DAMIETTA UNIVERSITY

CHEM-103:

BASIC ORGANIC CHEMISTRY

LECTURES 1-2

Dr Ali El-Agamey

LEARNING OUTCOMES

LECTURES 1-2

- Appreciate the importance of organic chemistry.
- Draw the structures of organic compounds using Lewis, condensed and skeletal structures.
- Identify various functional groups.
- Identify the hybridization of various atoms.

Reading

Wade LG, Organic Chemistry, Prentice Hall, Upper Saddle River, 2010.

J Clayden et al, Organic Chemistry, Oxford University Press, 2001.

Morrison & Boyd, Organic Chemistry, Allyn and Bacon, Inc., Boston, 1987.

P Sykes, A Guidebook to Mechanism in Organic Chemistry, 1991.

Electronic Configurations of Atoms

- ***Valence electrons*** are electrons on the outermost shell of the atom.

TABLE 1-1

Electronic Configurations of the Elements of the First and Second Rows

Element	Configuration	Valence Electrons
H	$1s^1$	1
He	$1s^2$	2
Li	$1s^2 2s^1$	1
Be	$1s^2 2s^2$	2
B	$1s^2 2s^2 2p_x^1$	3
C	$1s^2 2s^2 2p_x^1 2p_y^1$	4
N	$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$	5
O	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$	6
F	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$	7
Ne	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$	8

Bonding Patterns

	Valence electrons	# Bonds	# Lone Pair Electrons
C	4	4	0
N	5	3	1
O	6	2	2
Halides (F, Cl, Br, I)	7	1	3

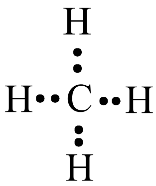
Drawing molecules

- (1) **Lewis structure**: a structural formula that shows all valence electrons, with the bonds symbolized by dashes (–) or by pairs of dots, and nonbonding electrons symbolized by dots.
- (2) **Condensed structural formulas**:
- (3) **Skeletal structure (Line-Angle Formula)**: (i) Draw chains of atoms as zig-zags (ii) Show functional groups (iii) Miss out H and C atoms

Lewis Structures

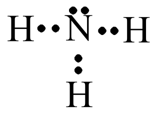
CH_4

Carbon: 4 *e*
4 H@1 *e* ea: 4 *e*
8 *e*



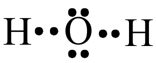
NH_3

Nitrogen: 5 *e*
3 H@1 *e* ea: 3 *e*
8 *e*



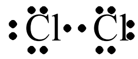
H_2O

Oxygen: 6 *e*
2 H@1 *e* ea: 2 *e*
8 *e*

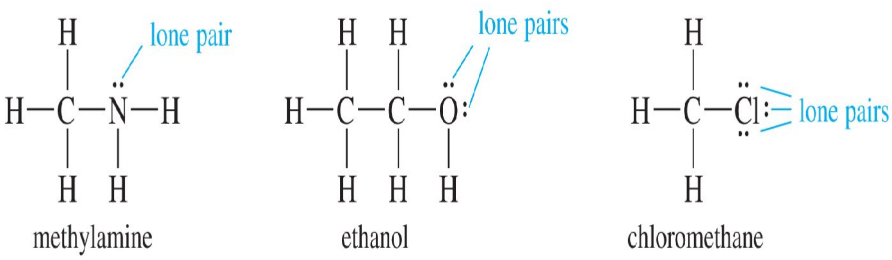


Cl_2

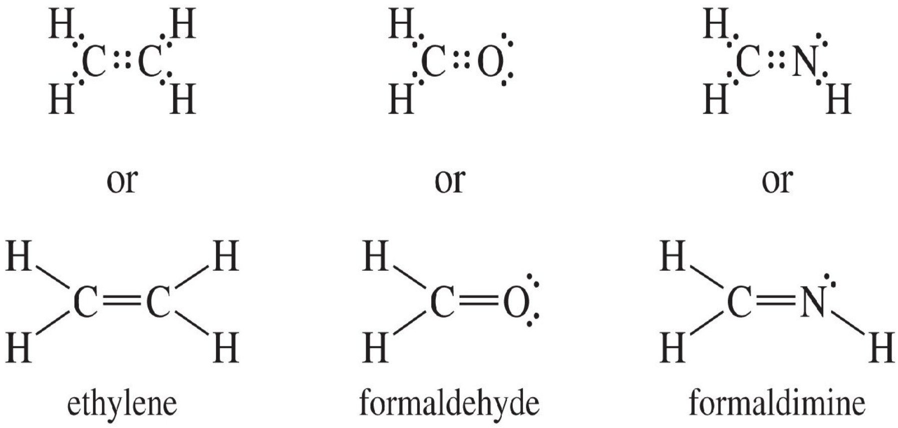
2 Cl @7 *e* ea: 14 *e*



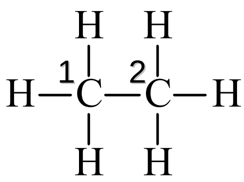
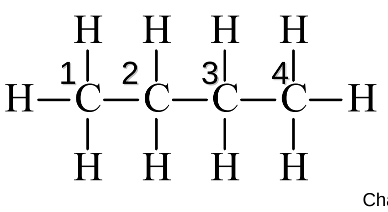
Lone Pairs



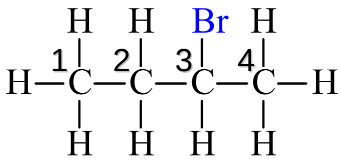
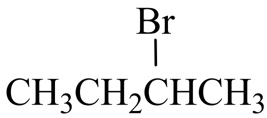
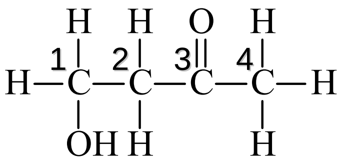
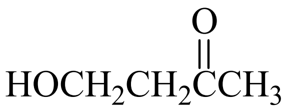
Double and Triple Bonds



(2) Condensed structural formulas

Lewis (Extended)	Condensed
	CH_3CH_3
	$CH_3CH_2CH_2CH_3$

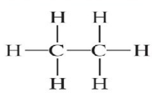
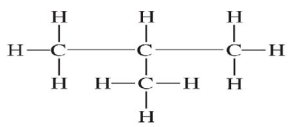
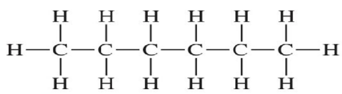
(2) Condensed structural formulas

Lewis (Extended)	Condensed
	
	

Condensed structural formulas

TABLE 1-2

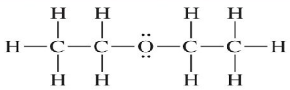
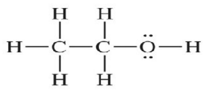
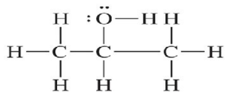
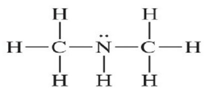
Examples of Condensed Structural Formulas

Compound	Lewis Structure	Condensed Structural Formula
ethane		CH_3CH_3
isobutane		$(CH_3)_3CH$
n-hexane		$CH_3(CH_2)_4CH_3$

(Continued)

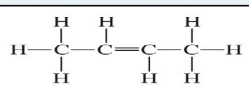
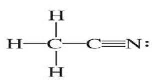
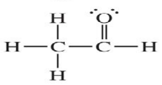
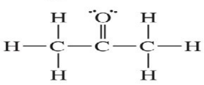
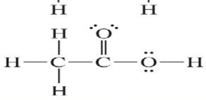
Condensed structural formulas

TABLE 1-2
Continued

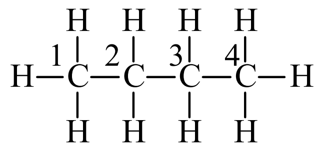
Compound	Lewis Structure	Condensed Structural Formula
diethyl ether		$CH_3CH_2OCH_2CH_3$ or $CH_3CH_2-O-CH_2CH_3$ or $(CH_3CH_2)_2O$
ethanol		CH_3CH_2OH
isopropyl alcohol		$(CH_3)_2CHOH$
dimethylamine		$(CH_3)_2NH$

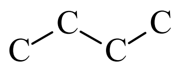
Condensed structural formulas

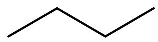
TABLE 1-3
Condensed Structural Formulas for Double and Triple Bonds

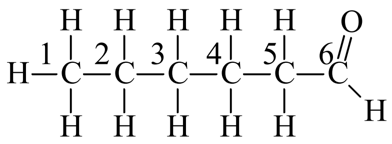
Compound	Lewis Structure	Condensed Structural Formula
2-butene		$CH_3CHCHCH_3$ or $CH_3CH{=}CHCH_3$
acetonitrile		CH_3CN or $CH_3C{\equiv}N$
acetaldehyde		CH_3CHO or $CH_3\overset{O}{\overset{\|}{C}}H$
acetone		CH_3COCH_3 or $CH_3\overset{O}{\overset{\|}{C}}CH_3$
acetic acid		CH_3COOH or $CH_3\overset{O}{\overset{\|}{C}}-OH$ or CH_3CO_2H

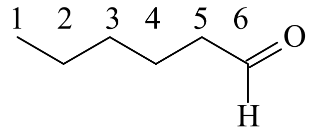
(3) Skeletal structure (line-angle formula)







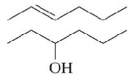
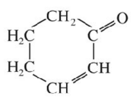
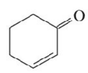
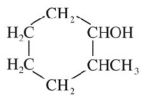
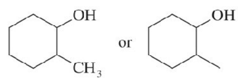
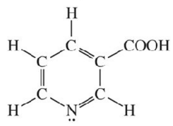
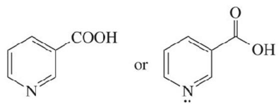




Skeletal structure (line-angle formula)

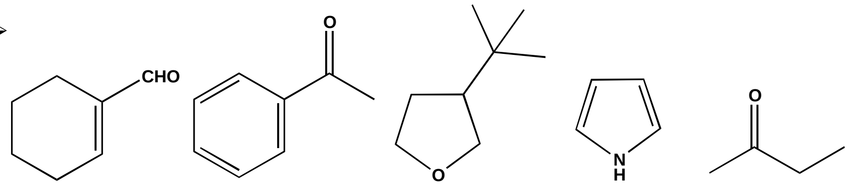
TABLE 1-4

Examples of Line–Angle Drawings

Compound	Condensed Structure	Line–Angle Formula
hexane	$CH_3(CH_2)_4CH_3$	
2-hexene	$CH_3CH{=}CHCH_2CH_2CH_3$	
3-hexanol	$CH_3CH_2CH(OH)CH_2CH_2CH_3$	
2-cyclohexenone		
2-methylcyclohexanol		
nicotinic acid (a vitamin, also called niacin)		

Problem

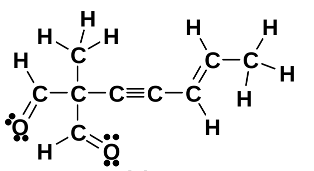
- 1-Draw the complete Lewis structures for the following condensed structural formulas.
- (i) $CH_3(CH_2)_3CH(CH_3)_2$ (ii) $CH_3COCOOH$
- (iii) $(CH_3CH_2)_2CO$ (iv) $(CH_3)_2CHCH_2Cl$
- **Homework:** Give Lewis structures corresponding to the following skeletal structures.
-



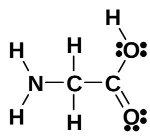
(a) (b) (c) (d) (e)

Homework

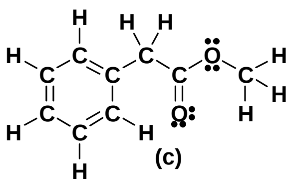
- Draw the skeletal structures for the following Lewis structures.



(a)



(b)



(c)

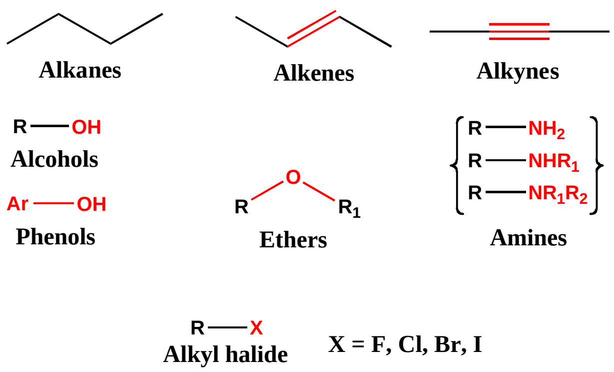
Names of normal alkanes

- **Homework:** Draw the skeletal structures for the following compounds except methane.

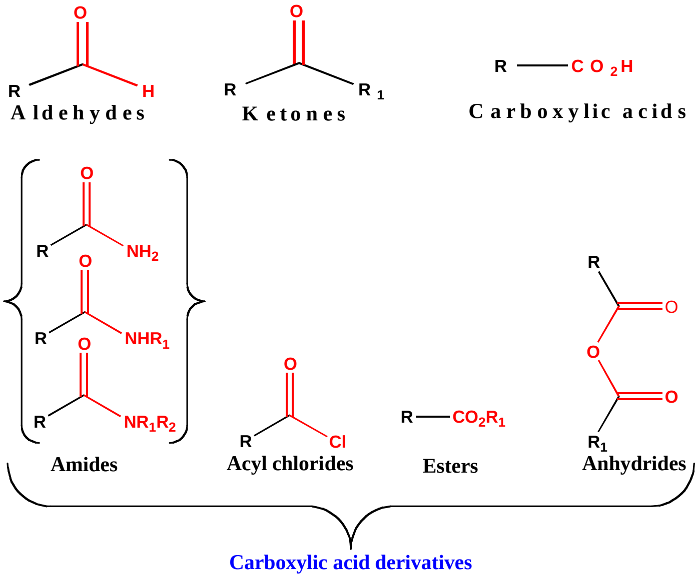
CH_4	Methane	$CH_3(CH_2)_6CH_3$	Octane
CH_3CH_3	Ethane	$CH_3(CH_2)_7CH_3$	Nonane
$CH_3CH_2CH_3$	Propane	$CH_3(CH_2)_8CH_3$	Decane
$CH_3(CH_2)_2CH_3$	Butane	$CH_3(CH_2)_9CH_3$	Undecane
$CH_3(CH_2)_3CH_3$	Pentane	$CH_3(CH_2)_{10}CH_3$	Dodecane
$CH_3(CH_2)_4CH_3$	Hexane	$CH_3(CH_2)_{11}CH_3$	Tridecane
$CH_3(CH_2)_5CH_3$	Heptane	$CH_3(CH_2)_{12}CH_3$	Tetradecane

Functional groups

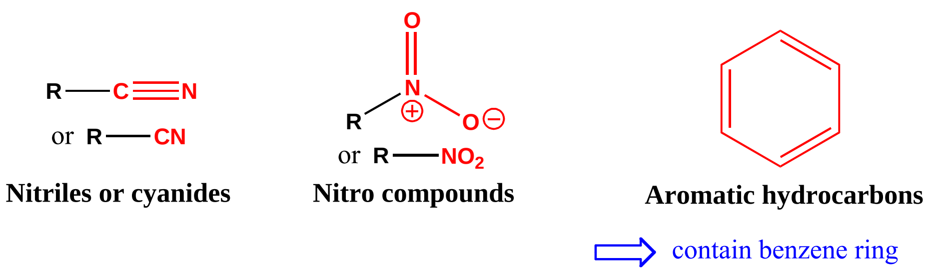
- R = Alkyl; Ar = Aryl.



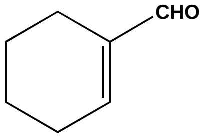
Functional groups



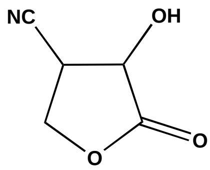
Functional groups



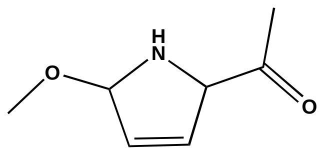
Problem

- 1-Draw the skeletal structures for the following compounds and name the functional groups. .
- (i) $CH_3(CH_2)_3CH(CH_3)_2$ (ii) $CH_3COCOOH$
- (iii) $(CH_3CH_2)_2CO$ (iv) $(CH_3)_2CHCH_2Cl$
- **Homework**: Identify the functional groups in the following structures.
- 

(a)



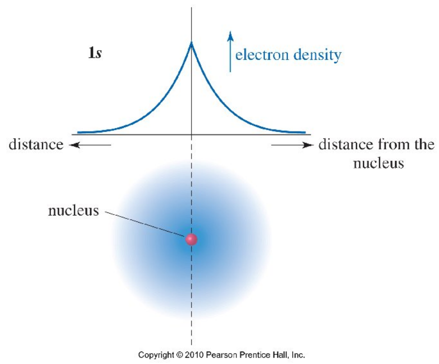
(b)



(c)

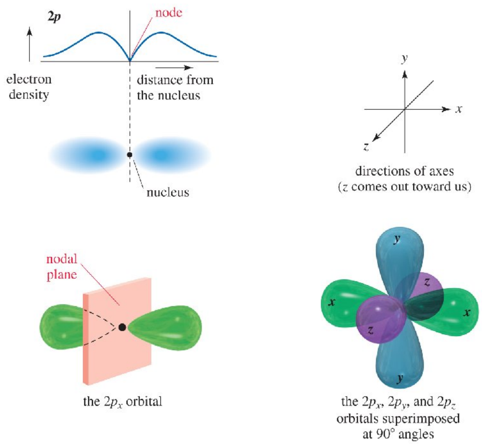
Electronic Structure of the Atom

- An atom has a dense, positively charged nucleus surrounded by a cloud of electrons.
- The electron density is highest at the nucleus and drops off exponentially with increasing distance from the nucleus in any direction.

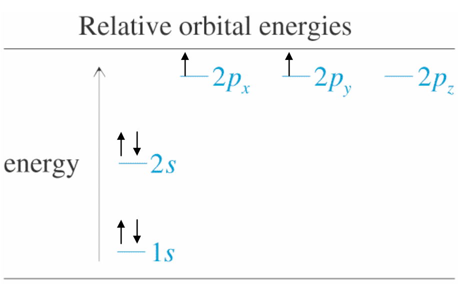


The 2*p* Orbitals

- There are three 2*p* orbitals, oriented at right angles to each other.
- Each *p* orbital consists of two lobes.
- Each is labeled according to its orientation along the *x*, *y*, or *z* axis.



Electronic Configurations



Electronic configuration of carbon

- The ***aufbau principle*** states to fill the lowest energy orbitals first.
- ***Hund's rule*** states that when there are two or more orbitals of the same energy (**degenerate**), electrons will go into different orbitals rather than pairing up in the same orbital.

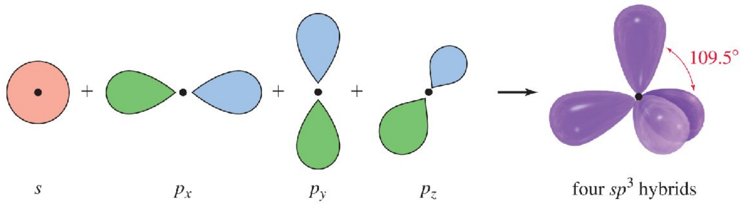
Hybridization

- Experimental results show that the bond angles of H_2O and NH_3 are roughly tetrahedral (104^o and 107^o respectively) and CH_4 is exactly tetrahedral (109.5^o) !!!
- Problem: Orbitals available for bonding are 2*s* () and 2*p* (right angles to each other)
- In order to account for the observed geometry, hybridization was proposed as a convenient model.
- Hybridization of atomic orbitals is a mathematical **mixing** of two or more different orbitals on a given atom to give the **same number** of new hybrid atomic orbitals, each of which has **some of the character** of the original component orbitals.

Hybridization

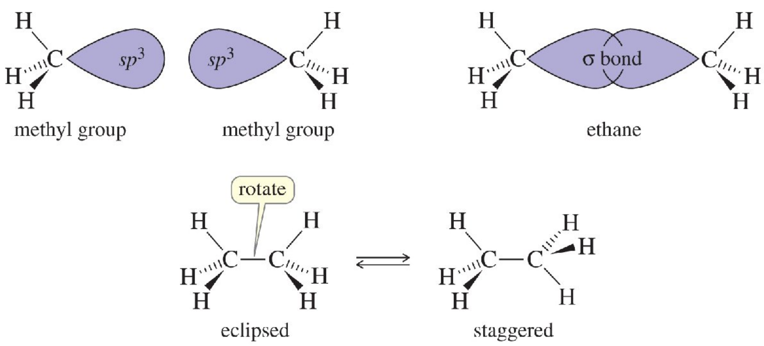
- Also, the resulting hybrid orbitals have **directional character** and when used to bond with atomic orbitals of other atoms, they help to determine the shape of the molecule formed.
- Hybridization involves **(i) promotion** and **(ii) mixing** (hybridization), For example; CH_4
- $2s^2\ 2p_x^1\ 2p_y^1 \xrightarrow{(i)} 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1 \xrightarrow{(ii)}$ $4sp^3$ hybrid atomic orbitals

sp^3 Hybrid Orbitals



- There are 4 sp^3 hybrid atomic orbitals.
- The atoms has tetrahedral electron pair geometry.
- 109.5° bond angle

Bonding in Ethane

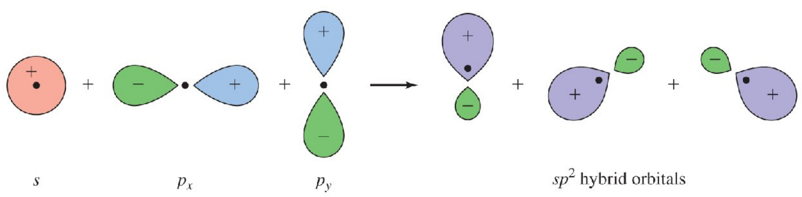


- Ethane is composed of two methyl groups bonded by the overlap of their sp^3 hybrid orbitals.
- There is free rotation along single bonds.

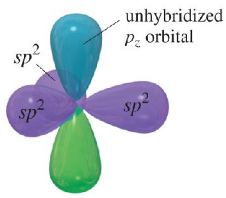
Hybridization

- Ethylene: $H_2C{=}CH_2$
- $\boxed{2s^1\ 2p_x^1\ 2p_y^1}\,2p_z^1 \xrightarrow{\text{(ii)}}$ 3 sp^2 hybrid atomic orbitals and $2p_z^1$
- In ethylene, the whole skeleton is in one plane and the central π-bond is above and below the plane.

sp^2 Hybrid Orbitals

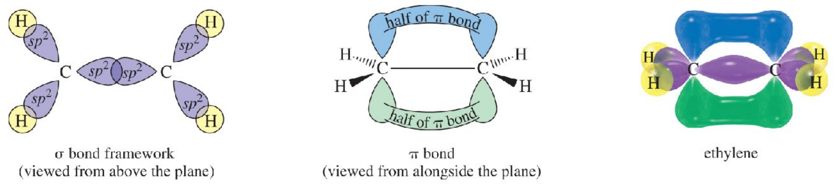


- 3 sp^2 hybrid atomic orbitals.
- Trigonal planar geometry
- 120° bond angle



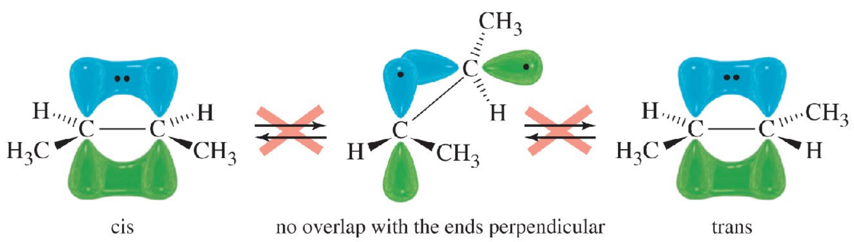
sp^2 hybrid carbon atom (viewed from the side)

Bonding in Ethylene



- Ethylene has three (3) **sigma** bonds formed by its sp^2 hybrid orbitals in a trigonal planar geometry.
- The unhybridized *p* orbital of one carbon is **perpendicular** to its sp^2 hybrid orbitals and it is parallel to the unhybridized *p* orbital of the second carbon.
- Overlap of these two *p* orbitals will produce a pi bond (double bond) which is located **above and below** the sigma bond.

Rotation Around Double Bonds



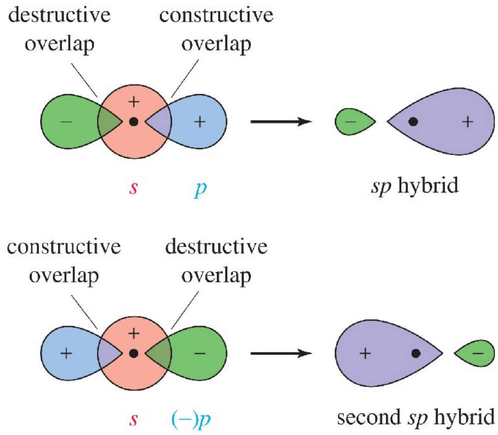
- Single bonds can rotate freely.
- Double bonds cannot rotate.

Hybridization

- Acetylene: HC≡CH
- $2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1 \xrightarrow{\text{(ii)}}$ 2 *sp* hybrid atomic orbitals plus $2p_y^1$ and $2p_z^1$
- In acetylene, the whole skeleton is linear.

sp Hybrid Orbitals

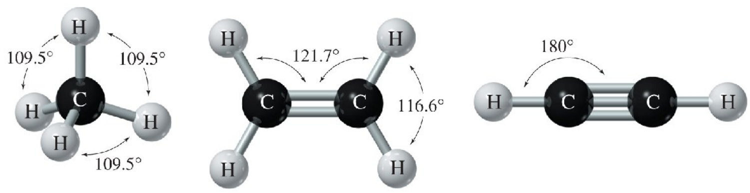
- Have 2 *sp* hybrid atomic orbitals.
- Linear electron pair geometry.
- 180° bond angle.



Valence-shell electron-pair repulsion theory (VSEPR)

- Electron pairs repel each other, and the bonds and lone pairs around a central atom generally are separated by the largest possible angles.
- An angle of 109.5º is the largest possible separation for four pairs of electrons; 120º is the largest separation for three pairs; and 180º is the largest separation for two pairs.

Molecular Shapes



methane, 109.5° ethylene, close to 120° acetylene, 180°

- As mentioned earlier, bond angles cannot be explained with simple *s* and *p* orbitals.
- Valence-shell electron-pair repulsion theory (VSEPR) is used to explain the molecular shape of molecules.

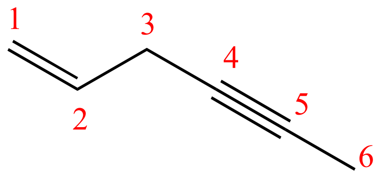
General rules of hybridization and geometry

- **Rule 1:** Both sigma bonding electrons and lone pairs can occupy hybrid orbitals. Therefore,
- The no. of hybrid orbitals on an atom = no. of sigma bonds + no. of lone pairs of electrons
- The no. of hybrid orbitals on an atom = no. of atoms bonded to the central atom + no. of lone pairs of electrons
- **Rule 2:** Use the hybridization and geometry that give the widest possible separation of the calculated number of bonds and lone pairs.

General rules of hybridization and geometry

- **Rule 3:** If two or three pairs of electrons form a multiple bond between two atoms, the first bond is a sigma bond formed by a hybrid orbital. **The second bond** is a **pi bond**, consisting of two lobes above and below the sigma bond, formed by unhybridized *p* orbitals. **The third bond** of a triple bond is **another pi bond**, perpendicular to the first pi bond.

Specify the hybridization of each atom in the following compound?

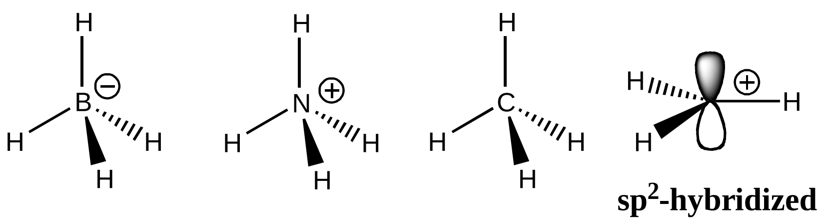


hex-1-en-4-yne

- C1, C2 are sp^2; C3, C6 are sp^3 and C4, C5 are sp
- More Examples

What is the hybridization of BH_4^-, CH_4, NH_4^+ and CH_3^+ ?

- BH_4^-, CH_4 and NH_4^+ are sp^3-hybridized and CH_3^+ is sp^2-hybridized.

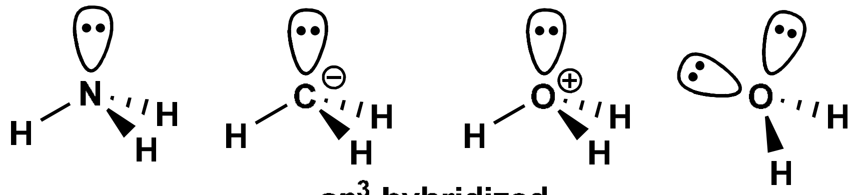


sp^3-hybridized

sp^2-hybridized

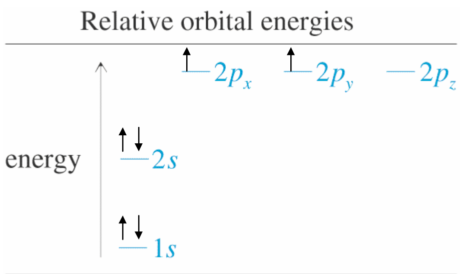
What is the hybridization of NH_3, CH_3^-, H_3O^+, and H_2O ?

- All molecules are ***sp*³**-hybridized.



***sp*³-hybridized**

Energy of various orbitals



Electronic configuration of carbon

- The greater the s character, the lower the energy, the greater stability.

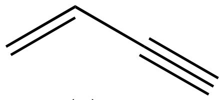
Increasing of energy →

sp sp^2 sp^3 p

- We need to populate the lowest energy orbital.

Homework

- Specify the hybridization of each atom and if the atom has lone pair, specify the type of orbitals which include them?
-



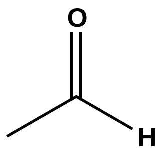
(a)

BeH_2

(b)

BH_3

(c)



(d)

Homework

- Specify the hybridization of each atom and if the atom has lone pair, specify the type of orbitals which include them?
-

$H_3C-C\equiv N$

(a)

$H_2C=C=CH_2$

(b)