Chapter 24. Organic Chemistry

What we will learn:

- Chemical bonding
- Molecular geometry
- Molecular orbitals
- Calsses of organic compounds
- Aliphatic hydrocarbons
- Aromatic hydrocarbons
- Chemistry of functional groups

Chemical bonding (Review of Chapters 9 and 10)

Ionic bond

The bond which involves an electrostatic force between ions

Example

LiF, NaCl, $MgCl_2$

Covalen bond

The bond which involves two electrons sharing two atoms

Example

Lewis structure

A representation of covalent bonding in which shared electron pairs are shown either as lines or as pairs of dots between two atoms

Example

Water molecule

$$\mathrm{H} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}} : \mathrm{H} \qquad\qquad \mathrm{H} - \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}} - \mathrm{H}$$

Octet rule

An atom other than hydrogen tends to form bonds until it is surrounded by eight valence electrons

By sharing electrons atoms tend to keep eight valence electrons in molecules

Atoms can form different forms of covalent bonds depending on the number of sharing electron pairs

Single covalent bond

Two atoms are held together by one electron pair

Double covalent bond

Two atoms are held together by two electron pairs

Example

Carbon dioxide

$$\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} :: C :: \underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} \qquad \underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} = C = \underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}$$

Triple covalent bond

Two atoms are held together by three electron pairs

Example

Acetylene

H : C ::: C : H   H - C ≡ C - H

Bond length

A distance between atoms held together by a covalent bond

Bond type	Bond length (pm)
C - C	154
C = C	133
C ≡ C	120

Electronegativity

An ability of an atom to attract toward itself the electron cloud in a chemical bond

Electronegativity is a relative concept, meaning that an electronegativilty of one atom can be measured relative to another atom

Generally electronegativity increases from left to right acros a period in the periodic table.

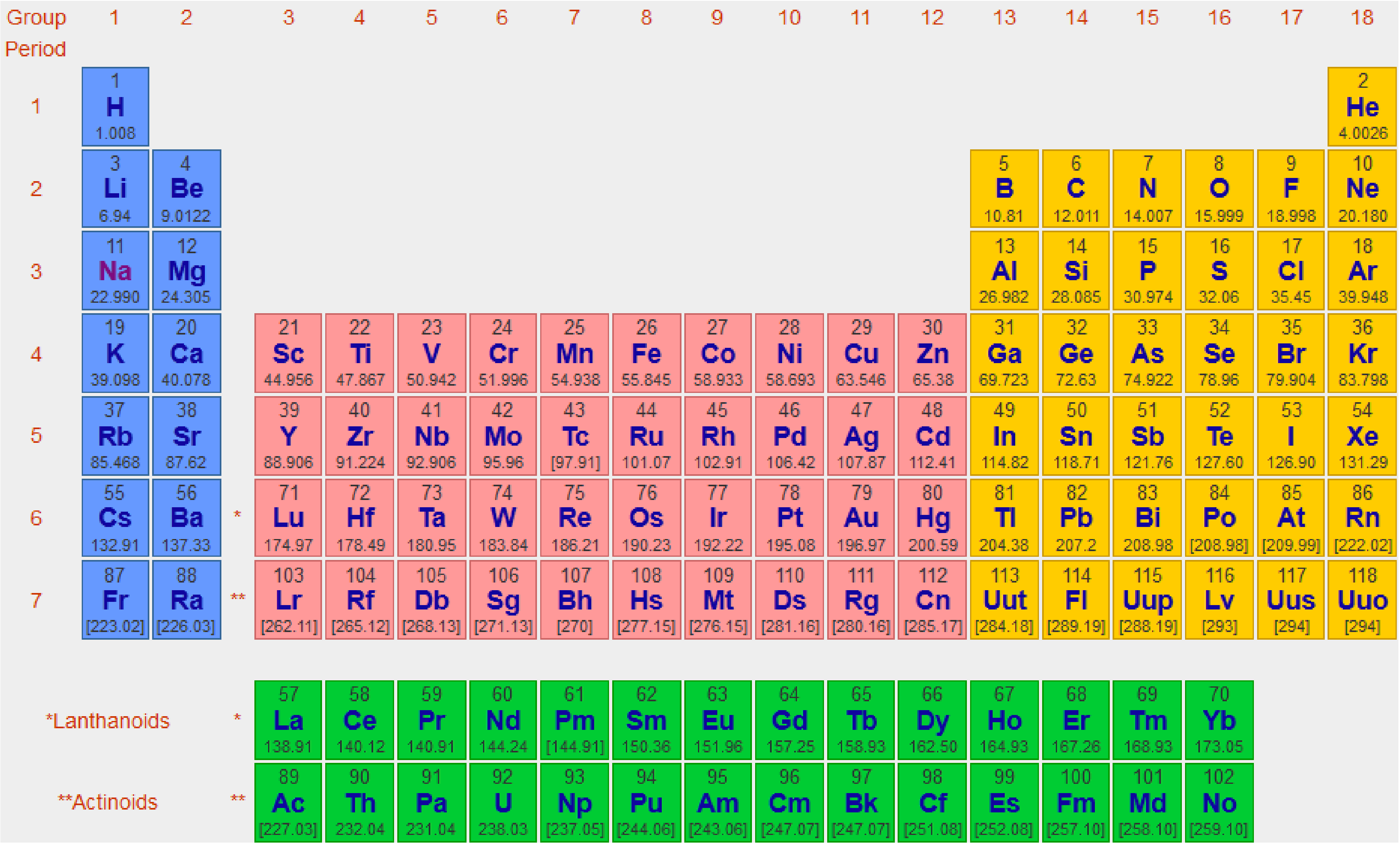
Within each group, electronegativity decreases with increasing atomic number

The most electrogegative atom is F

The less electronegative atom is Cs

Oxidation number

The number of charges that an atom would have if electrons were transferred completely to the more electronegative atoms in the bond



Group Period	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008																		2 He 4.0026
2	3 Li 6.94	4 Be 9.0122												5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
3	11 Na 22.990	12 Mg 24.305												13 Al 26.982	14 Si 28.085	15 P 30.974	16 S 32.06	17 Cl 35.45	18 Ar 39.948
4	19 K 39.098	20 Ca 40.078		21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.63	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.798
5	37 Rb 85.468	38 Sr 87.62		39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.96	43 Tc [97.91]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	*	71 Lu 174.97	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [208.98]	85 At [209.99]	86 Rn [222.02]
7	87 Fr [223.02]	88 Ra [226.03]	**	103 Lr [262.11]	104 Rf [265.12]	105 Db [268.13]	106 Sg [271.13]	107 Bh [270]	108 Hs [277.15]	109 Mt [276.15]	110 Ds [281.16]	111 Rg [280.16]	112 Cn [285.17]	113 Uut [284.18]	114 Fl [289.19]	115 Uup [288.19]	116 Lv [293]	117 Uus [294]	118 Uuo [294]
*Lanthanoids			*	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [144.91]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05		
**Actinoids			**	89 Ac [227.03]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237.05]	94 Pu [244.06]	95 Am [243.06]	96 Cm [247.07]	97 Bk [247.07]	98 Cf [251.08]	99 Es [252.08]	100 Fm [257.10]	101 Md [258.10]	102 No [259.10]		

Example

Oxidation numbers and electronegativity

NH_3 molecule

N atom forms three bonds with three H atoms. N is more electronegative than H therefore the elctron cloud will be shifted to N. If the transfer of electrons were complete, each H would donate an electron to N, which would have a total charge of -3, and each H would have a charge +1

CH_4 molecule

C atom forms four bonds with four H atoms. C is more electronegative therefore the elctron cloud will be shifted to C. If the transfer of electrons were complete, each H would donate an electron to C, which would have a total charge of -4, and each H would have a charge +1

Resonance

Lewis structures of ozone O_3

$$\overset{..}{\underset{..}{O}} = \overset{..+}{O} - \overset{..-}{\underset{..}{O}} \qquad \overset{..\,-}{\underset{..}{O}} - \overset{..+}{O} = \overset{..}{\underset{..}{O}}$$

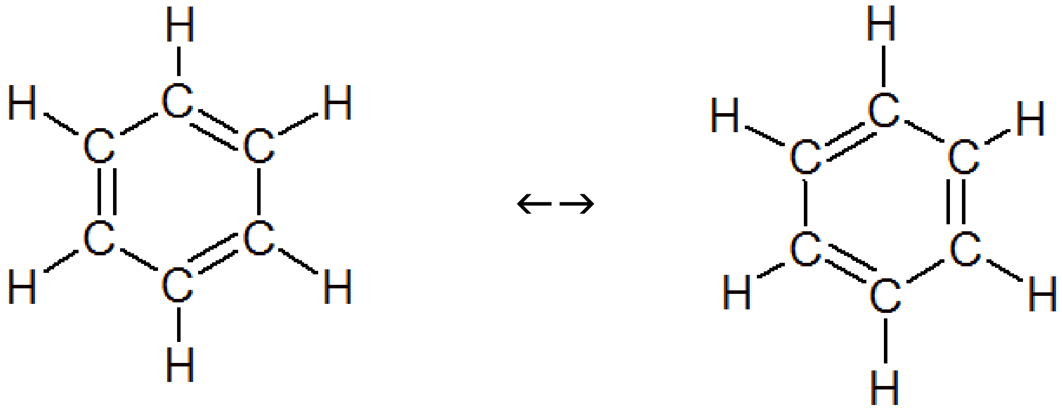
Two Lewis structures of ozone based on the octet rule

According to the rules, a double bond should be shorter, and a single bond should be longer. However experimentally, both bonds have the same length which is between the length of the single and double bond (128 pm)

Resonance structure

One of two or more Lewis structures for a single molecule that cannot be represented accurately by only one Lewis structure

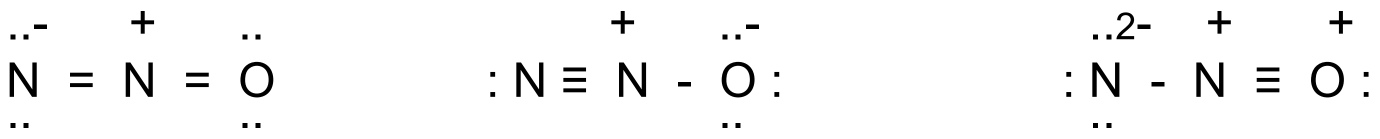
Lewis structures of benzene (C_6H_6)



Two Lewis structures of benzene based on the octet rule

According to the rules, a double bond should be shorter (140 pm), and a single bond should be longer (154 pm). However experimentally, both bonds have the same length which is between the length of the single and double bond (133 pm)

Lewis structures of nitrous oxide (N_2O)



$\overset{..-}{\underset{..}{N}} = \overset{+}{N} = \overset{..}{\underset{..}{O}}$

$:N \equiv \overset{+}{N} - \overset{..-}{\underset{..}{O}}:$

$:\overset{..2-}{\underset{..}{N}} - \overset{+}{N} \equiv \overset{+}{O}:$

The second structure is the most important because the negative charge is on the more electronegative atom

The last structure is the lest important because it has a large separation of formal charges

Bond enthalpy

The enthalpy change required to break a particular bond in 1 mole of gaseous molecules

Example

$$H_2\,(g) \rightarrow H\,(g) + H\,(g) \qquad \Delta H^0 = 436.4 \text{ kJ/mol}$$

The 436.4 kJ of energy is required to break the covalent bonds in 1 mole of gaseous H_2

$$Cl_2\,(g) \rightarrow Cl\,(g) + Cl\,(g) \qquad \Delta H^0 = 242.7 \text{ kJ/mol}$$

$$HCl\,(g) \rightarrow H\,(g) + Cl\,(g) \qquad \Delta H^0 = 431.9 \text{ kJ/mol}$$

Molecules with a double bond

$$O_2\,(g) \rightarrow O\,(g) + O\,(g) \qquad \Delta H^0 = 498.7 \text{ kJ/mol}$$

Breaking bonds in polyatomic molecules is more complex

$H_2O\ (g) \rightarrow H\ (g) + OH\ (g) \qquad \Delta H^0 = 502$ kJ/mol

$OH\ (g) \rightarrow H\ (g) + O\ (g) \qquad \Delta H^0 = 427$ kJ/mol

Different values of bond enthalpy in water are not related to different bond strength. They are related to different environments in H_2O and OH when the OH bond is breaking

Therefore the same bond can have different enthalpy in different moelcules

Example

CH_3OH and H_2O

Bond enthalpies of the O-H bond are different in those two molecules

Bond enthalpy in thermochemistry

In each chemical reaction some bonds are formed and some bonds are broken. Therefore, it is possible to predict the approximate enthalpy of a chemical reaction using the average bond enthalpies

$$\Delta H^0 \quad = \quad \Sigma\, BE(reactants) \; - \Sigma\, BE(products)$$

BE - average bond enthalpy

The positive value of ΔH^0 indicates that the reaction is endothermic (requires energy to proceed)

The equation is accurate for diatomic molecules, and is approximate for polyatomic molecules

Molecular geometry

Valence shell

The outermost electron-occupied shell of an atom

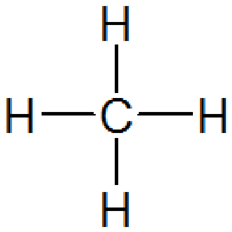
Valence electrons are mostly responsible for covalent bonding

Valence-shell electron-pair repulsion model

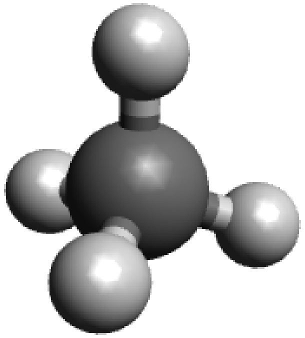
Geometric arrangement of electron pairs around a central atom in terms of the electrostatic repulsion between electron pairs

A molecule forms a geometry in which electrostatic repulsion between electron pairs is minimized

Methane

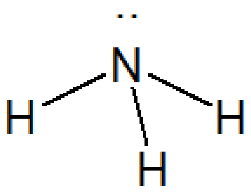


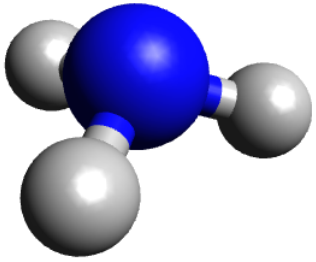
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$



There are four electron pairs in methane, forming bonds with hydrogen atoms. To minimize the repulsion interaction between electron pairs, the methane molecule forms a tetrahedral geometry, where the carbon atom is in the center, and there is the same angle between the bonds 109.5.

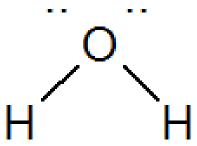
Ammonia

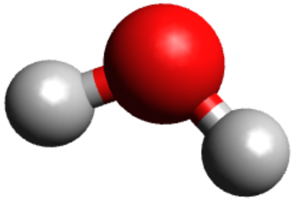




There are four electron pairs, three of them form bonds with hydrogen atoms, and one electron pair is a lone pair. To minimize electrostatic repulsion between the electron pairs, all four pairs form tetrahedral arrangement. The repulsion interaction between electron pairs involved in bonds is weaker than this interaction between a pair in a bond and a lone pair. Therefore the geometry of ammonia is trigonal pyramid. The angle between bonds is 107.3, which is smaller than in methane.

Water





The central oxygen atom is surrounded by four electron pairs. Two electron pairs form bonds with hydrogen atoms and other two are lone pairs. To minimize electrostatic repulsion between the electron pairs, all four pairs form tetrahedral arrangement. The repulsion interaction between pairs involved in bonds is weaker, and the repulsion interaction between lone pairs is stronger. Therefore the angle between bonds in water is 104.5, which is smaller than the similar angle in ammonia or in methane.

Dipole moment

A dipole moment is a product of a charge Q and a distance r

$$\mu = Q \cdot r$$

A unit of a dipole moment is 1 Debye

$$1\ \mathrm{D} = 3.336 \times 10^{-30}\ \mathrm{C\ m}$$

A dipole moment is a vector quantity it means it has a value and a direction

Polar and nonpolar molecules

Molecule have a dipole moment are polar, and those without a dipole moment are nonpolar

A convention is to draw a dipole moment from a positive pole of the dipole to a negative pole

Example

HF molecule

$$\underset{\rightarrow}{H - F}$$

The dipole moment of the HF molecule goes from hydrogen atom (a positive pole) to fluorine atom (a negative pole)

Carbon dioxide CO_2

$$\underset{\leftarrow \quad \rightarrow}{O = C = O}$$

There are nonzero dipole moments of individual bonds (C=O) in CO_2, however the resultant dipole moment of this molecule is zero

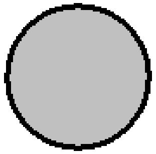
Resultant dipole moment

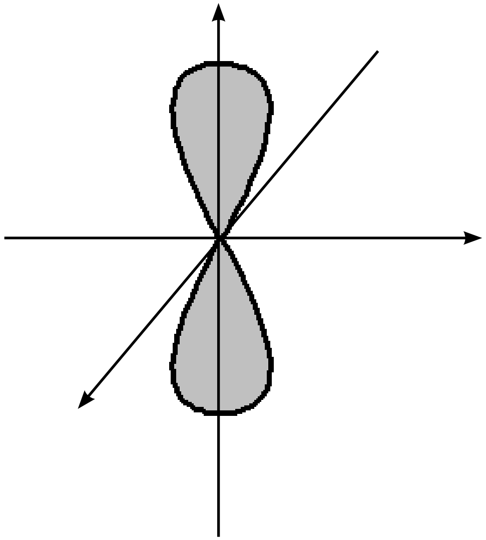
A dipole moment of a molecule is a resultant dipole moment from dipole moments of individual bonds

Atomic orbitals

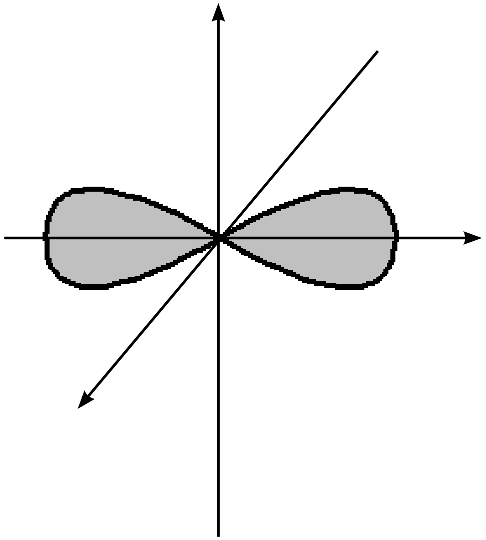
Atomic orbital is function describing electron clouds in atoms

2s

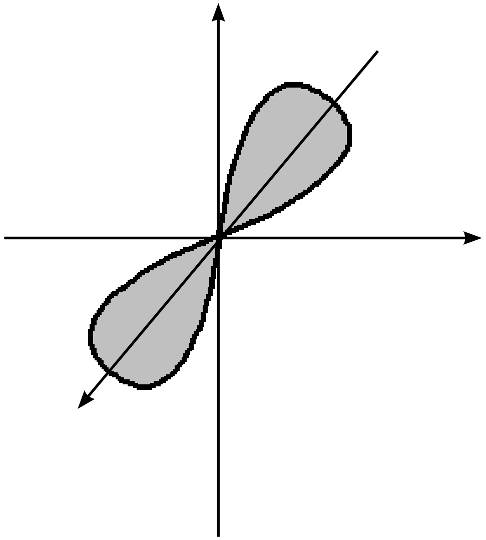




$2p_x$



$2p_y$



$2p_z$

Atomic orbitals describing valence electrons of carbon atom

Electron configuration

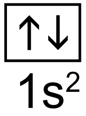
An arrangement of electrons on atomic orbitals

Rules of electron configuration and atom stability

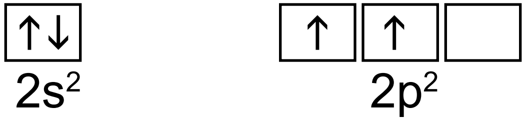
1. Atomic orbitals are filled out by electrons starting from the orbital of the lowest energy
2. Each atomic orbital can be occupied by two electrons with opposite spins
3. When two orbitals have the same energy, they are occupied by electrons with the same spin first, and next with the opposite spin

Example

The electron configuration of core electrons of a carbon atom (C)

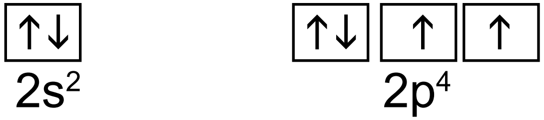


The electron configuration of valence electrons of a carbon atom (C)



Carbon atom has two electrons on an electron shell *s* (an atomic orbital s) and two electrons on a shell *p* (atomic orbitals p)

The electron configuration of valence electrons of an oxygen atom (O)



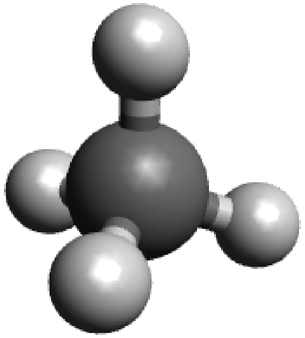
Oxygen atom has two electrons on an electron shell *s* (an atomic orbital s) and four electrons on a shell *p* (atomic orbitals p)

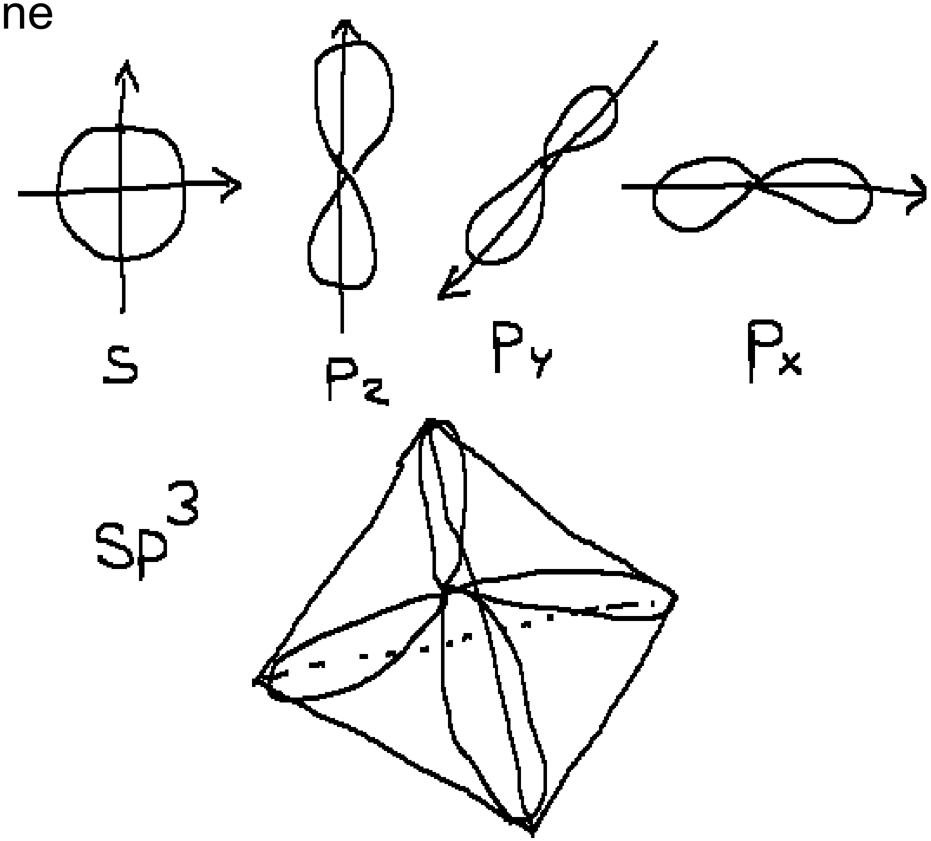
Hybridization

A mixture of atomic orbitals describing electron clouds of an atom in preparation for covalent bond formation

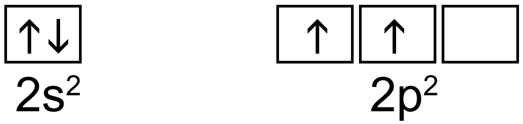
Example

sp^3 hybridization of carbon in methane

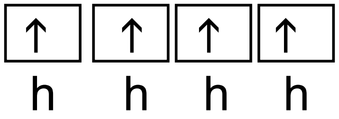




The electron configuration of a carbon atom before hybridization

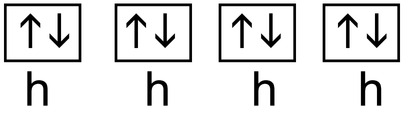


The electron configuration of a carbon atom after sp^3 hybridization



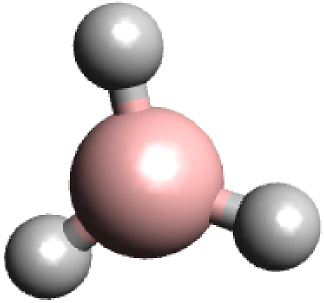
Each hybrid orbital contains one unpaired electron, which is ready to make a covalent bond with hydrogen atoms. The are four hydrogen atoms and each of them provides one electron

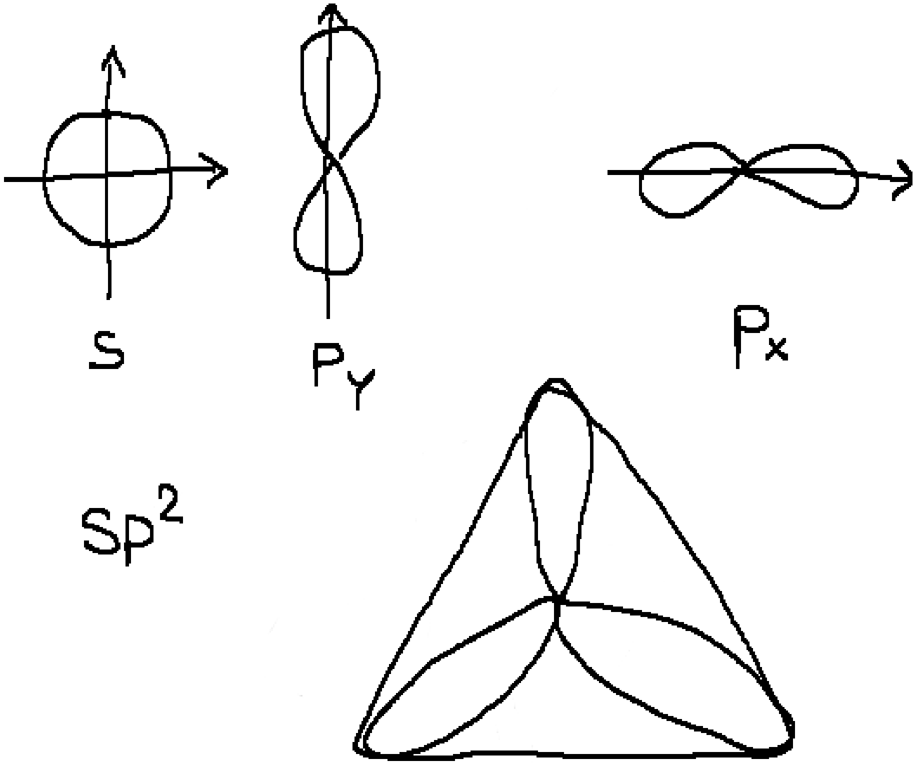
The electron configuration of methane



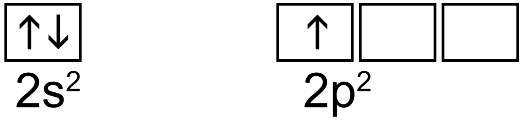
Example

sp^2 hybridization of B in BH_3

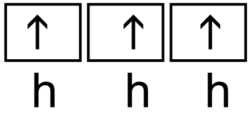




The electron configuration of a boron atom before hybridization

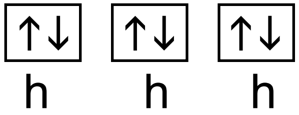


The electron configuration of a boron atom after sp^2 hybridization



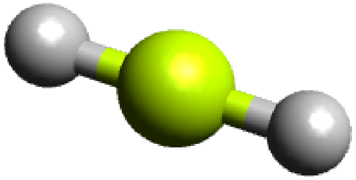
Each hybrid orbital contains one unpaired electron, which is ready to make a covalent bond with hydrogen atoms. The are three hydrogen atoms and each of them provides one electron

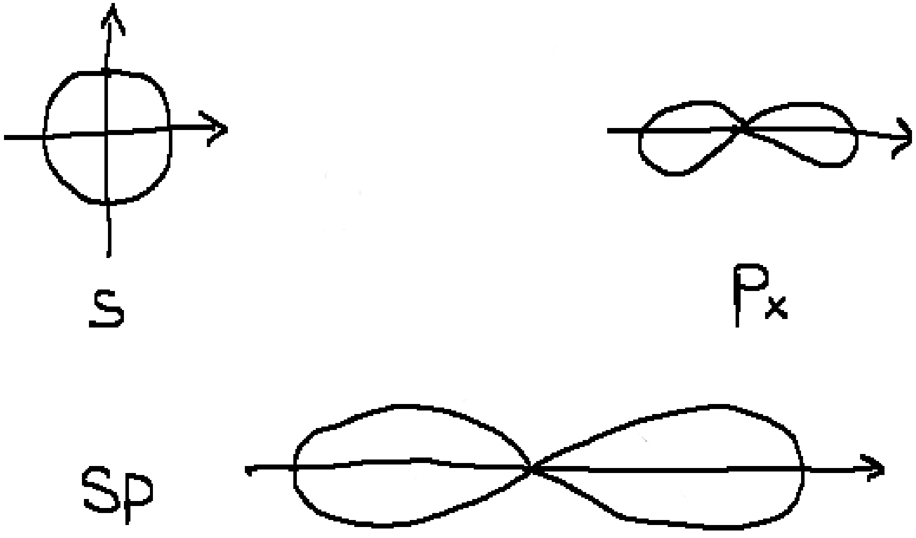
The electron configuration of BH_3



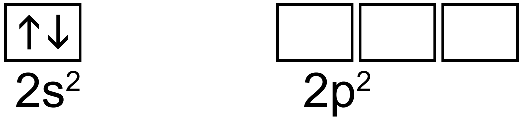
Example

sp hybridization of Be in BeH_2

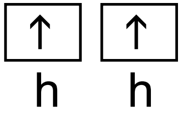




The electron configuration of a beryllium atom before hybridization

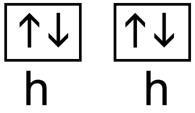


The electron configuration of a beryllium atom after sp hybridization



Each hybrid orbital contains one unpaired electron, which is ready to make a covalent bond with hydrogen atoms. The are two hydrogen atoms and each of them provides one electron

The electron configuration of BeH_2

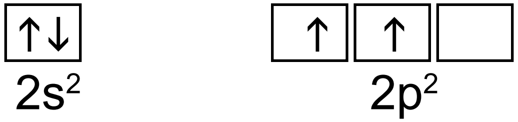


Hybridization with double and triple bonds

Ethylene molecule

Let us consider an ethylene molecule. Each carbon atom participates in three bonds (two bonds with hydrogens and one bond with another carbon). Therefore each carbon atom should undergo sp^2 hybridization, forming three hybrid orbitals

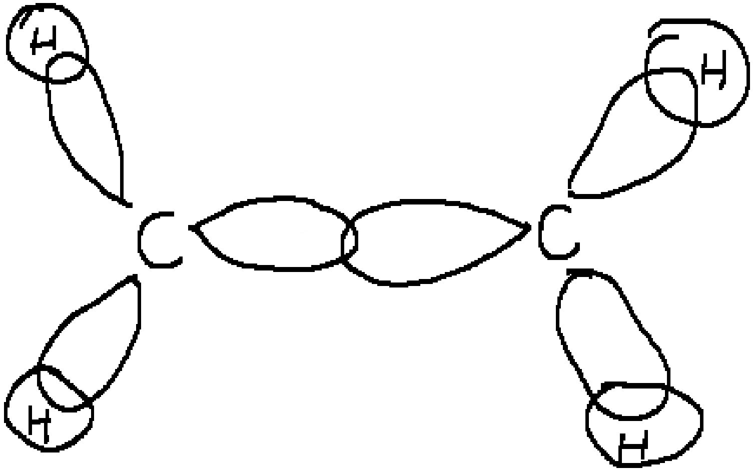
The electron configuration of a carbon atom before hybridization



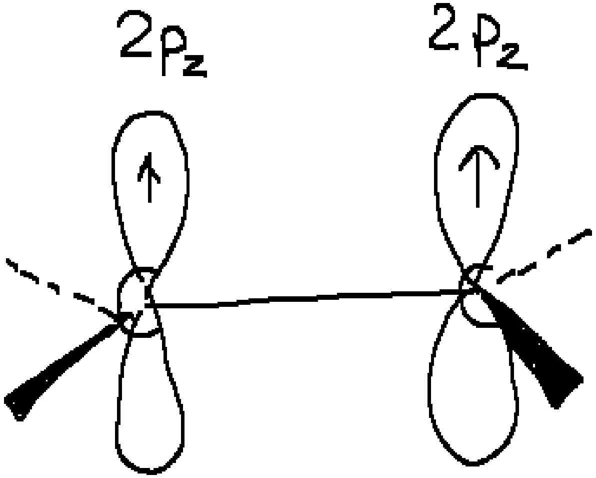
The electron configuration of a carbon atom after sp^2 hybridization

Three hybrid orbitals participate in covalent bonds, however there is one unpaired electron on an atomic orbital $2p_z$. This electron forms a different type of a covalent bond with an electron on the atomic orbital $2p_z$ of another carbon atom

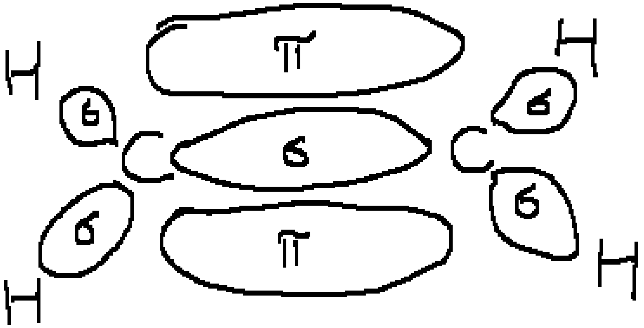
Two carbon atoms forming bonds based on sp^2 hybridization



Two $2p_z$ atomic orbitals of carbons forming a new covalent bond



The final structure of orbitals in ethylene molecule



A bond between carbon atoms from sp^2 hybrid orbitals is called a σ bond

The σ bond

A bond having a maximum of an electron cloud (electron density) on a line between atoms

A bond between carbon atom from $2p_z$ atomic orbitals is called a π bond

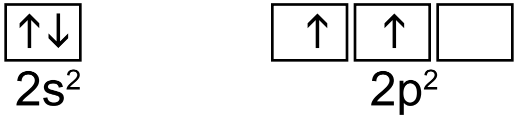
The π bond

A bond having a minimum of an electron cloud (electron density) on a line between atoms

Acetylene molecule

Let us consider an acetylene molecule. Each carbon atom participates in two bonds (one bond with a hydrogen and one bond with another carbon). Therefore each carbon atom should undergo sp hybridization, forming two hybrid orbitals

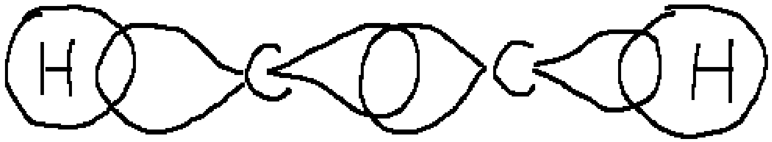
The electron configuration of a carbon atom before hybridization



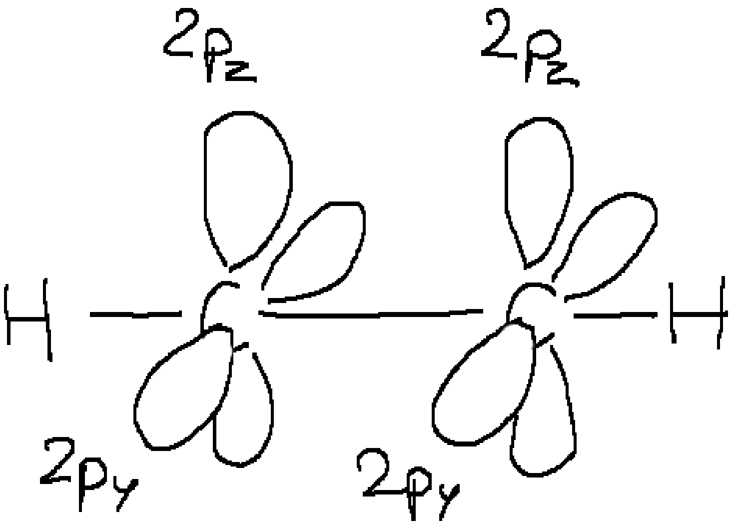
The electron configuration of a carbon atom after sp hybridization

Two hybrid orbitals participate in covalent bonds, however there are two unpaired electrons on an atomic orbitals $2p_z$, $2p_x$.These electron form a different type of a covalent bond with electrons on the atomic orbital $2p_z$ and $2p_x$ of another carbon atom

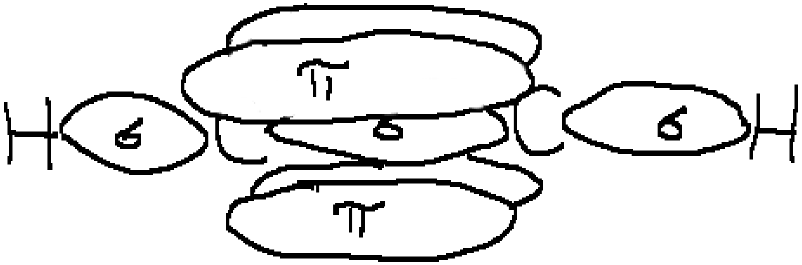
Two carbon atoms forming bonds based on sp hybridization



Two pairs of 2p atomic orbitals of carbons forming two new covalent bonds



The final structure of orbitals in acetylene molecule



Molecular orbitals

A mixture of atomic orbitals (or hybrids) which describes covalent bondings in molecules

From molecular orbital theory two atomic orbitals form two molecular orbitals, one of them is bonding and another is anibonding

Bonding molecular orbital

An orbital which has lower energy and grater stability than atomic orbitals from which it was formed

Antibonding molecular orbital

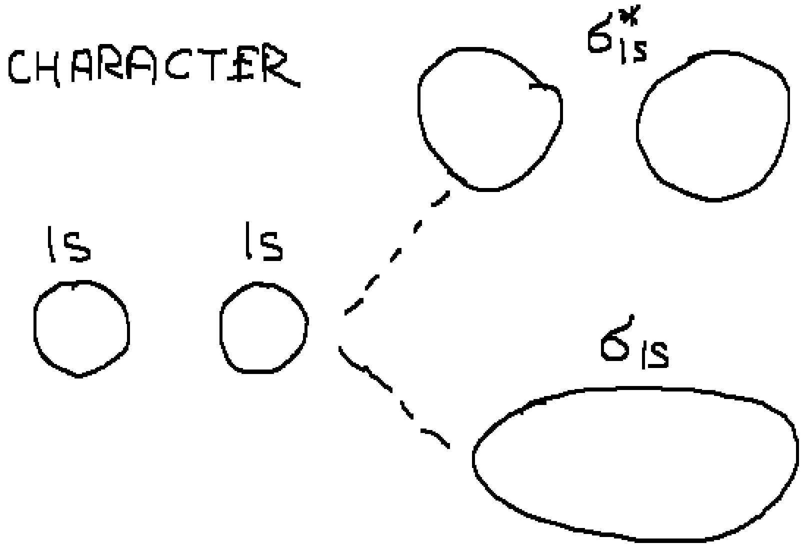
An orbital which has higher energy and lower stability than atomic orbitals from which it was formed

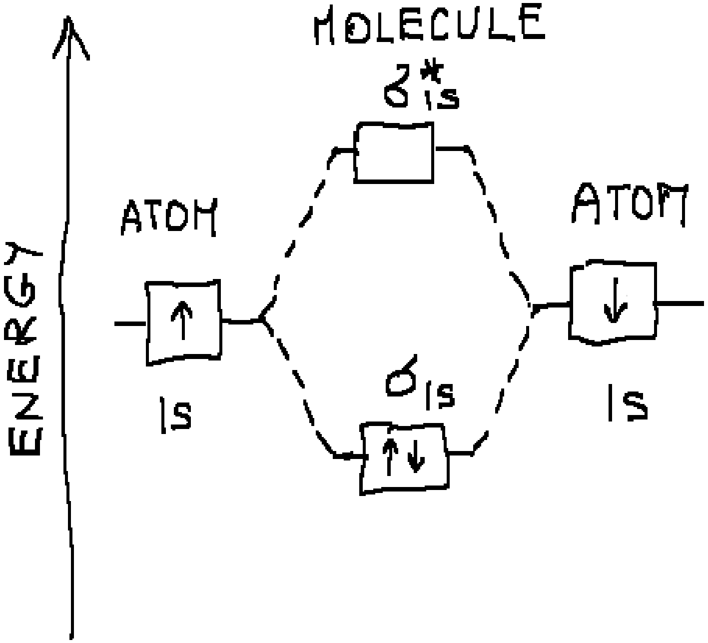
The σ molecular orbital

A molecular orbital describing a covalent bond with a maximum of an electron cloud (electron density) on a line between atoms

Example

σ_{1s}	bonding molecular orbital formed from 1s atomic orbitals
σ^*_{1s}	antibonding molecular orbital formed from 1s atomic orbitals



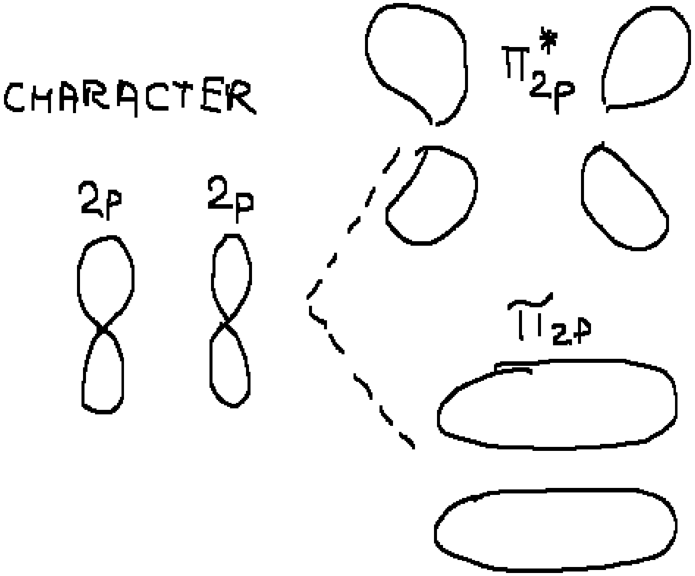


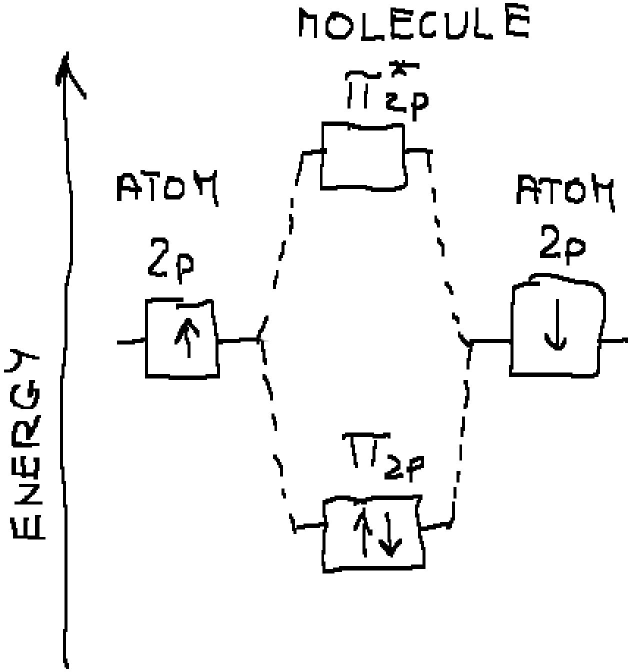
The π molecular orbital

A molecular orbital describing a covalent bond with a minimum of an electron cloud (electron density) on a line between atoms

Example

π_{2p}	bonding molecular orbital formed from 2p atomic orbitals
π^{*}_{2p}	antibonding molecular orbital formed from 2p atomic orbitals





Molecular orbital configuration

An arrangement of electrons on molecular orbitals

Rules of molecular electron configuration and stability

1. The number of molecular orbitals is always equal to the number of atomic orbitals (hybrids)

2. A bonding molecular orbital corresponds to a stabile bond, an antibonding orbital corresponds to an unstabile bond

3. Molecular orbitals are filled out by electrons starting from the orbital of the lowest energy

4. Each molecular orbital can be occupied by two electrons with opposite spins

5. When two orbitals have the same energy, they are occupied by electrons with the same spin first, and next with the opposite spin

6. The number of electrons in molecular orbitals must be the same as the sum of atomic electrons

Hydrogen and helium molecules

Bond order

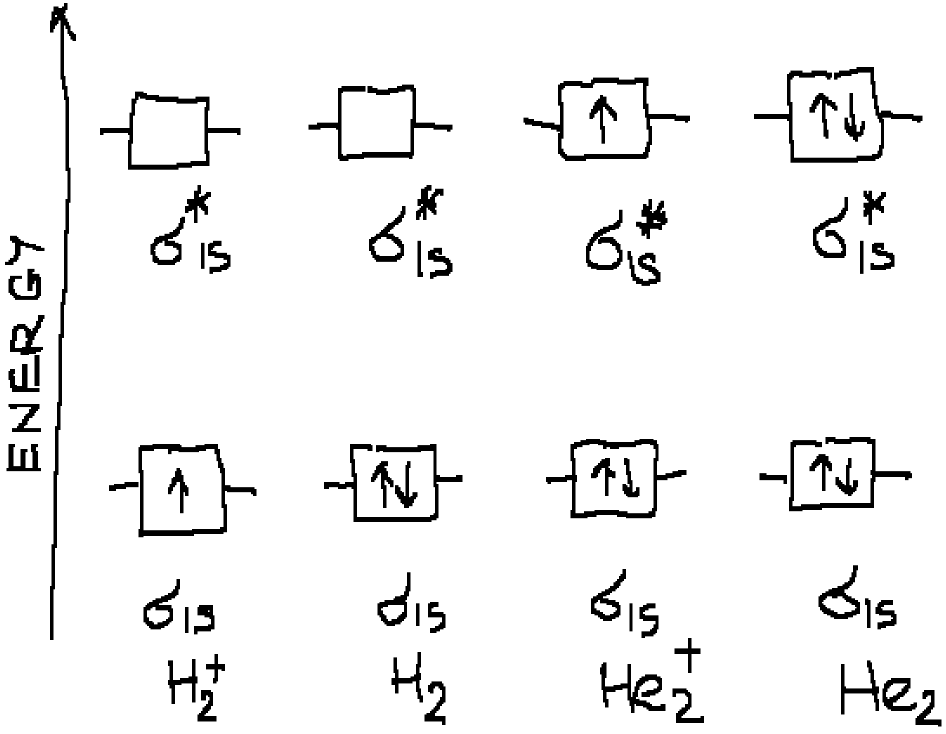
= 1/2 (electrons on bonding MOs - electrons on antionding MOs)

Bond order of H_2^+ is 1/2

Bond order of H_2 is 1

Bond order of He_2^+ is 1/2

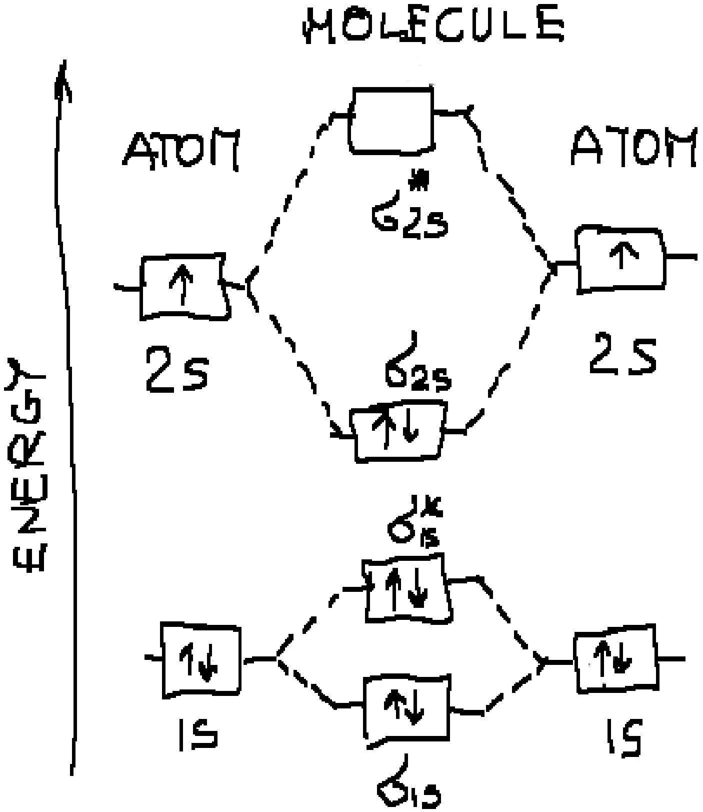
Bond order of H_2 is 0



Homonuclear diatomic molecules

Example

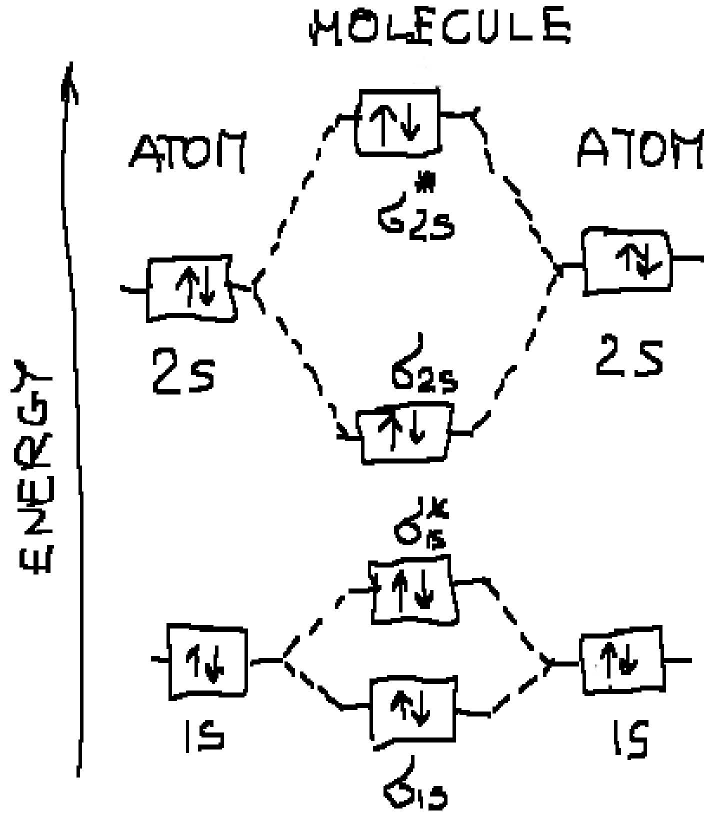
Li_2 molecule

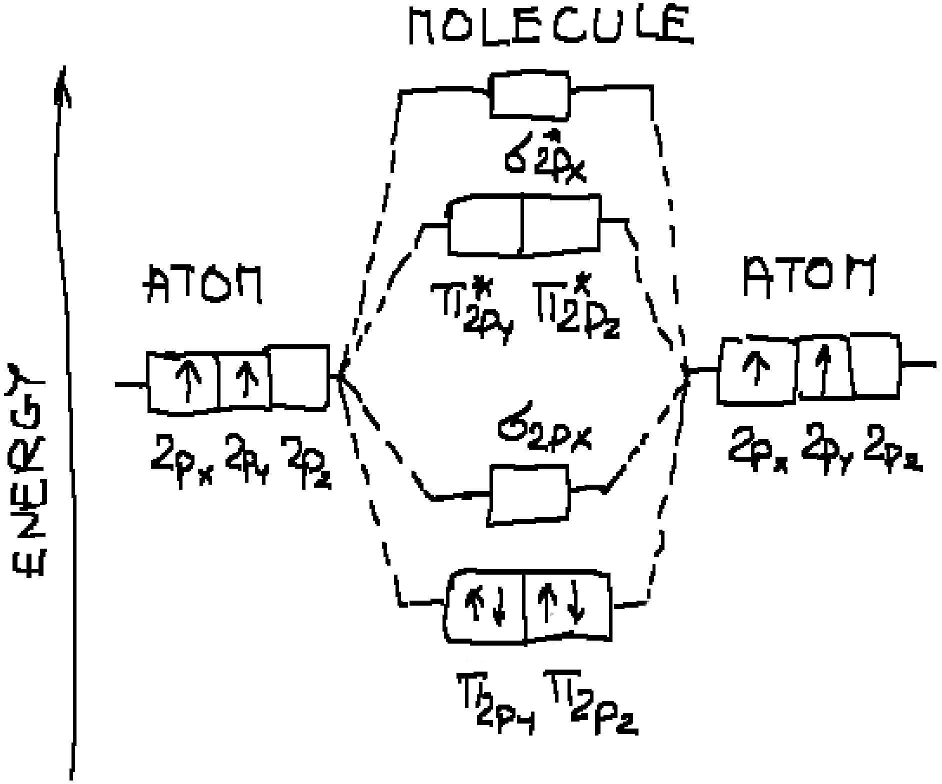


$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi_{2py} = \pi_{2pz} < \sigma_{2px} < \pi_{2py} = \pi_{2pz} < \sigma_{2px}^*$$

Example

C_2 molecule

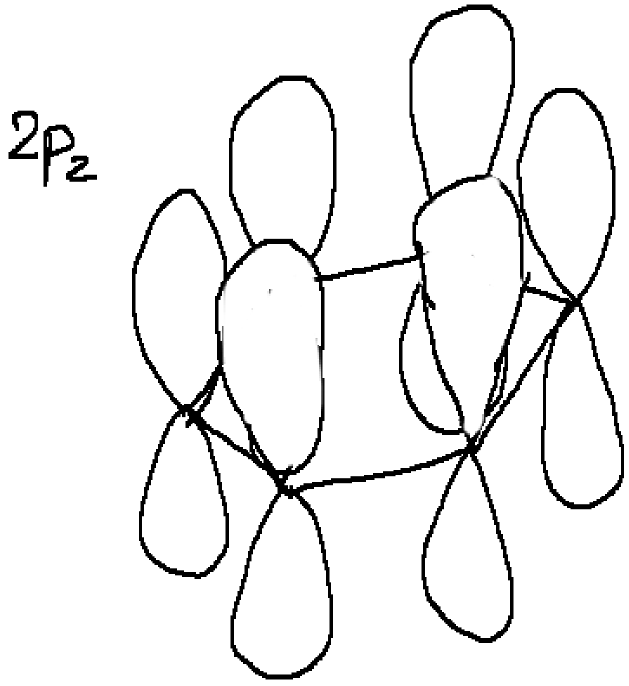


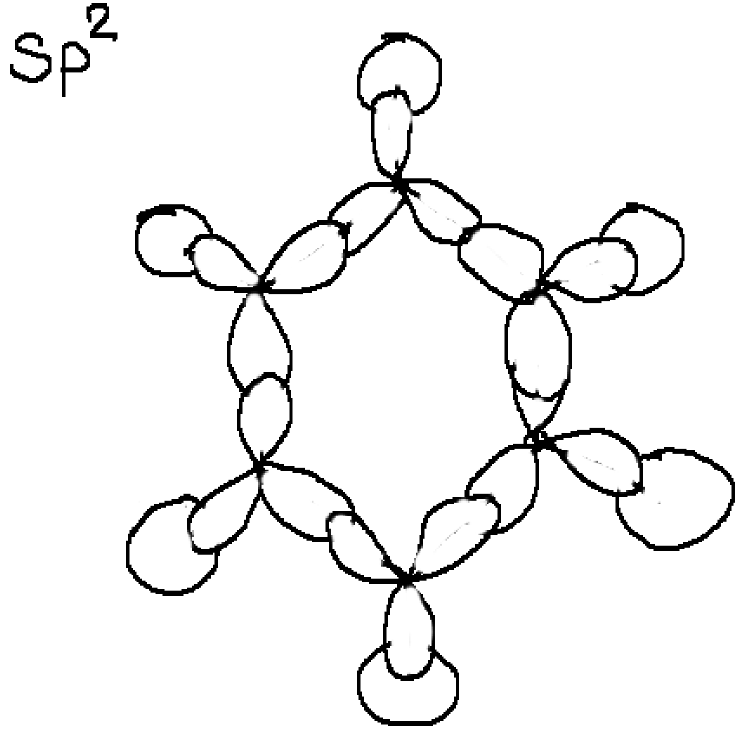


Delocalized molecular orbitals

Example

Benzene (C_6H_6)





Each carbon atom forms sp^2 hybrids from one s and two p atomic orbitals. Those hybrid orbitals form σ molecular orbitals in benzene. The remaining $2p_z$ orbitals from all carbon atoms form delocalized π molecular orbitals

Organic chemistry

A branch of chemistry that deals with carbon compounds

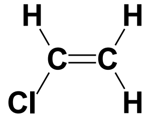
Tremendous variety of organic molecular structures and properties are possible

Functional group

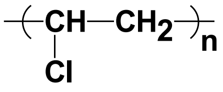
A group of atoms that is largely responsible for the chemical properties of the parent molecule

Hydrocarbons

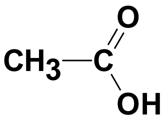
Molecules made up of only carbon and hydrogen atoms



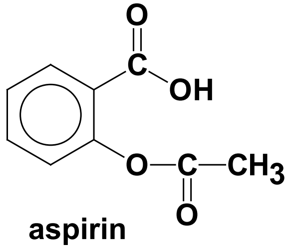
vinyl chloride



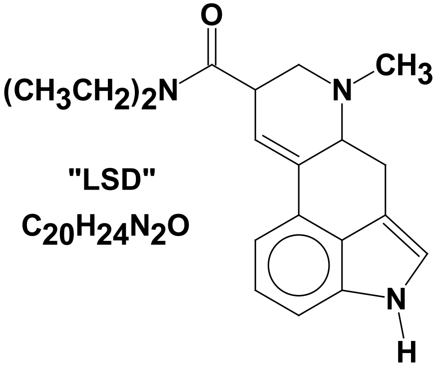
poly(vinyl chloride)
"PVC"



acetic acid

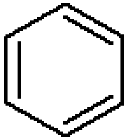
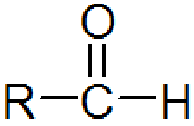
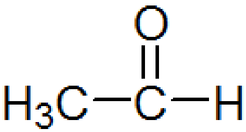
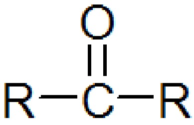
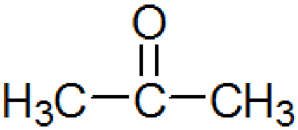


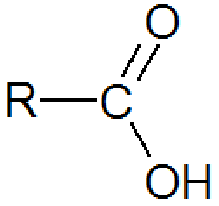
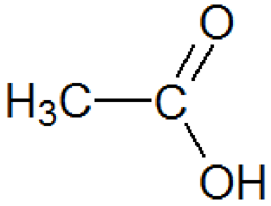
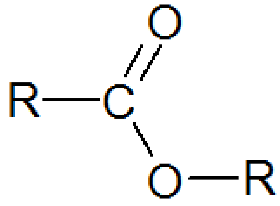
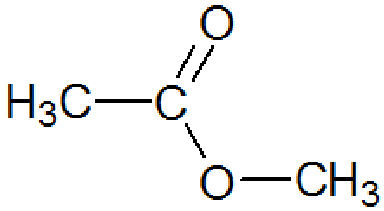
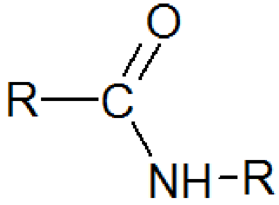
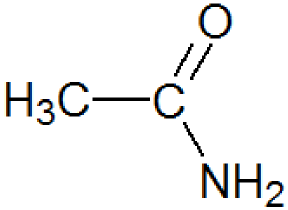
aspirin
(acetylsalicyclic acid)



"LSD"
$C_{20}H_{24}N_2O$

$(CH_3CH_2)_2N-H$
diethyl amine

Family	**Characteristic Structural Feature**	**Examples**
Hydrocarbons		
• Alkanes	C -C	CH_3CH_3
• Alkenes	C=C	$CH_2=CH_2$
• Alkynes	C≡C	CH≡CH
• Aromatic	Benzene ring	
Alcohols	R-OH	CH_3CH_2-OH
Ethers	R-O-R’	CH_3-O-CH_3
Aldehydes	 $R-\overset{\overset{O}{\parallel}}{C}-H$	 $H_3C-\overset{\overset{O}{\parallel}}{C}-H$
Ketons	 $R-\overset{\overset{O}{\parallel}}{C}-R$	 $H_3C-\overset{\overset{O}{\parallel}}{C}-CH_3$

Family	**Characteristic Structural Feature**	**Examples**
Carboxylic acids		
Esters		
Amines (1°)	R-NH_2	CH_3-NH_2
Amines (2°)	R-NHR’	$(CH_3)_2NH$
Amines (3°)	R-NR’R”	$(CH_3)_3N$
Amides		

Alkanes

Known also as saturated hydrocarbons. Hydrocarbons in which only a single covalent bond (C-C) is present

$$C_nH_{2n+2}$$

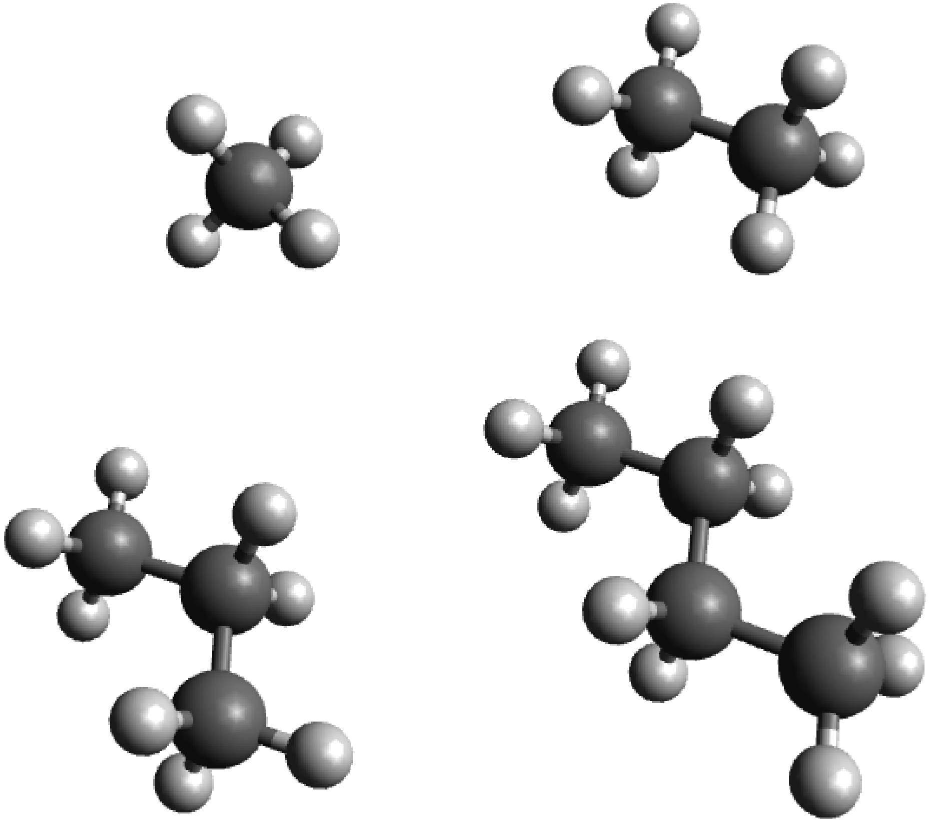
The simplest alkan is methane where carbon atoms have sp^3 hybridization. The bond angles are 109.5, therefore for this hybridization the carbon bonds are in tetrahedral geometry

CH_4	methane	C_6H_{14}	hexane
C_2H_6	ethane	C_7H_{16}	heptane
C_3H_8	propane	C_8H_{18}	octane
C_4H_{10}	butane	C_9H_{20}	nonane
C_5H_{12}	pentane	$C_{10}H_{22}$	decane, etc......

Properties of alkanes

All carbon atoms are in its sp^3 hybridization forming only σ bonds with other carbons atoms and hydrogen atoms

There is an almost free rotation around C - C σ bond



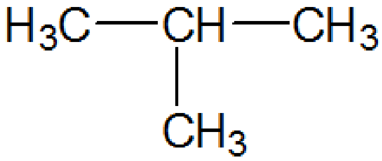
Structural isomers

The same chemical formula, but different arrangement (connectivity) of atoms

Example

n-butane $H_3C-CH_2-CH_2-CH_3$

iso-butane



$$\begin{array}{c}H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3\end{array}$$

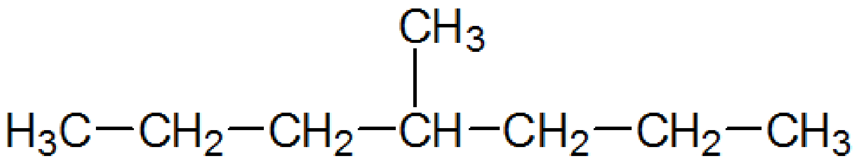
Number of possible isomers can be very large, e.g.:

C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_8H_{18}	$C_{10}H_{22}$	$C_{20}H_{42}$
1	2	3	5	18	75	> 105

Nomenclature of alkanes

The nomenclature is based on the Union of Pure and Applied Chemistry (UPAC) rules

1. The parent name of the hydrocarbon is that given to the longest continuous chain of carbon atoms



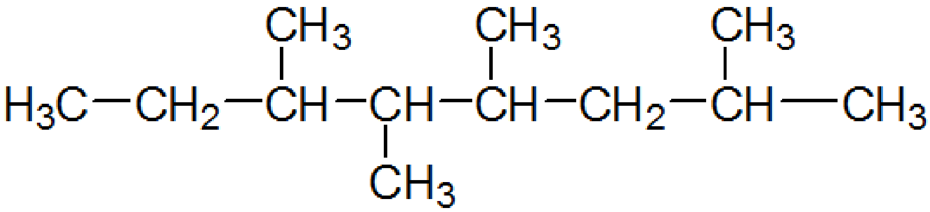
$$H_3C-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2-CH_2-CH_3$$

2. An alkane which has less on hydrogen is an alkyl group

Methyl	CH_3-
Ethyl	CH_3-CH_2-
n-Propyl	CH_3-CH_2-CH_2-
Phenyl	C_6H_5-

3. When one hydrogen is repalced by other group the name indicates the location of the group in the chain and the name of the group

4. When there is more than one alkyl branch, we use prefix *di-, tri-, tetra-*

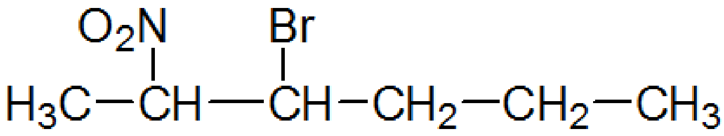


$$H_3C-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_3$$

2,4,5,6-tetramethyloctane

5. When there is another group, the name indicates the location of the group in the chain and the name of the group

Amino	NH_2-
Fluoro	F-
Chloro	Cl-
Bromo	Br-
Iodo	I-
Nitro	NO_2-



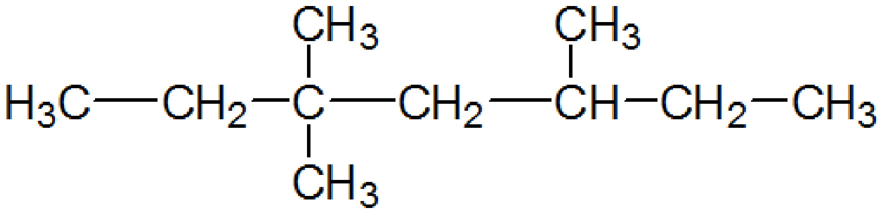
$$H_3C-\overset{\overset{\displaystyle O_2N}{|}}{C}H-\overset{\overset{\displaystyle Br}{|}}{C}H-CH_2-CH_2-CH_3$$

3-bromo-2-nitrohexane

The substituents are listed alphabetically in the name

Problem

Give the name of the following compound



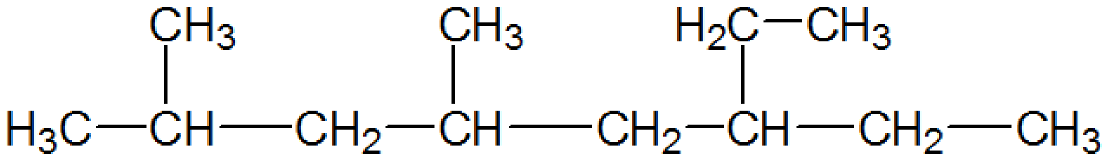
$$H_3C-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2-CH_3$$

The longest chain has 7 carbons in one chain (heptane), two methyl groups at position 3 and one methyl group at position 5

Therefore the name is: 3,3,5-trimethylheptane

Problem

Give the name of the following compound



$$H_3C-CH(CH_3)-CH_2-CH(CH_3)-CH_2-CH(CH_2-CH_3)-CH_2-CH_3$$

The longest chain has 8 carbons in one chain (octane), two methyl groups at positions 2 and 4, and one ethyl group at position 6

Therefore the name is: 2,4-dimethyl-6-ethyloctane

Reactions of alkanes

Alkanes are generally not very reactive. Methane reacts with oxygen

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) \qquad \Delta H^0 = -890 \text{ kJ/mol}$$

This reaction is a combustion reaction of methane, and it generates a relatively big amount of heat. Methane is the main compound of a natural gas used in industry and in domestic heating and cooking

Halogenation reaction

The replacement of one or more hydrogen atoms by halogen atoms

$$CH_4\,(g) + Cl_2\,(g) \rightarrow CH_3Cl\,(g) + HCl\,(g)$$

The reaction can proceed further

$$CH_3Cl\,(g) + Cl_2\,(g) \rightarrow CH_2Cl_2\,(g) + HCl\,(g)$$

$$CH_2Cl_2\,(g) + Cl_2\,(g) \rightarrow CHCl_3\,(g) + HCl\,(g)$$

$CHCl_3\,(g) + Cl_2\,(g) \rightarrow CCl_4\,(g) + HCl\,(g)$

The reaction starts forming radicals

$Cl_2\,(g) + \text{energy} \rightarrow {}^{\cdot}Cl\,(g) + {}^{\cdot}Cl\,(g)$

Each radical has one unpaired electron and is very reactive

$CH_4\,(g) + {}^{\cdot}Cl\,(g) \rightarrow {}^{\cdot}CH_3\,(g) + HCl\,(g)$

${}^{\cdot}CH_3\,(g) + Cl_2\,(g) \rightarrow CH_3Cl\,(g) + {}^{\cdot}Cl\,(g)$

However there are “side reactions”, which stop this process

${}^{\cdot}Cl\,(g) + {}^{\cdot}Cl\,(g) \rightarrow Cl_2\,(g)$

${}^{\cdot}CH_3\,(g) + {}^{\cdot}CH_3\,(g) \rightarrow C_2H_6\,(g)$

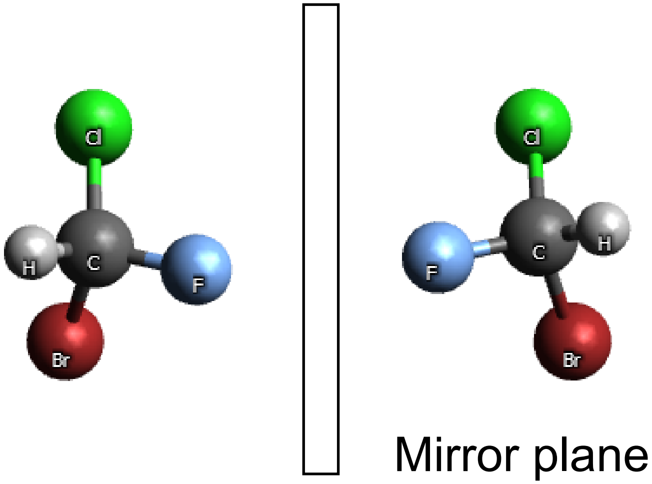
Optical isomers

Compouns that are nonsuperimposable mirror images of each other

Chiral molecules contain at least one asymmetric carbon atom

Asymmetric atom

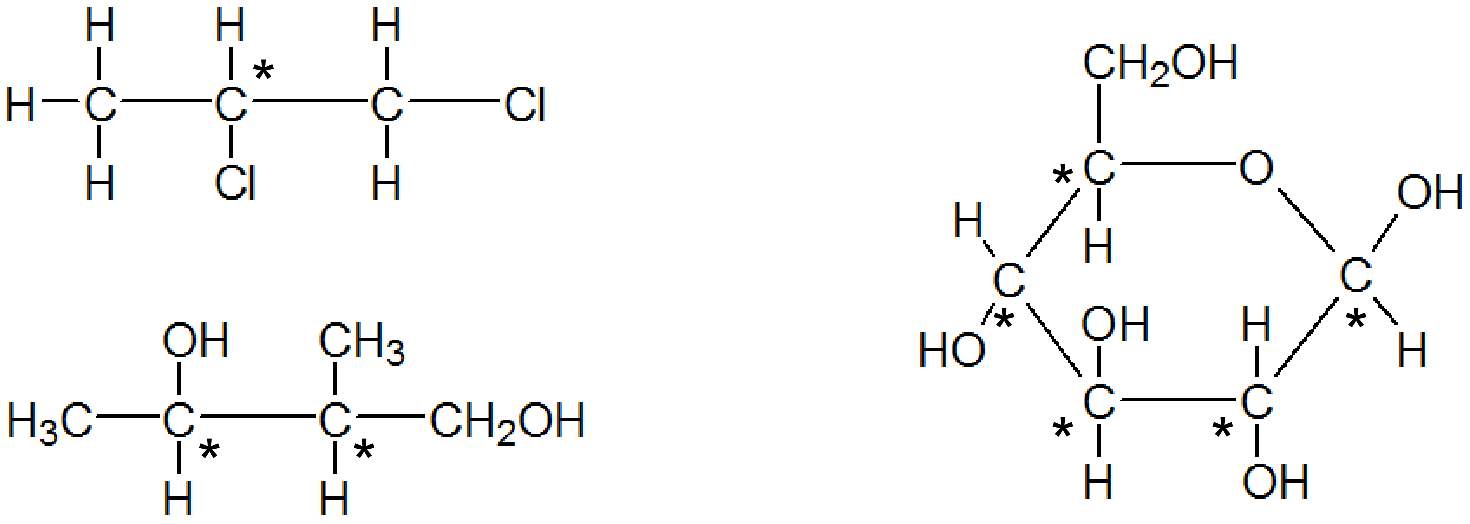
Atom bonded to four different groups



Chiral isomers turn light in the opposite directions

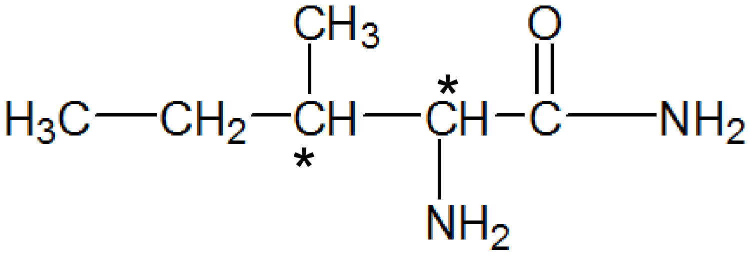
Problem

How many asymmetric carbons are present in each of the following compounds

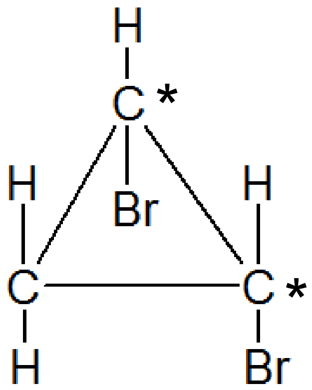


Problem

Indicate the asymmetric carbon atoms in the following compounds



$H_3C-CH_2-\underset{*}{C}H(CH_3)-\overset{*}{C}H(NH_2)-C(=O)-NH_2$

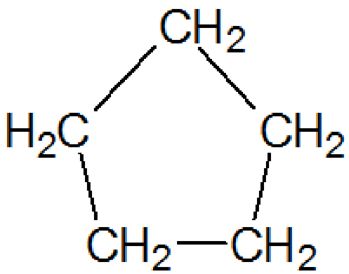
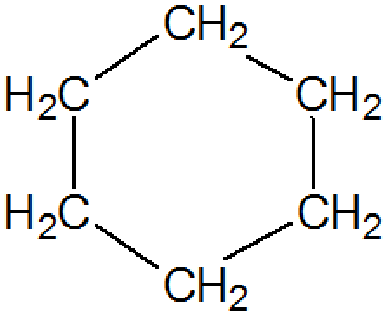


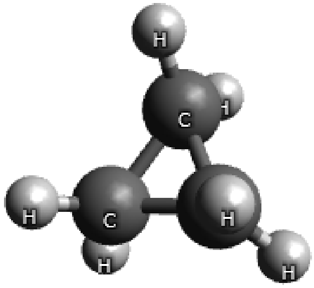
Cyclic alkanes

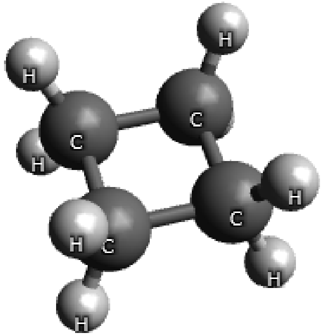
Alkanes whose carbon atoms are joined in rings

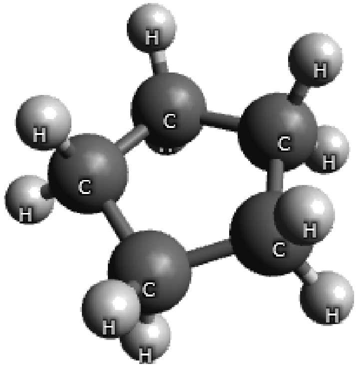
In cyclic alkanes there is a strain between bonds forming a cyclic structure

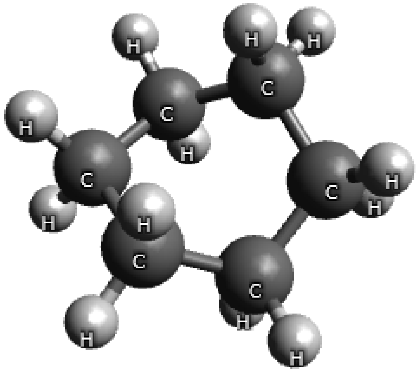
This strain becoms smaller as the size of the ring increases

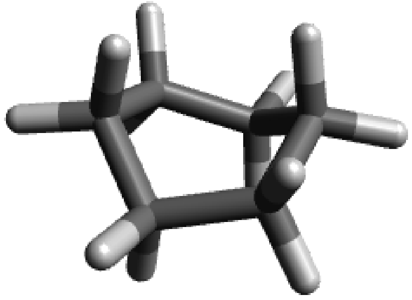

cyclopropan


cyclobutan

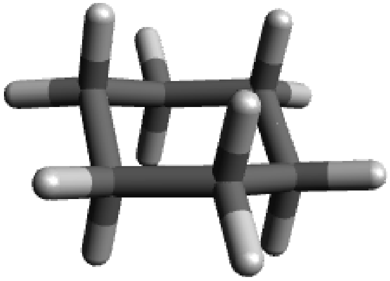

cyclopropan


cyclohexan

Cyclohexane conformers



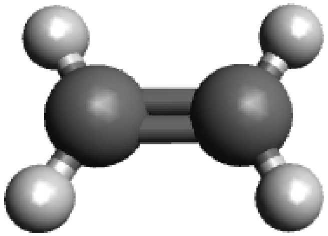
Boat form



Chair form

The chair conformation is more stable because there are bigger distances between hydrogen atoms than in the boat conformation. The repulsive interaction between hydrogen atoms changes the boat conformation into the chair conformation

Alkenes



Hydrocarbons involving at least one double bond (C=C), which are also known as unsaturated hydrocarbons

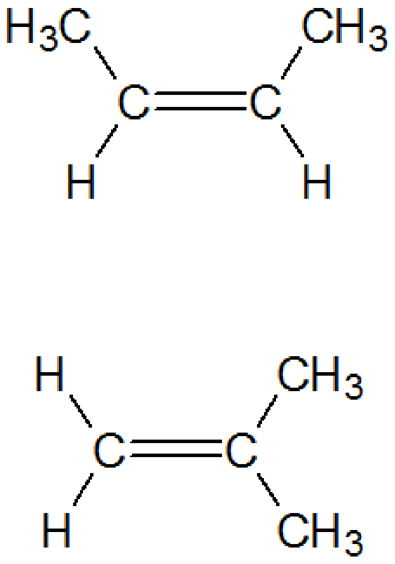
$$C_nH_{2n}$$

The simplest alken is ethene (ethylene) where carbon atoms have sp^2 hybridization. The bond angles are close to 120, therefore for this hybridization the carbon bonds are in one plane

C_2H_4	ethene	C_7H_{14}	heptene
C_3H_6	propene	C_8H_{16}	octene ...

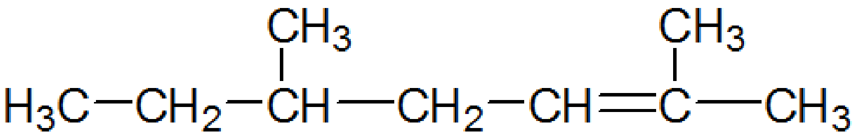
Properties of alkenes

- Restricted C=C bond rotation
- Trigonal planar geometry at C=C carbons
- sp^2 hybridization at C=C carbons
- Possible geometrical isomerization



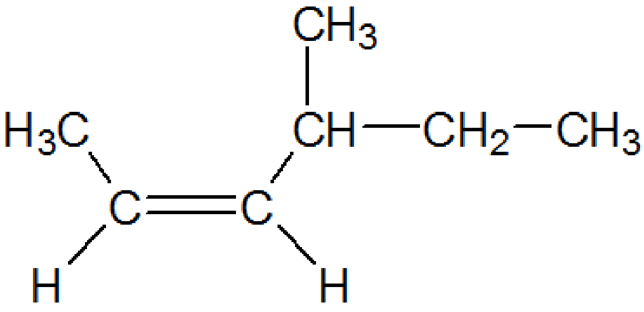
Nomenclature

The names of compounds containing a C=C bond end with *-ene*. The position of a double bond is indicated using the same rules. The double bond has the biggest priority

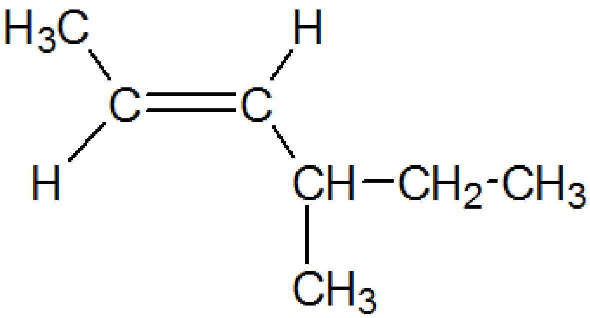


$$H_3C-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-CH=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_3$$

2,5-dimethyl-2-heptene



4-methyl-*cis*-2-hexene



4-methyl-*trans*-2-hexene

Reactions of alkenes

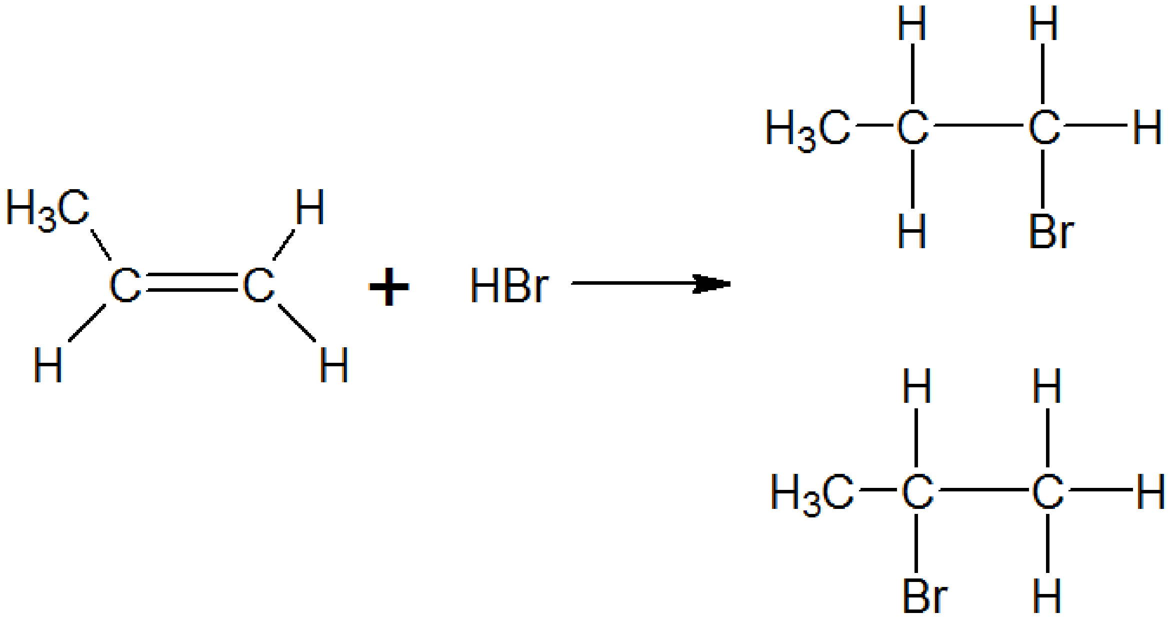
Reactivity of alkenes are related to an addition to the double bond

$$H_2C{=}CH_2 \quad + \quad HX \quad \rightarrow \quad CH_3\text{-}CH_3X$$

$$H_2C{=}CH_2 \quad + \quad X_2 \quad \rightarrow \quad CH_2X\text{-}CH_2X$$

where X = Cl, Br, I

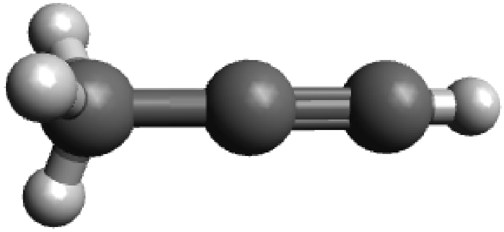
Addition of HBr



Markovnikov’s rule: H goes on the C atom that already has the most H’s

Alkynes

Hydrocarbons involving at least one triple bond (C≡C)



$$C_nH_{2n-2}$$

The simplest alkyn is acetylene where carbon atoms have sp^1 hybridization. The bond angles are close to 180, therefore for this hybridization the carbon bonds are linear

C_2H_2	acetylene	C_7H_{12}	heptyne
C_3H_4	propyne	C_8H_{14}	octyne ...

Nomenclature

The names of compounds containing a C≡C bond end with *-yne*. The position of a triple bond is indicated using the same rules. The triple bond has the biggest priority

$HC\equiv C-CH_2-CH_3$

1-butyne

$H_3C-C\equiv C-CH_3$

2-butyne

Reactions of alkynes

Reactivity of alkynes are related to an addition to the triple bond

Addition of HX to the triple bond

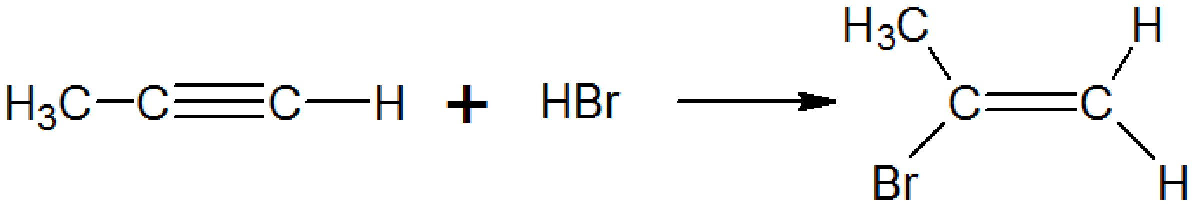
$$HC{\equiv}CH + HX \rightarrow CH_2{=}CHX$$

$$HC{\equiv}CH + X_2 \rightarrow CHX{=}CHX$$

$$HC{\equiv}CH + 2X_2 \rightarrow CHX_2\text{-}CHX_2$$

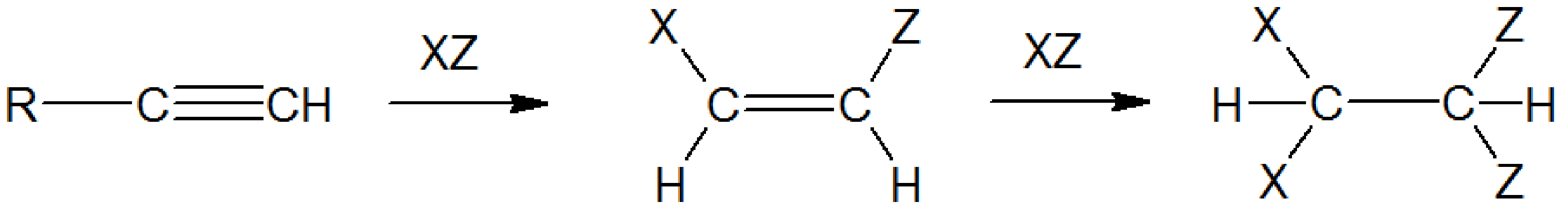
where X = Cl, Br, I

The reactions obey Markovnikov’s rule



General addition to the triple bond

$$RCH{\equiv}CH \;+\; ZX \;\rightarrow\; RZCH{=}CHZ$$



Problem

How many chloropentanes $C_5H_{11}Cl$ could be produced in chlorination of n-pentane $CH_3(CH_2)_3CH_3$. Draw the structures.

n-pentane

CH_3-CH_2-CH_2-CH_2-CH_3

All posible isomers

$ClCH_2$-CH_2-CH_2-CH_2-CH_3

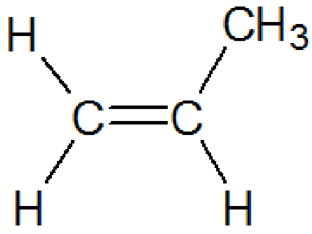
CH_3-CH-$ClCH_2$-CH_2-CH_3

CH_3-CH_2-CHCl-CH_2-CH_3

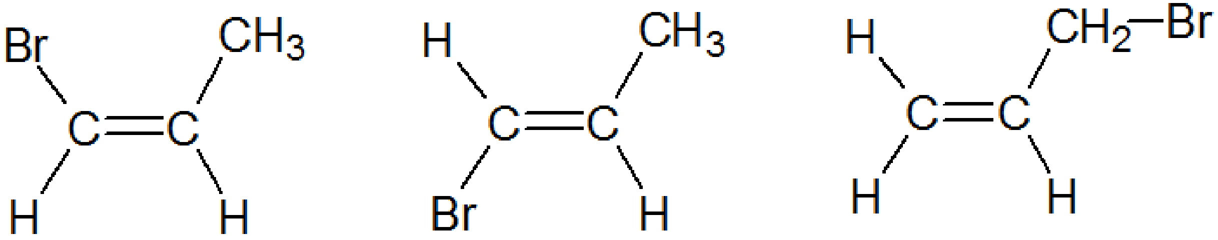
Problem

Draw all posible isomers for the noncyclic molecule C_3H_5Br

C_3H_6



C_3H_5Br

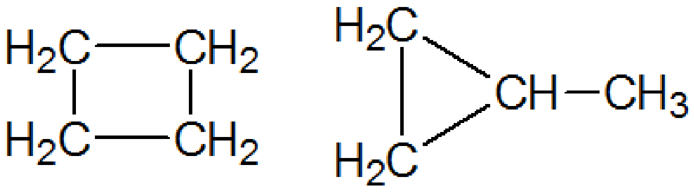


Problem

Draw all posible isomers for the molecule C_4H_8

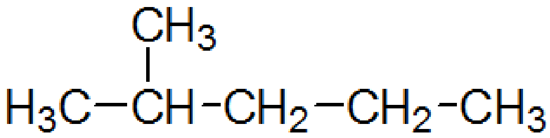
There is one linear isomer and two cyclic isomers

$H_3C-CH=CH-CH_3$



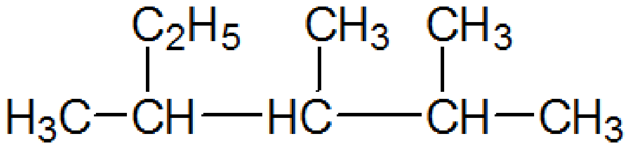
Problem

Name the following compounds



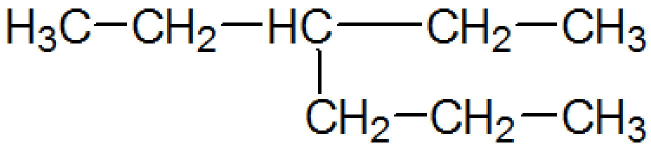
$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2-CH_2-CH_3$$

2-methylpentane



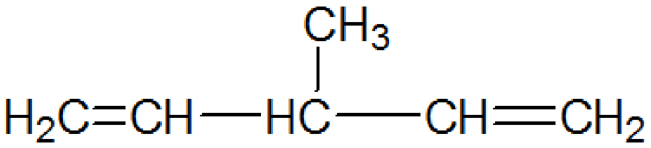
$$H_3C-\overset{\overset{\displaystyle C_2H_5}{|}}{C}H-H\overset{\overset{\displaystyle CH_3}{|}}{C}-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3$$

2,3,4-trimethylhexane



$$H_3C-CH_2-\underset{\underset{\displaystyle CH_2-CH_2-CH_3}{|}}{HC}-CH_2-CH_3$$

3-ethylhexane

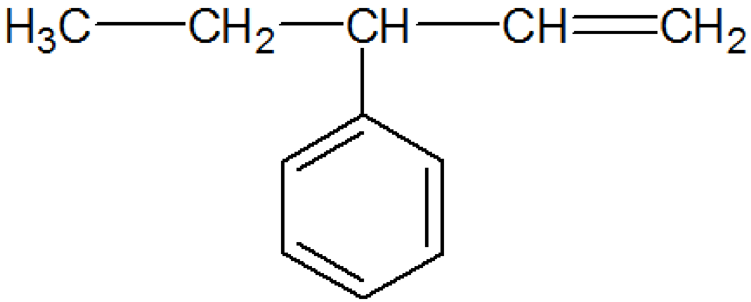


$$H_2C{=}CH{-}\overset{\displaystyle CH_3}{\overset{|}{HC}}{-}CH{=}CH_2$$

3-methyl-1,4-pentadiene

$$H_3C{-}C{\equiv}C{-}CH_2{-}CH_3$$

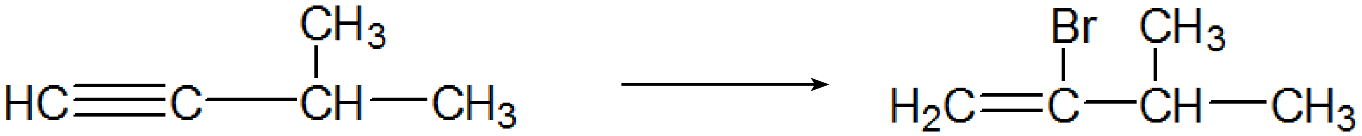
2-pentyne



3-phenyl-1-pentene

Problem

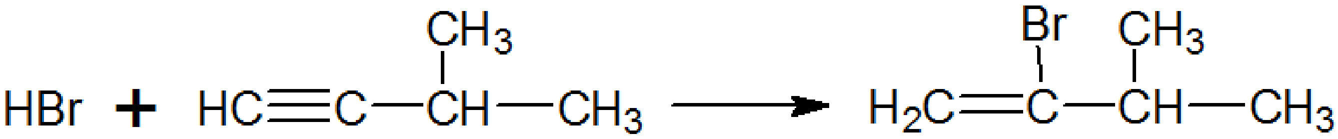
Beginning with 3-methyl-1-butyne show how you would prepare the following compounds



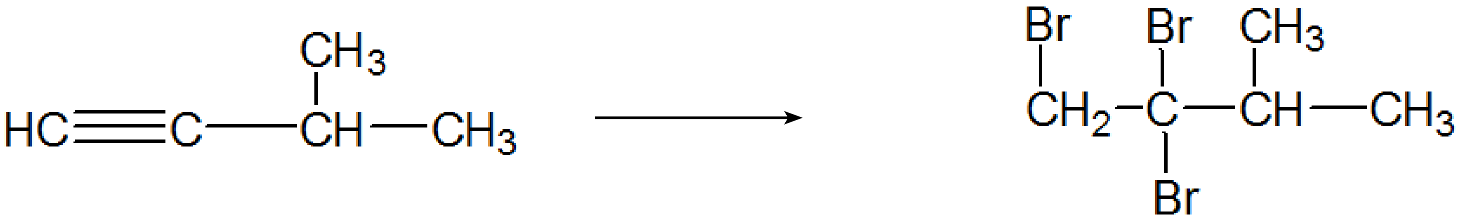
$$HC\equiv C-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3 \longrightarrow H_2C=\overset{\overset{\displaystyle Br}{|}}{C}-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3$$

3-methyl-1-butyne

2-bromo-3-methyl-1-butene

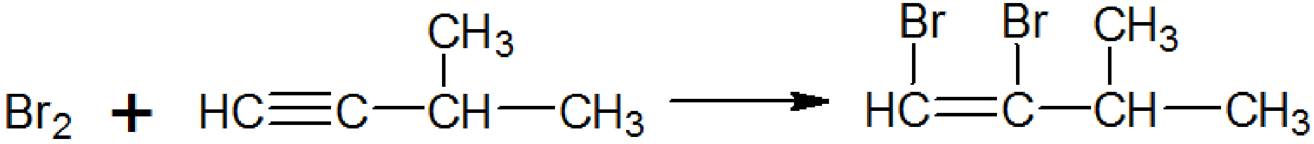


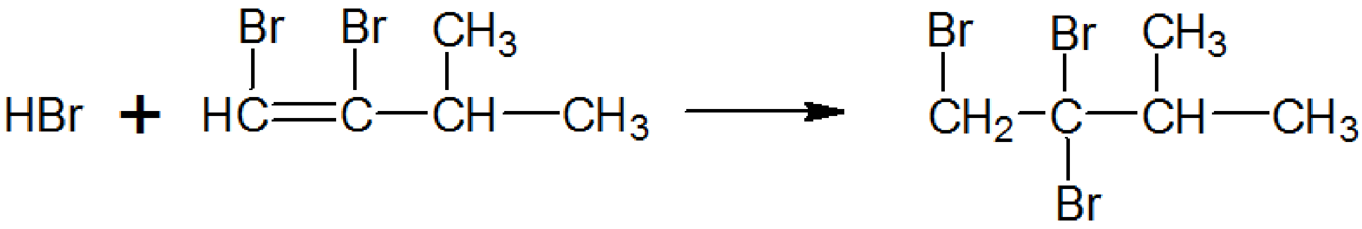
$$HBr + HC\equiv C-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3 \longrightarrow H_2C=\overset{\overset{\displaystyle Br}{|}}{C}-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3$$



3-methyl-1-butyne

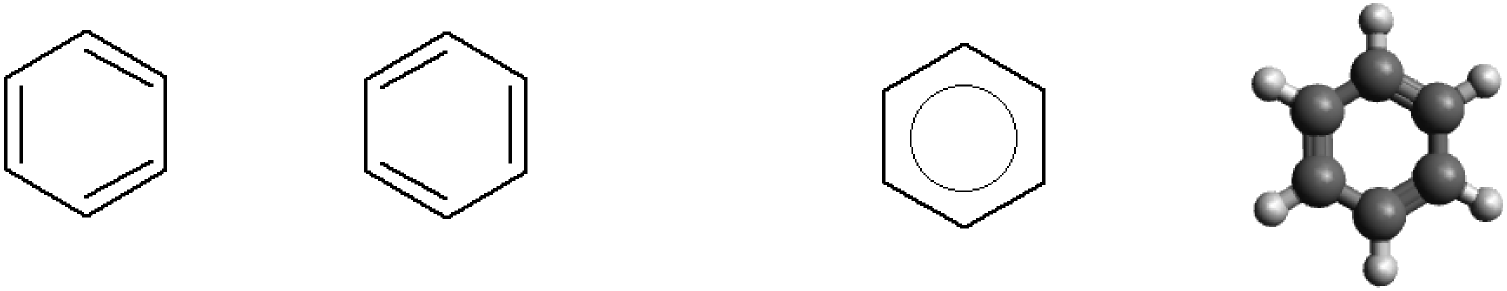
1,2,2-tribromo-3-methylbutane





Aromatic hydrocarbons

Aromatic hydrocarbons are made up of benzene and its derivatives

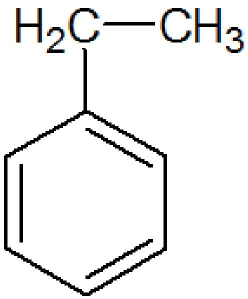


Each carbon atom of benzene has sp^2 hybridization forming σ bonds with hydrogen and other carbon atoms. $2p_z$ atomic of each carbon forms π bonds which are delocalized around the ring

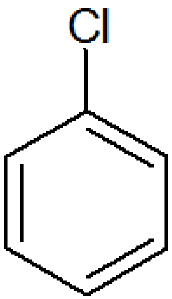
- All C-C distances equivalent
- sp^2 hybridization at all carbons
- Delocalized set of 3 double bonds (6 π electrons)

Nomenclature of aromatic compounds

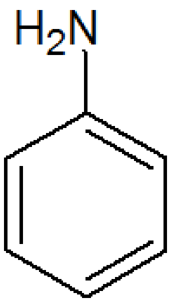
When hydrogen atom is replaced by a group, we use the following names



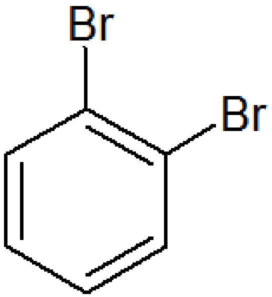
ethylbenzene



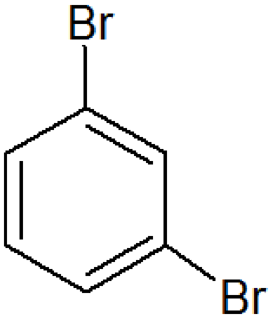
chlorobenzene



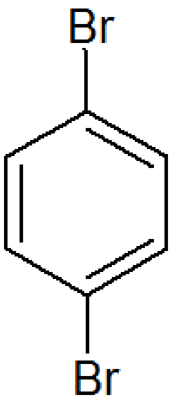
aminobenzene



o-dibromobenzene
(ortho)



m-dibromobenzene
(meta)

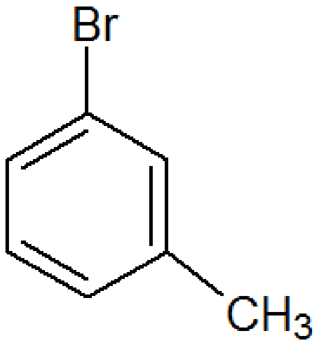


p-dibromobenzene
(para)

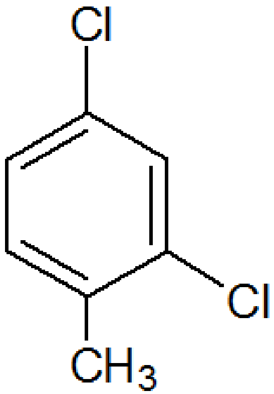
Problem

Write structures for the following compounds

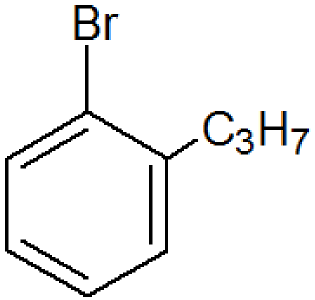
1-bromo-3-methylbenzene



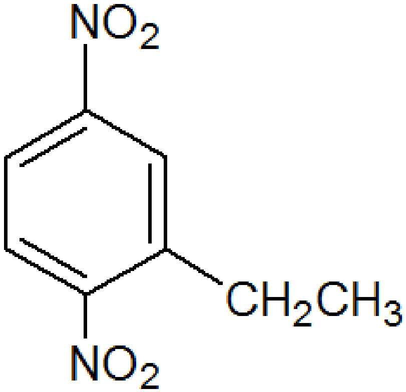
1,3-dichloro-4-methylbenzene



1-chloro-2-propylbenzene



1,4-dinitro-2-ethylbenzene

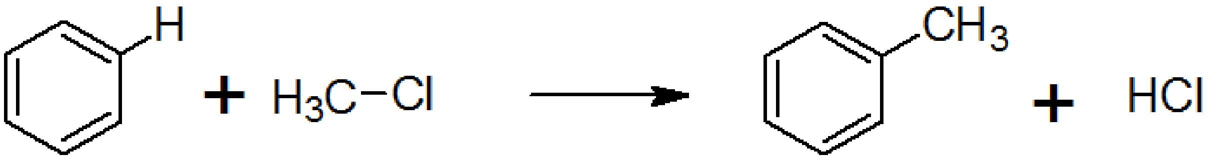


Reactions of aromatic compounds

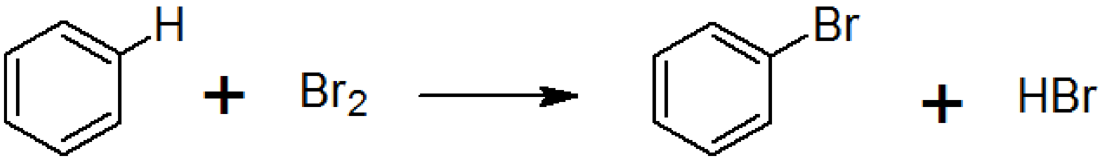
Substitution

The reaction where one atom (or a group) is replaced by another atom (or a group)

Reaction with haloalkanes



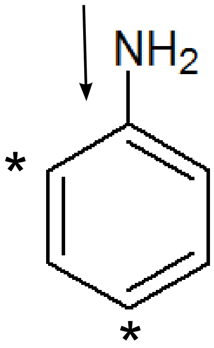
Reaction with halogens



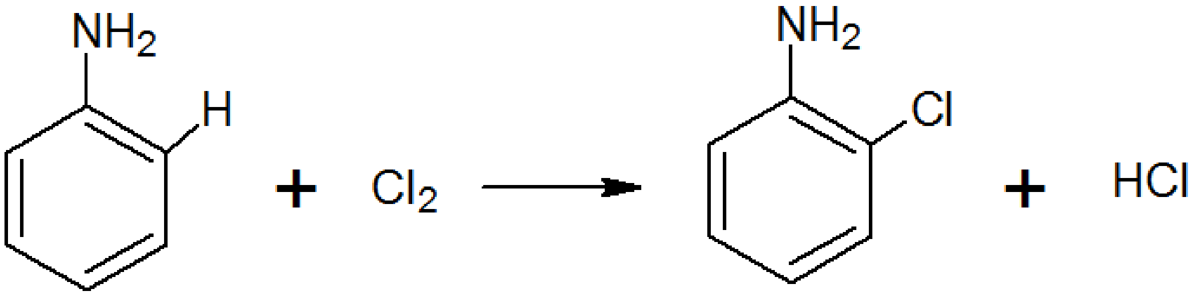
Electrophilic subtitutions in benzene

Substitution by a group which likes electrons

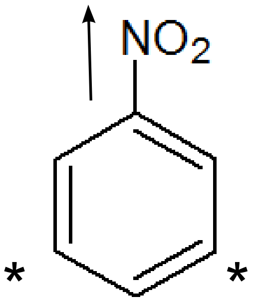
Activating functional group



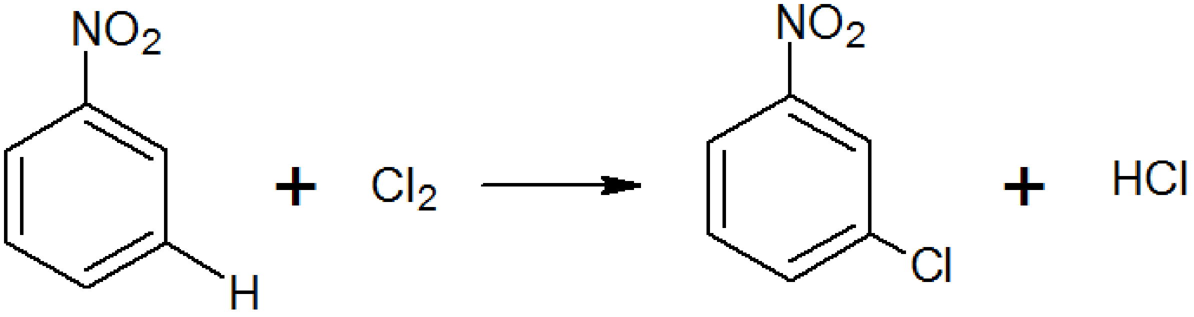
An activating functional group (-NH_2) activates positions *ortho* and *para* for electrophilic substitution, by donating electrons to the π system of benzene



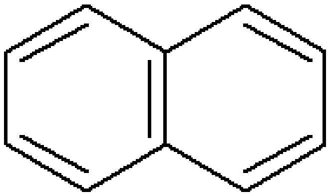
Deactivating functional group



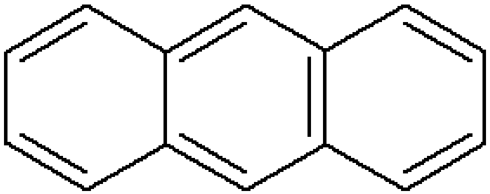
A deactivating functional group (-NO_2) deactivates positions *ortho* and *para* for electrophilic substitution, by withdrawing electrons from the π system of benzene, therefore the position *meta* is prefered



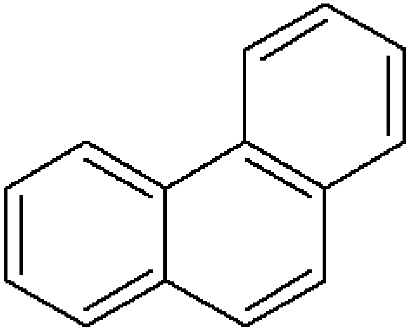
Other common aromatic hydrocarbons:



Naphtalene



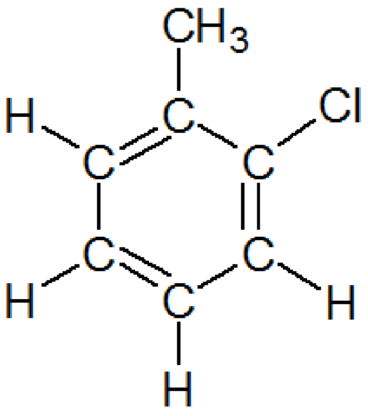
Anthracene

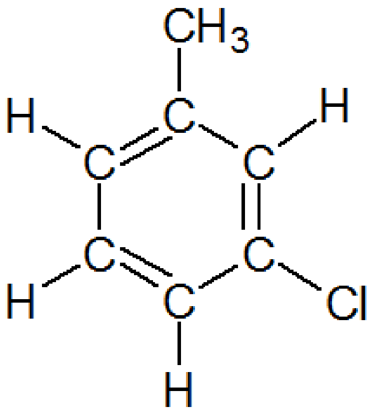


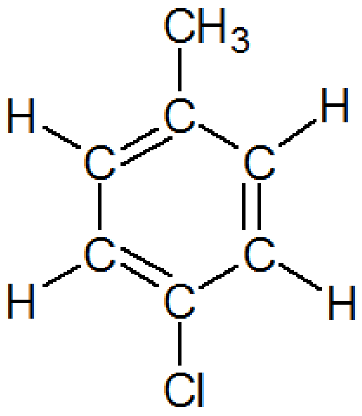
Phenanthrene

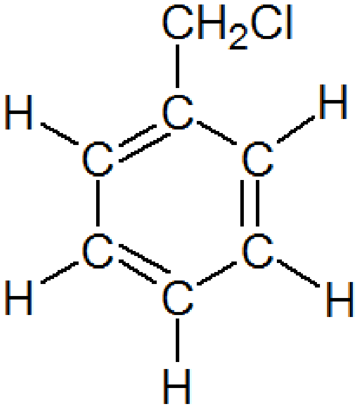
Problem

Draw all posible structural isomers for the molecule having the formula C_7H_7Cl. The molecule has one benzene ring.



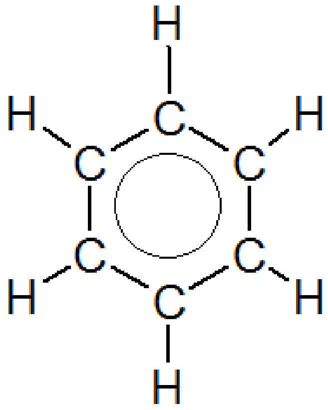




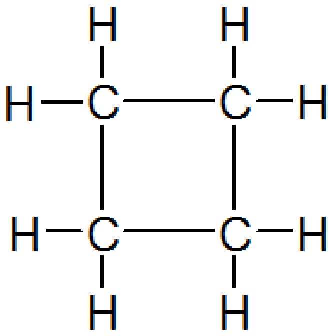


Problem

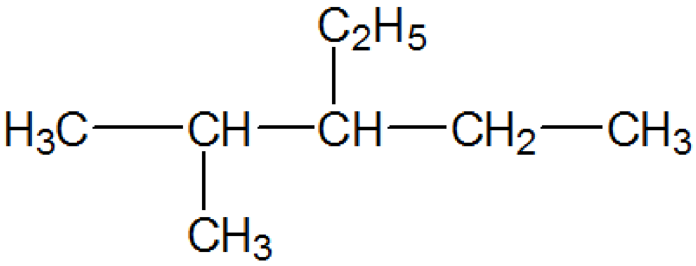
How many carbon-carbon σ bonds are present in each of the following molecules



6 σ *C-C* bonds



4 σ *C-C* bonds



$$H_3C-\underset{CH_3}{CH}-\overset{C_2H_5}{CH}-CH_2-CH_3$$

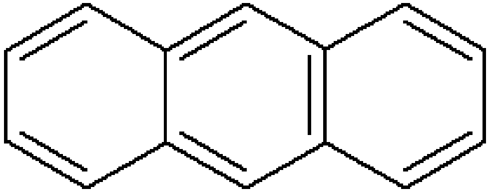
7 σ *C-C* bonds

Problem

How many carbon-carbon σ bonds are present in each of the following molecules

$H_3C—C≡C—CH_3$

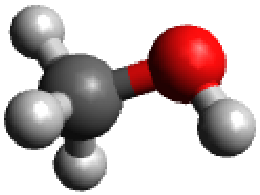
2-butyne, 3 σ *C-C* bonds



anthracene, 16 σ *C-C* bonds

Chemistry of functional groups

Alcohols



Functional group *-OH*

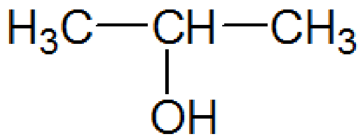
Nomenclature (*-ol*)

R-O-H

R = $-CH_3$ methanol

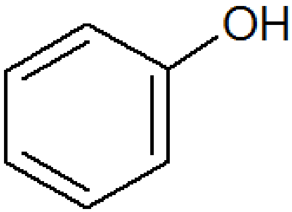
R = $-CH_3CH_2$ ethanol

R = $-CH_3CH_2CH_2$ 1-propanol (n-propanol)



$H_3C-CH(OH)-CH_3$

2-propanol

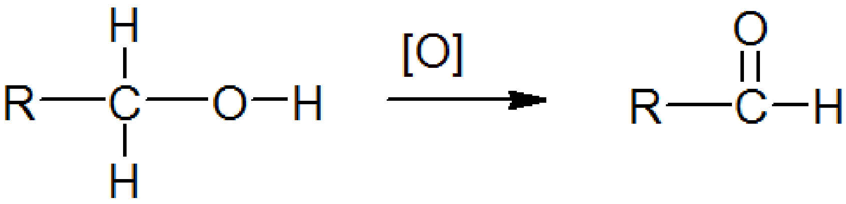


phenol

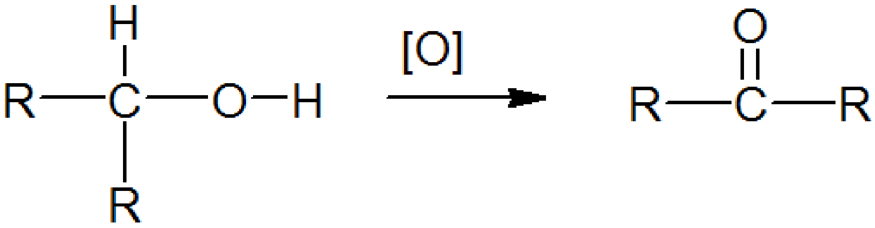
Reactions

Oxidation of alcohols

Alkohols can be oxidized by inorganic oxidizing agents ($Cr_2O_7^{2-}$)



primary alcohol aldehyde



secondary alcohol ketone

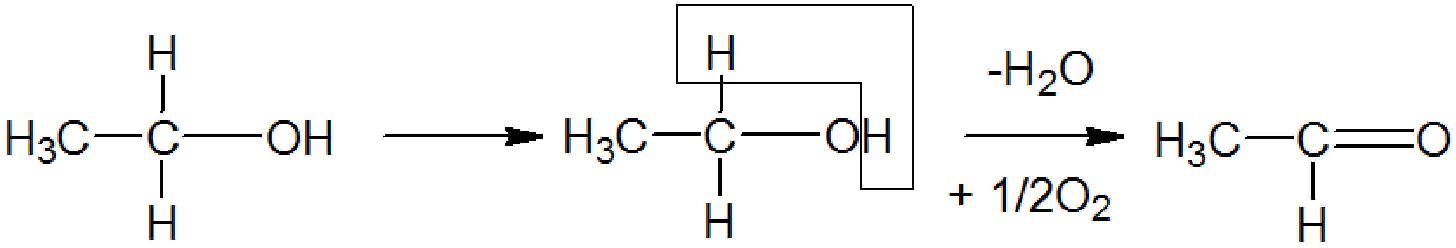
Examples

$CH_3OH + 1/2\ O_2 \rightarrow H_2C{=}O + H_2O$

aldehyde

$C_2H_5OH + 1/2\ O_2 \rightarrow CH_3HC{=}O + H_2O$

aldehyde



Reactions with Na

Alcohols are very weak acids, and they react with Na forming molecular hydrogen

$$2\ CH_3OH\ +\ 2\ Na\ \rightarrow\ 2\ CH_3ONa\ +\ H_2$$

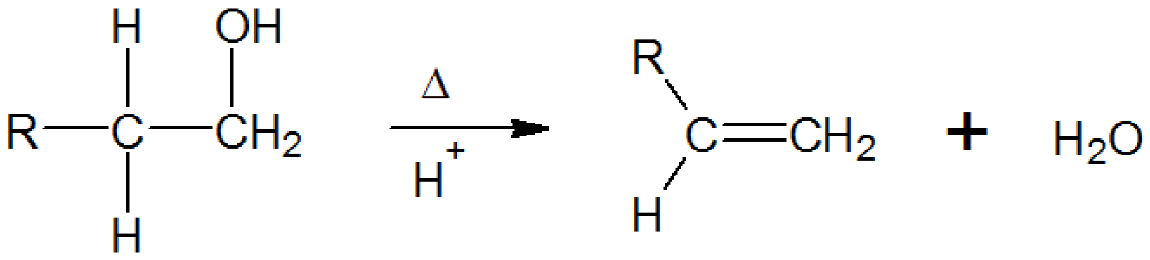
(Sodium methoxide)

However this reaction is much less violent than the reaction of Na with water

$$2\ H_2O\ +\ 2\ Na\ \rightarrow\ 2\ NaOH\ +\ H_2$$

Elimination reactions of alcohols

Removing the -OH group and one hydrogen forming H_2O



alcohol

alkene

Substitution reactions of alcohols

The -OH group is substituted by a halogen forming H_2O

$$R-CH_2-OH + H-X \xrightarrow[-H_2O]{\Delta} R-CH_2-X$$

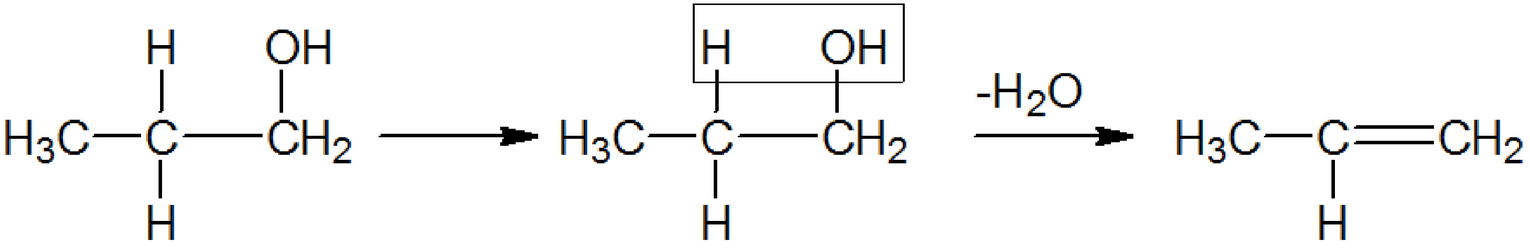
alcohol

X = Cl, Br, I

alkyl halide

Example

Elimination reaction of alcohols

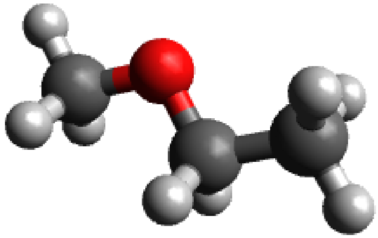


$$H_3C-\underset{H}{\overset{H}{C}}-\overset{OH}{CH_2} \longrightarrow H_3C-\underset{H}{\overset{H}{C}}-\overset{OH}{CH_2} \xrightarrow{-H_2O} H_3C-\underset{H}{C}=CH_2$$

Substitution reaction of alcohols

$$H_3C-CH_2-OH + HCl \longrightarrow H_3C-CH_2-Cl + H_2O$$

Ethers



Functional group *R-O-R’*

Nomenclature *(... ... ether)*

$CH_3CH_2\text{-}O\text{-}CH_2CH_3$	diethyl ether
$CH_3\text{-}O\text{-}CH_2CH_2CH_3$	methyl propyl ether

Formation of ethers

$$R{-}O{-}H + H{-}O{-}R \xrightarrow[-H_2O]{\Delta} R{-}O{-}R$$

Condensation reaction

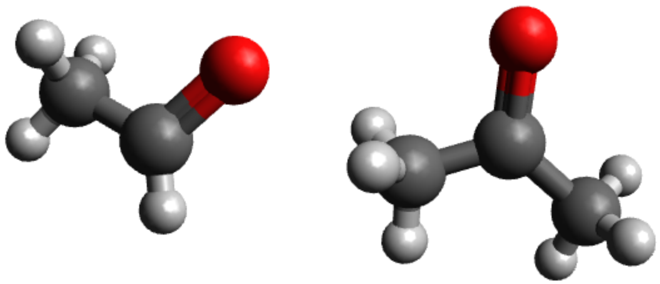
The reaction which is characterized by joining of two molecules and the elimination of a small molecule, usually water

$$\mathrm{H_3C{-}O{-}\boxed{H \;+\; H{-}O}{-}C_2H_5 \xrightarrow{-H_2O} H_3C{-}O{-}C_2H_5}$$

Reaction of alcohol salts with haloalkanes

$$\mathrm{H_3C{-}O{-}\boxed{Na \;+\; Br}{-}CH_3 \longrightarrow H_3C{-}O{-}CH_3 + NaBr}$$

Aldehydes and ketones

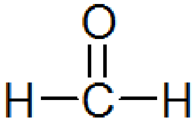


Functional group *-CHO, -CRO*

Nomenclature

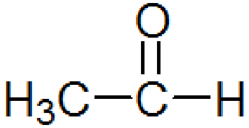
Alehydes *(-al)*

Ketones *(-one)*



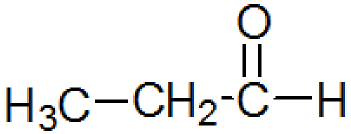
$$H-\overset{\overset{O}{\|}}{C}-H$$

methanal



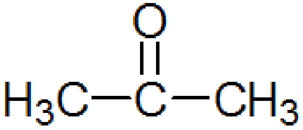
$$H_3C-\overset{\overset{O}{\|}}{C}-H$$

ethanal



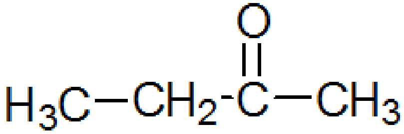
$$H_3C-CH_2\text{-}\overset{\overset{O}{\|}}{C}-H$$

propanal



$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3$$

propanone

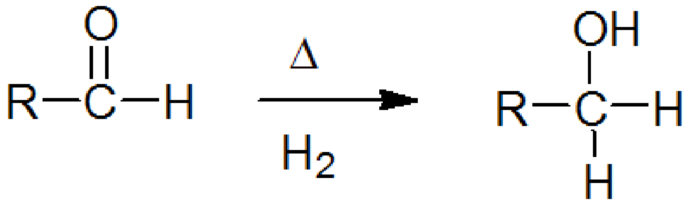


$$H_3C-CH_2\text{-}\overset{\overset{O}{\|}}{C}-CH_3$$

butanone

Reactions

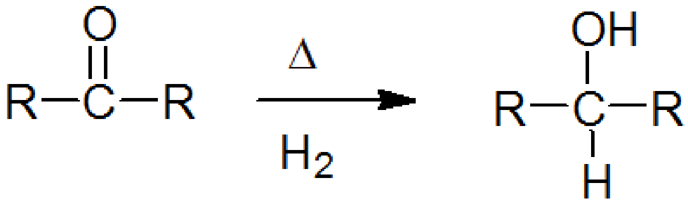
Hydrogenation (reduction) of aldehydes and ketones



$$R-\overset{\overset{O}{\|}}{C}-H \xrightarrow[H_2]{\Delta} R-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-H$$

aledyde

primary
alcohol

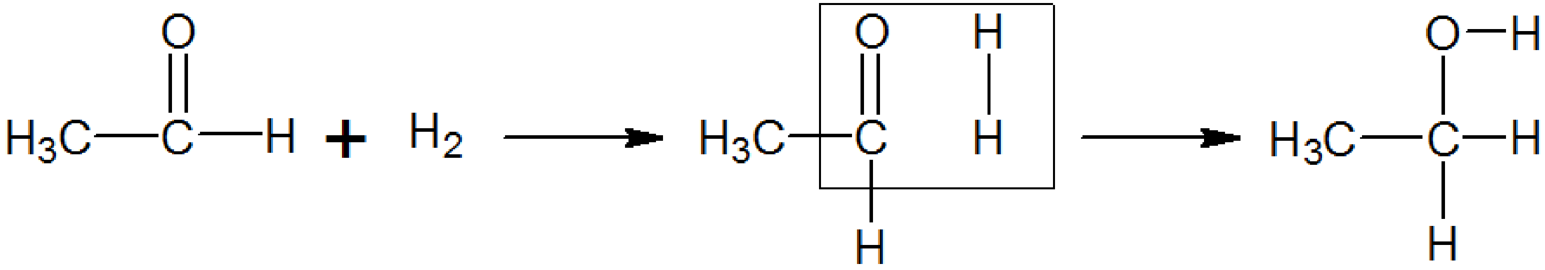


$$R-\overset{\overset{O}{\|}}{C}-R \xrightarrow[H_2]{\Delta} R-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-R$$

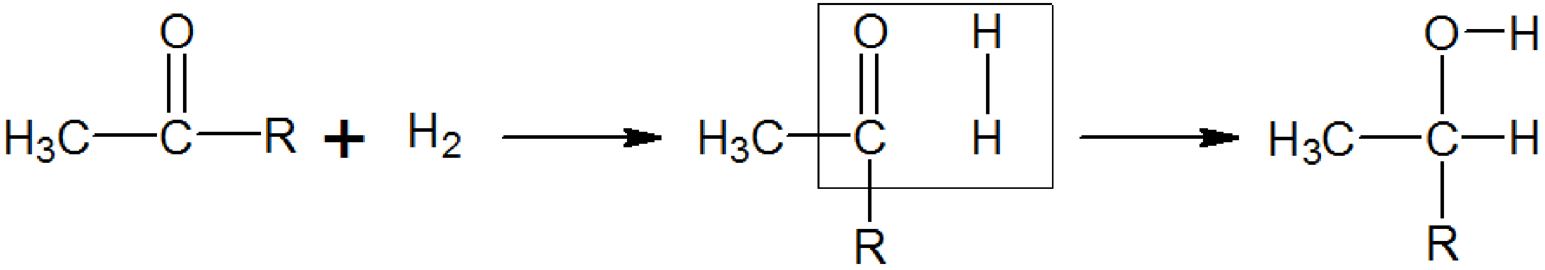
ketone

secondary
alcohol

Hydrogenation of aldehydes

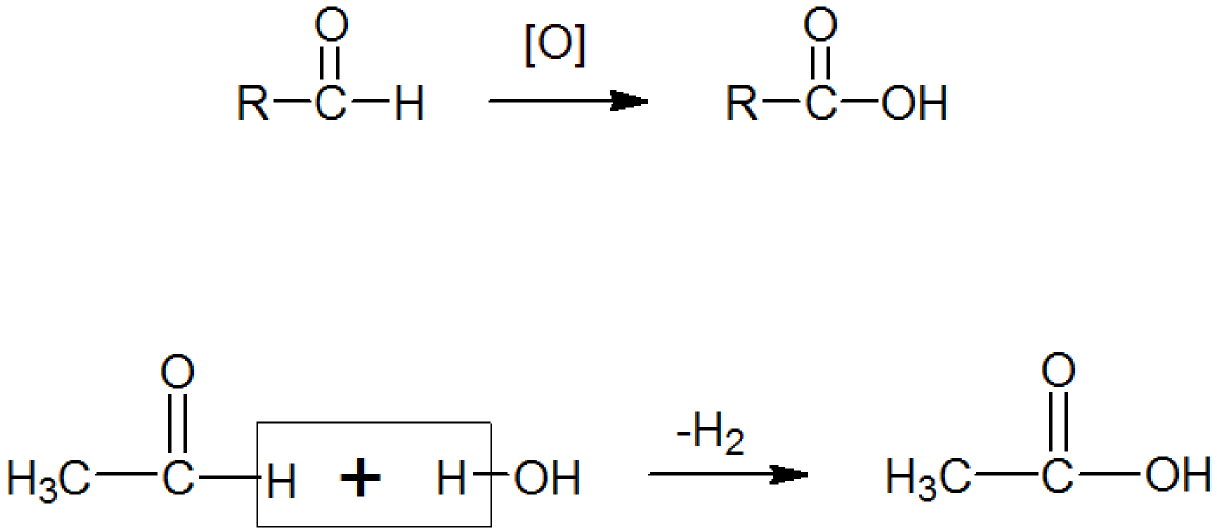


Hydrogenation of ketones



Oxidation of aldehydes

(very easy to form carbocylic acids)



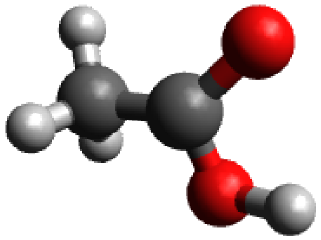
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{[O]} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

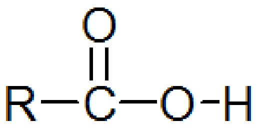
$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-\boxed{H + H}-OH \xrightarrow{-H_2} H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Carboxylic Acids

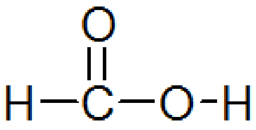
Functional group *-COOH*

Nomenclature *(... acid)*



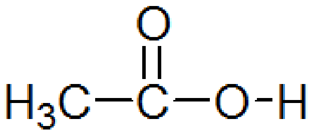


$$\mathrm{R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H}$$



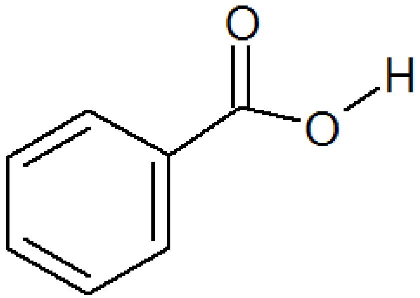
$$\mathrm{H-\overset{\overset{\displaystyle O}{\|}}{C}-O-H}$$

formic acid



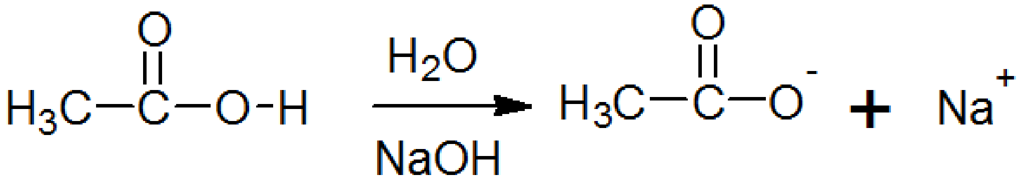
$$\mathrm{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-O-H}$$

acetic acid



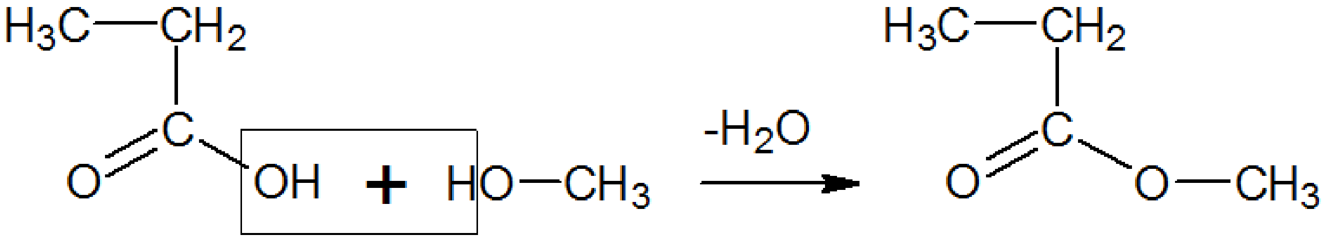
benzoic acid

Salts of Acids



acetic acid sodium acetate

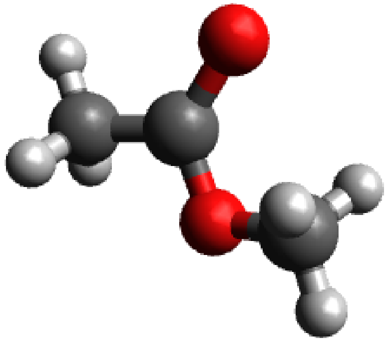
Reaction of acids with alcohols

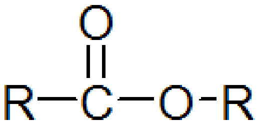


Esters

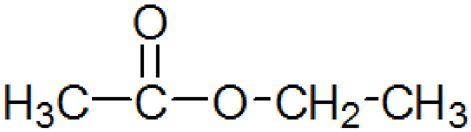
Functional group *R - COO - R'*

Nomenclature *(... ... -ate)*



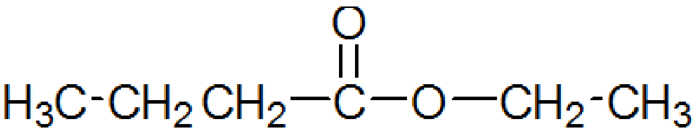


$R-\overset{\overset{O}{\|}}{C}-O-R$



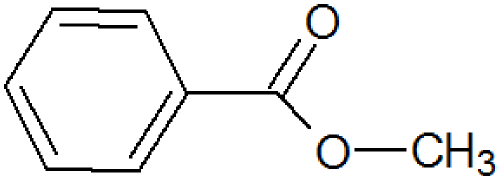
$H_3C-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$

ethyl acetate



$H_3C-CH_2\,CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$

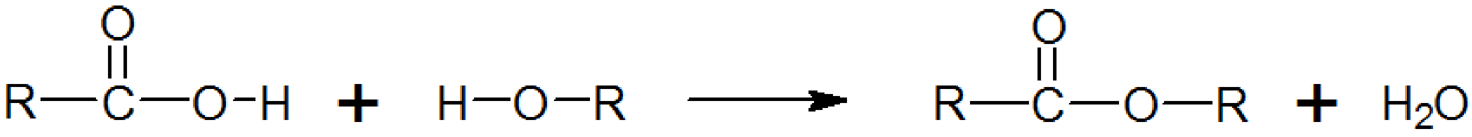
ethyl butanoate



methyl benzaoate

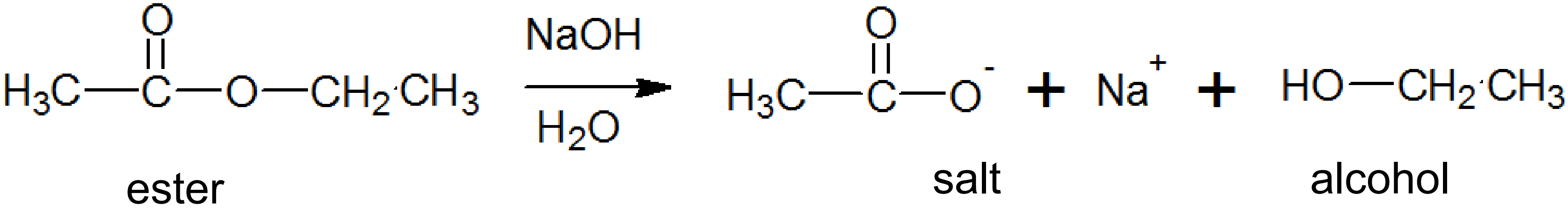
Reactions of esters

Formation of esters (from acid + alcohol)



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H + H-O-R \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R + H_2O$$

Hydrolysis of esters



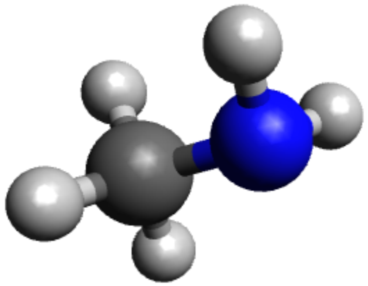
$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2CH_3 \xrightarrow[H_2O]{NaOH} H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + Na^+ + HO-CH_2CH_3$$

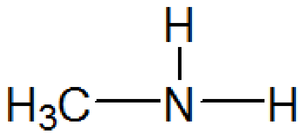
Amines

Functional group *$-NH_2$*

Nomenclature *(... -amine)*

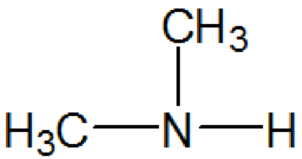
Organic derivatives of ammonia, NH_3





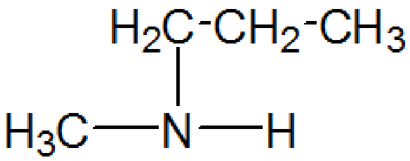
$H_3C-\overset{\overset{H}{|}}{N}-H$

methylamine



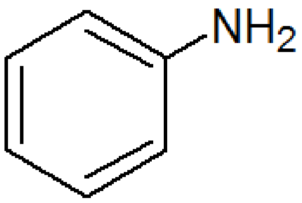
$H_3C-\overset{\overset{CH_3}{|}}{N}-H$

dimethylamine



$H_3C-\overset{\overset{H_2C-CH_2-CH_3}{|}}{N}-H$

methylpropylamine

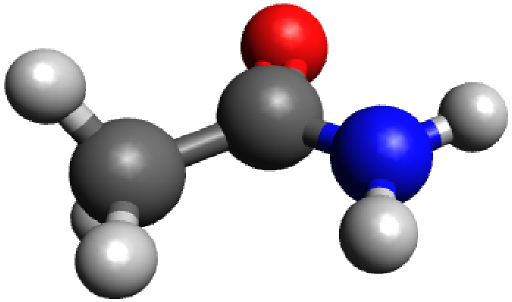


aniline

Like ammonia, amines are weak bases

$$RNH_2 + H^+ \rightarrow RNH_3^+$$

Amides



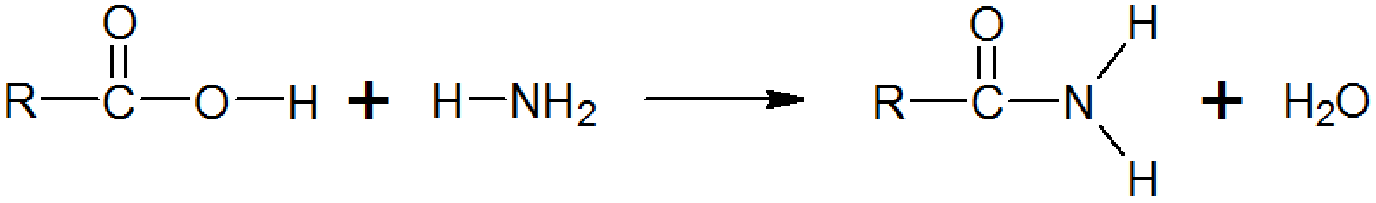
Functional group *$-CO-NH_2$*

Nomenclature *(... -amide)*

$R-CO-NH_2$

$R = -CH_3$	ethanamide
$R = -CH_2CH_2CH_2CH_3$	pentanamide, etc.

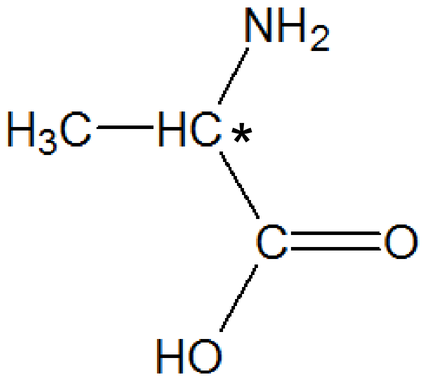
Formation of amides



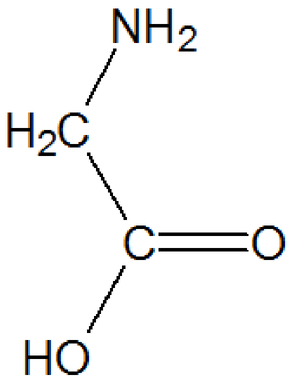
$$R-\overset{O}{\overset{\|}{C}}-O-H + H-NH_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-N\begin{matrix}\diagup H\\ \diagdown H\end{matrix} + H_2O$$

Problem

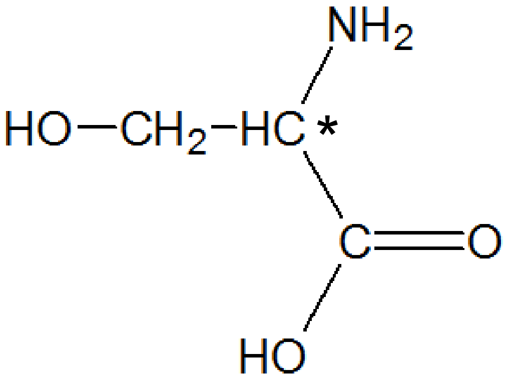
Which of the following aminoacids are chiral



chiral



non-chiral



chiral

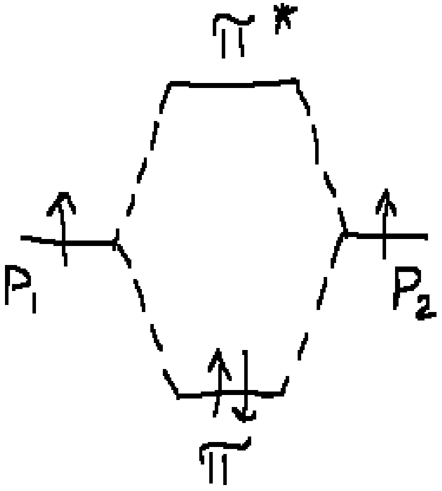
Aromaticity and Huckel method

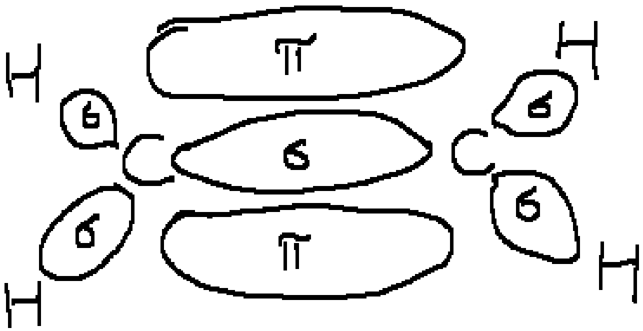
Proposed by Erich Huckel in 1930, is a very simple linear combination of atomic orbitals molecular orbitals method for the determination of energies of molecular orbitals of π electrons in conjugated hydrocarbon systems, such as ethene, benzene and butadiene

1. It limits itself to conjugated hydrocarbons
2. Only π electron MO's are included (separation of σ and π)
3. The method predicts how many energy levels exist for a given molecule

Ethylene

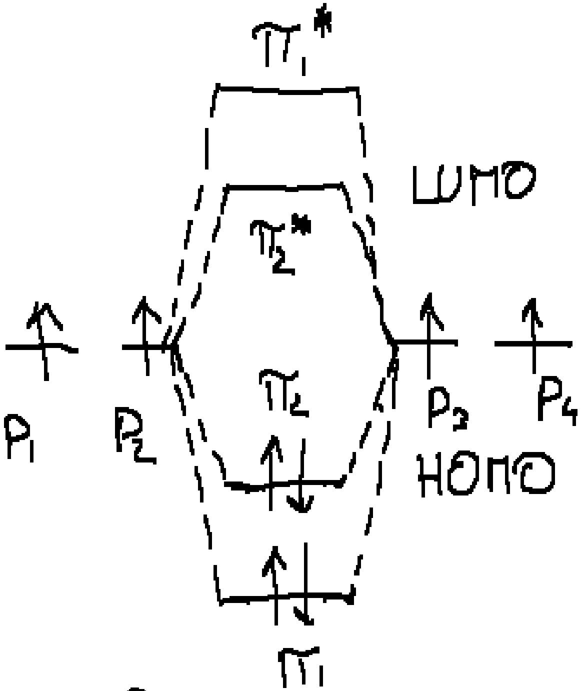
$H_2C = CH_2$





Butadien

$H_2C{=}CH{-}CH{=}CH_2$



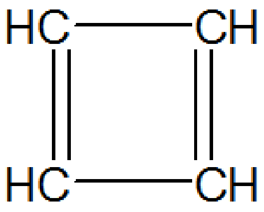
Homo orbital

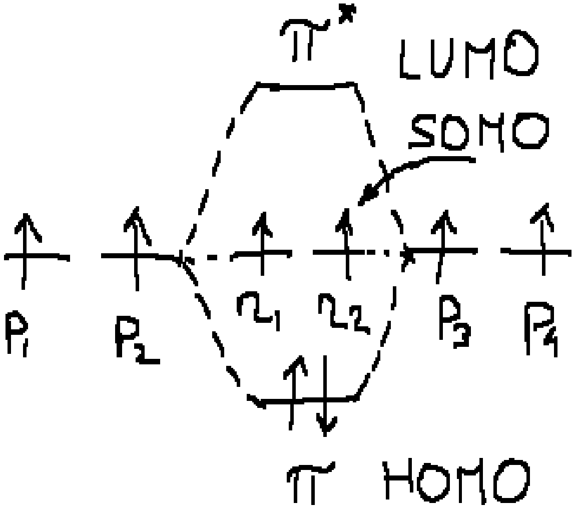
The highest occupied orbital

Lumo orbital

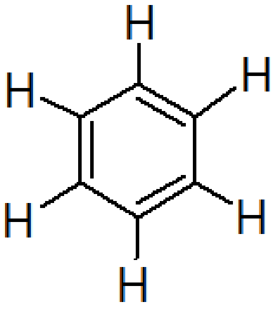
The lowest non occupied orbital

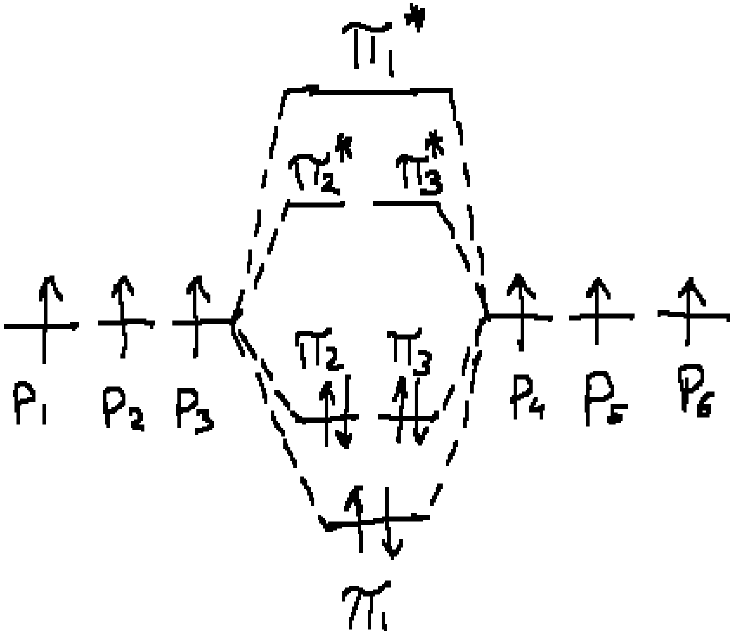
Cyclobutadien





Benzene

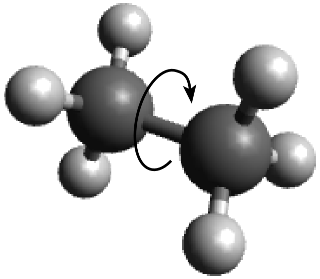




Spectroscopy of organic molecules

Microwave spectroscopy

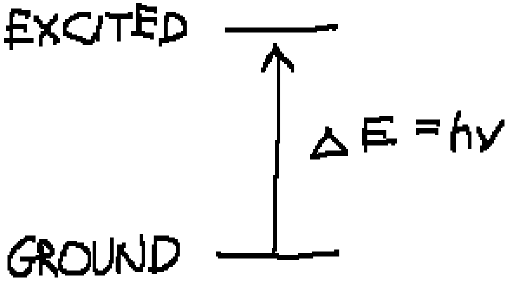
Ethane torsion motion

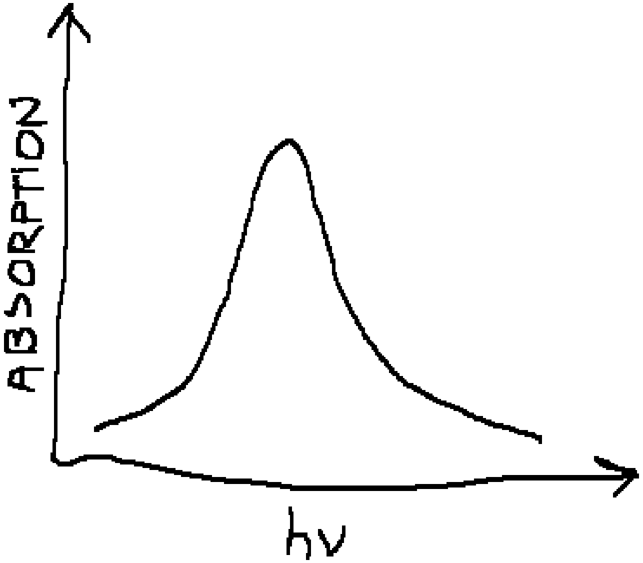


Absorbed energy

ΔE =~ 100 cm^{-1}

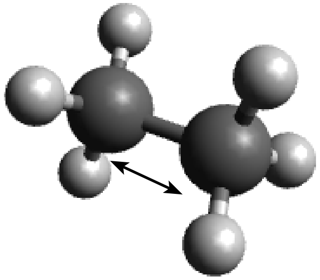
C ↻ C TORSION MOTION





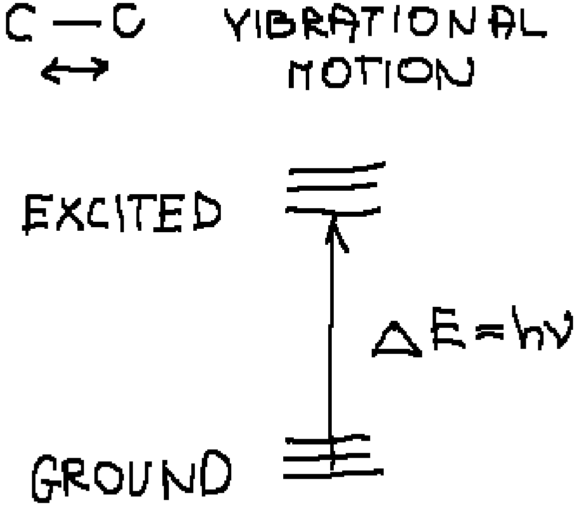
Vibrational spectroscopy

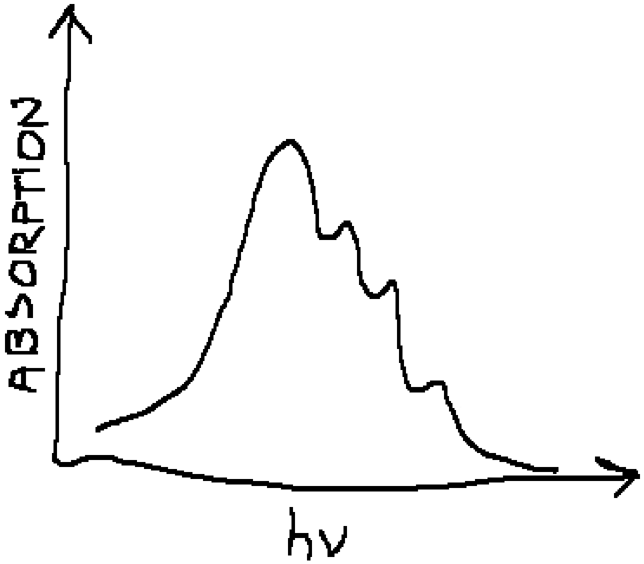
Ethane vibrational motion



Absorbed energy

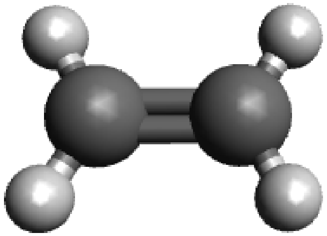
ΔE =~ 1000 cm^{-1}

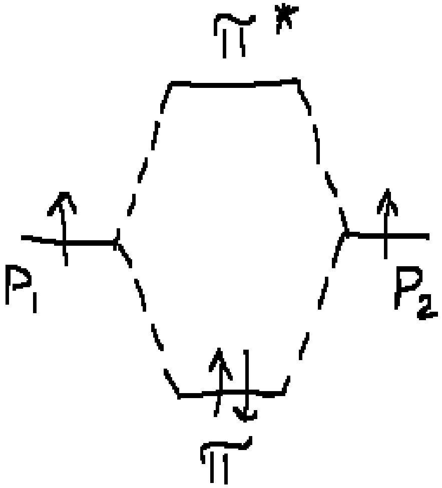




Electronic spectroscopy

Ethene electronic motion





Absorbed energy

ΔE =~ 10000 cm^{-1}