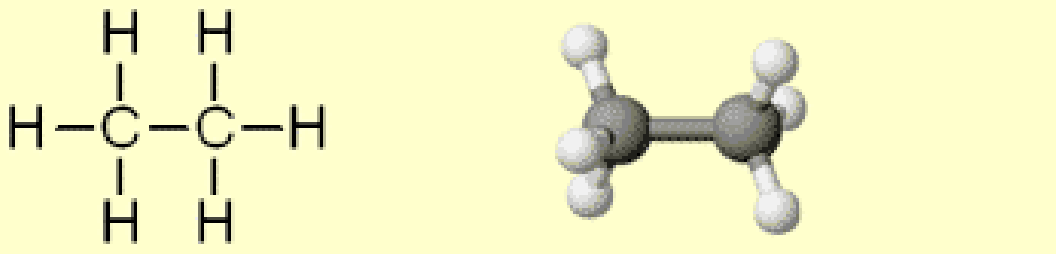
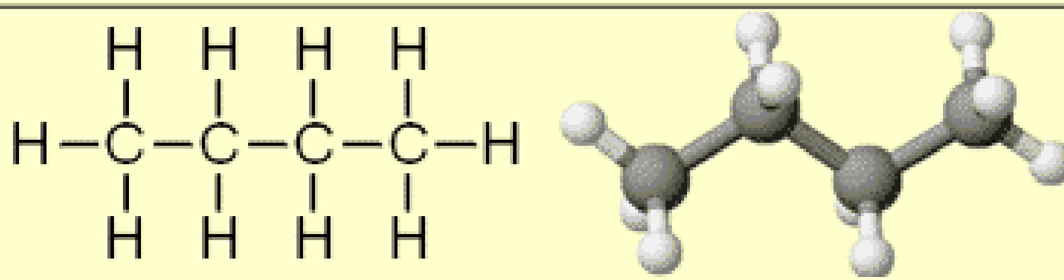
BUT the silicon-silicon covalent bond is not strong enough for it to form long stable chains.

So, it can not form molecules of the complexity needed to make up cells like carbon can!

Long Chain Hydrocarbons & their Names

- **<u>The alkanes</u> make up a series of saturated hydrocarbons, called an <u>homologous series</u> because they have similar properties and have the same general formula:**
- **The first four members of the series are gases at room temperature and are called:**
- **<u>methane,</u> CH_4**
- **<u>ethane,</u> C_2H_6**
- **<u>propane,</u> C_3H_8**
- **<u>butane,</u> C_4H_{10}**

Alkanes molecule structure

methane CH_4	
ethane C_2H_6	
propane C_3H_8	
butane C_4H_{10}	

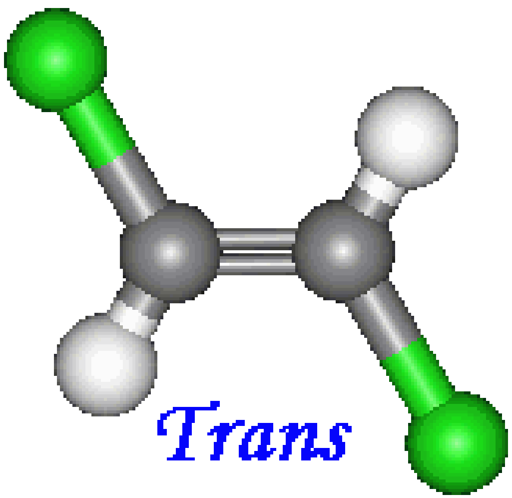
- Alkanes with increasing numbers of carbon atoms have names are based on the Greek word for the number of carbon atoms in the chain of each molecule.
- So you can get, for example,
- **pentane (5),**
- **hexane (6),**
- **heptane (7)**
- **and octane (8).**

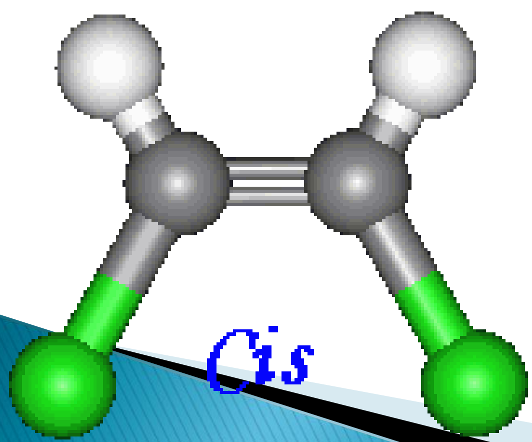
- From pentane onwards, approximately the next thirty alkanes in the series are liquids.
- Alkanes with even longer chains are waxy solids.
- They are typical covalent compounds, insoluble in water but able to mix with each other.
- Alkanes burn in oxygen to produce carbon dioxide and steam.

Lots of carbon compounds seem to be isomers. What is an isomer?

- In organic chemistry, there are many examples of different compounds which have the same molecular formula as each other,
- **But different arrangements (structures)** of the atoms in their molecules.
- These are called **isomers.**

What is an isomer?



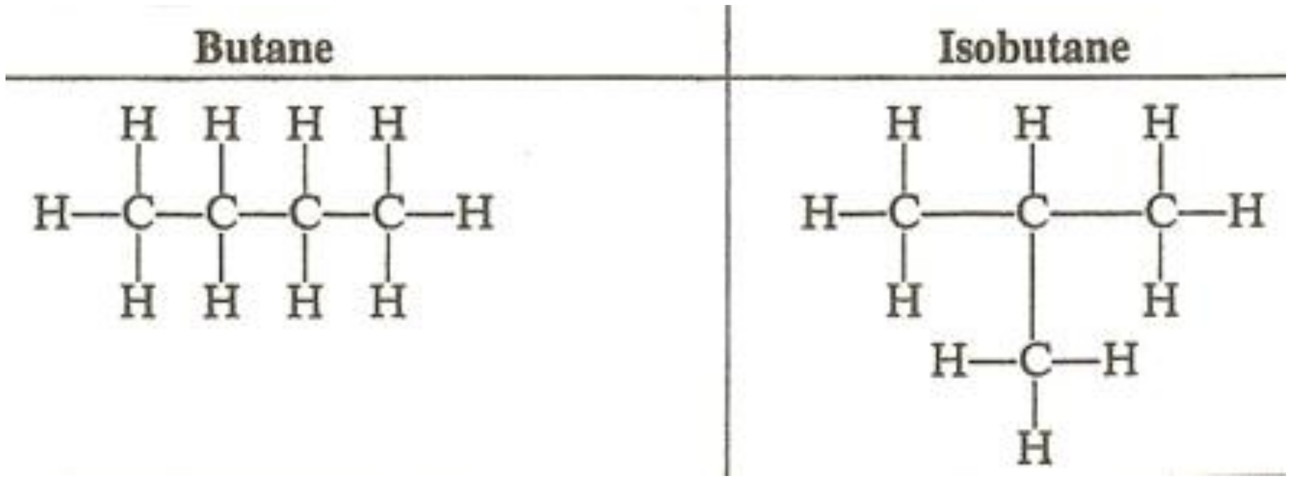


- These compounds are said to be isomers of one another.
- Isomerism also occurs in inorganic chemistry, but it is less common.

If isomers have the same atoms in them, surely they have the same properties, so what's the point?

- It is important to realize that this can have significant effects in a living system.
- One optical isomer of glucose, for example, can be used by a living cell, but the other isomer cannot.
- This is because the enzyme in the cell which recognizes glucose is sensitive to only one form.

Chain Isomerism

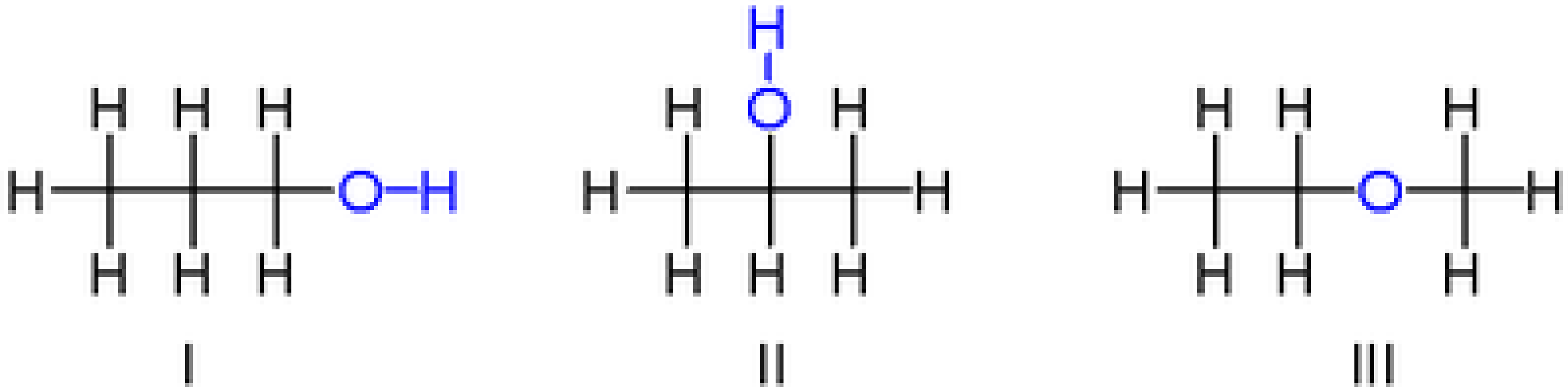


<u>Chain isomers</u> of the same compound are very similar.

There may be small difference in physical properties such as melting or boiling point due to different strengths of intermolecular bonding.

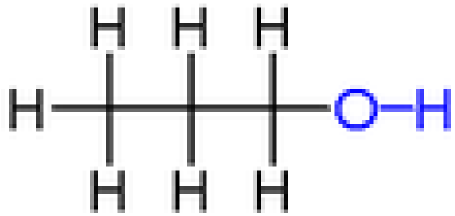
Their chemistry is likely to be identical.

Positional Isomers

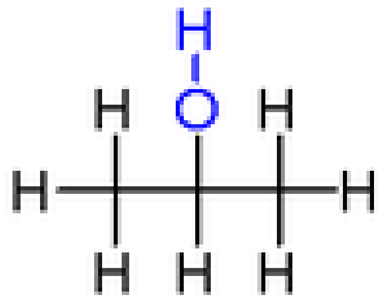


- **<u>Positional isomers</u>** are also usually similar.
- There are slight physical differences, but the chemical properties are usually very similar.
- However, occasionally, positional isomers can have quite different properties

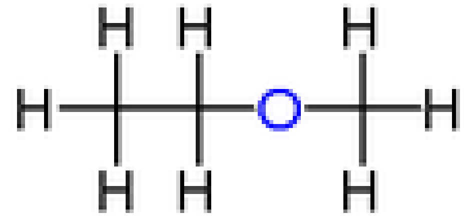
Positional Isomers



I



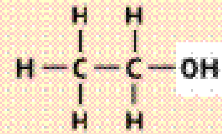
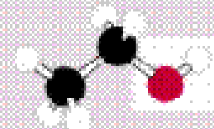
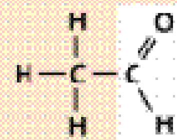
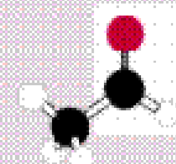
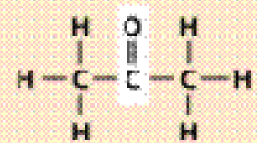
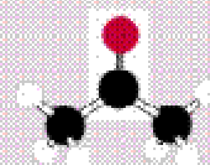
II



III

- A simple example of **isomerism** is given by propanol:
- it has the formula C_3H_8O (or C_3H_7OH) and two isomers propan-1-ol (n-propyl alcohol; **I**) and propan-2-ol (isopropyl alcohol; **II**)
- Note that the position of the oxygen atom differs between the two: it is attached to an end carbon in the first isomer, and to the center carbon in the second.
- The number of possible isomers increases rapidly as the number of atoms increases; for example the next largest alcohol, named butanol ($C_4H_{10}O$), has four different structural isomers.

Functional Group Isomers

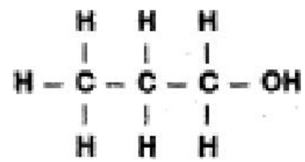
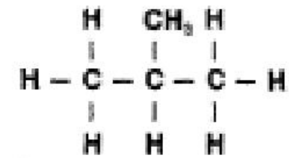
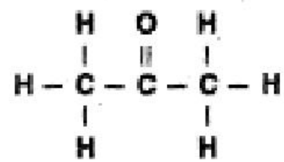
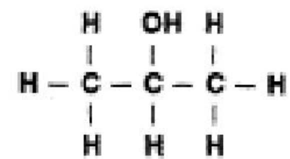
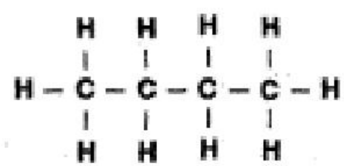
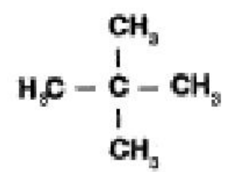
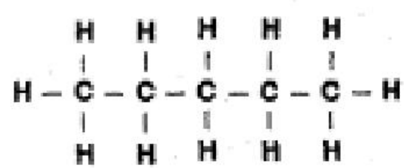
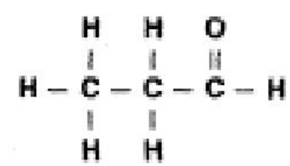
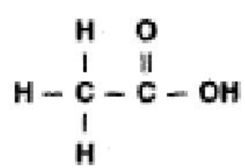
Functional group	Class of compounds	Structural formula	Example	Ball-and-stick model
Hydroxyl —OH	Alcohols	R— OH	 Ethanol	
Carbonyl —CHO	Aldehydes	R—C(=O)—H	 Acetaldehyde	
Carbonyl >CO	Ketones	R—C(=O)—R	 Acetone	

<u>Functional group isomers</u> are likely to be both physically and chemically dissimilar.

Naming the following

ISOMERS Name ____________

Isomers have the same chemical formula but different structural formulas. Match the structure in Column I with its isomer in Column II.

I		II
1. 	______	a) 
2. 	______	b) 
3. 	______	c) 
4. 	______	d) 
5. 	______	e)