TOPIC 1. STRUCTURE AND BONDING

OBJECTIVES

1. Introduction to organic chemistry and review of terms
1. Describe distribution of electrons in organic molecules (atomic electronic configurations, Lewis structures, resonance)
2. Describe bonding C-C and C-H bonds in organic molecules (hybridization, overlap of atomic orbitals).
3. Describe molecular geometry.

ORGANIC CHEMISTRY: YESTERDAY, TODAY AND TOMORROW

Yesterday

Pre-1820: "Vitalism" - belief that "natural compounds" possessed special properties, could not be made by man

1828: Wöhler: preparation of urea (organic) from ammonium cyanate (inorganic)

$$NH_4^+OCN^- \xrightarrow{\text{heat}} CH_4N_2O$$

1908: First production of a synthetic plastic, Bakelite
(1930s-50s: Commercialization of commodity plastics: nylon, polyester, PVC, polyethylene, polypropylene)

1928: Discovery of penicillin (1954: Celphalosporin)

1948: α-helix of protein structure determined
(1952: Determination of double helix structure of DNA)

1950s: Oral contraceptives

Today

Major commodities
(annual US production)

	billion lb
Ethylene	55
Propylene	32
Dichloroethane	22
Urea	15
Ethybenzene	13
Styrene	12
Ethylene oxide	9
p-Xylene	8
Cumene	8
1,3-Butadiene	4
Acrylonitrile	3
Benzene	2
Aniline	2
Isopropanol	1
o-Xylene	1
2-Ethylhexanol	1

Major US commodity Producers
(Annual Sales)

	billion$
Dow	28
DuPont	27
BASF	25
Bayer	18
Total	18
ExxonMobil	16
Shell Oil	15
BP Amoco	13
Degussa	11
Akzo Nobel	9
ICI Americas	9
SABIC	8
China Petroleum	8
Mitsui	8
General Electric	7
Huntsman	7
Union Carbide	6
Air Products	5

Major Pharmaceuticals

Prilosec
(Astra Pharm Inc., acid reflux)

Lipitor
(Parke-Davis, high cholesterol)

Propecia
(antibaldness)

AZT
(Burroughs Wellcome, HIV)

Prozac (Fluoxetine)
(Antidepresent. Lillv)

Viagra
(Pfizer)

Zantac (Ranitidine)
(Antiulcer, Glaxo)

Claratin
(Schering, allergies)

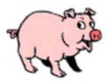
Amoxicillin
(Antibiotic; SKB, Squibb)

Acetaminophen
Ibuprophen

Recently
Taxol (anticancer), C60-buckyball, Organic electronic materials (LCDs)

Tomorrow

Better food:
- Nutrients
- Pesticides
- Fertilizers



Better health:
- Pharmaceuticals
- Biomedical engineered implants/replacements

Better environment:
- Cleaner processes

Better living….

Better Living Through Chemistry

…through responsible care and stewardship.

SOME BASIC STRUCTURAL FEATURES

Empirical Formula
- Ratio of atoms in a compound.

Molecular Formula
- Number of each atom in a molecule.

Valency
- Elements form a fixed number of bonds (H 1, O 2, N 3, C 4).

Structure
- Arrangement of atoms and bonds in a molecule.

Isomers
- Different compounds with the same molecular formula.

Constitutional isomers
- Compounds with the same formula, but with different connectivities of atoms.

A VERY GOOD PLACE TO START:
ELECTRONIC CONFIGURATION OF ATOMS

H	$1s^1$	
He	$1s^2$	
Li	$1s^2, 2s^1$	
Be	$1s^2, 2s^2$	
B	$1s^2, 2s^2, 2p^1$	$1s^2, 2s^2, 2p_x^1$
C	$1s^2, 2s^2, 2p^2$	$1s^2, 2s^2, 2p_x^1 2p_y^1$
N	$1s^2, 2s^2, 2p^3$	$1s^2, 2s^2, 2p_x^1 2p_y^1 2p_z^1$
O	$1s^2, 2s^2, 2p^4$	$1s^2, 2s^2, 2p_x^2 2p_y^1 2p_z^1$
F	$1s^2, 2s^2, 2p^5$	$1s^2, 2s^2, 2p_x^2 2p_y^2 2p_z^1$
Ne	$1s^2, 2s^2, 2p^6$	$1s^2, 2s^2, 2p_x^2 2p_y^2 2p_z^2$

BONDING: LEWIS STRUCTURES AND FORMAL CHARGES

The Octet Rule

Atoms exchange or share electrons to complete the valence shell (adopt Noble gas electronic configuration)

H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca					Br	
						I	

Ionic Bonds

Atoms exchange electrons to form ions which are electrostatically attracted to one another.

Li + F ⟶ Li + F

Ionic bonds are typically formed between atoms which are highly electronegative and highly electropositive

Covalent Bonds

Atoms share valence shell electrons to form covalent bonds

C H H H H ⟶

O H H ⟶

Recommendation: ALWAYS *explicitly* show lone pairs of electrons

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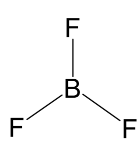
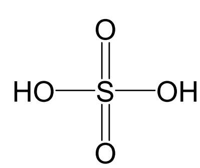
"Exceptions" to the Octet "Rule"

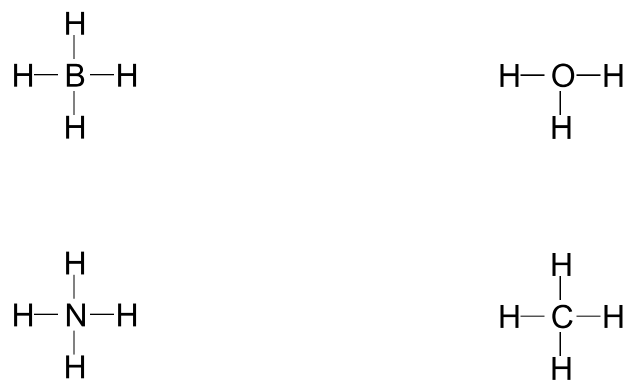
Octet rule is the tendency to have eight valance electrons - only applies strictly to second row elements





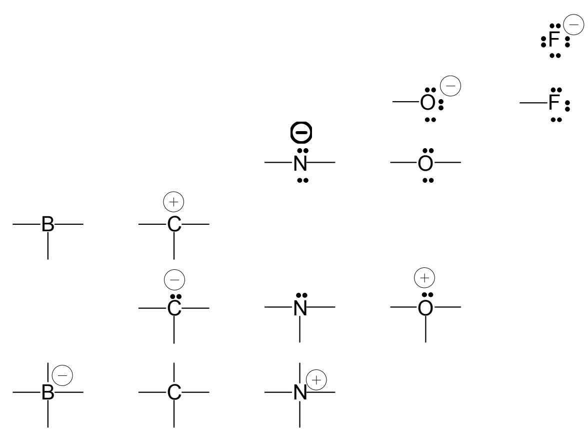
Formal Charge

$F = Z - (S/2) - U$



*Always show **all** formal charges in all structures!*

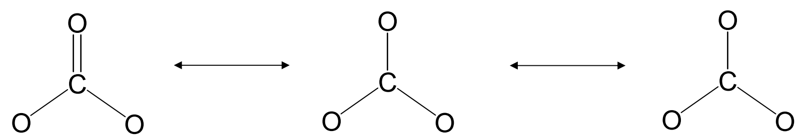
Some Common Valencies



Not:

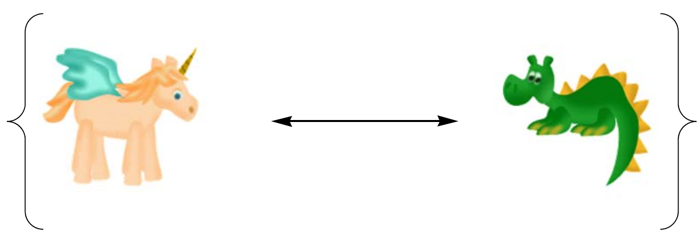
RESONANCE THEORY

e.g., Carbonate, CO_3^{2-}: A single Lewis structure does not accurately describe the structure of the carbonate dianion.

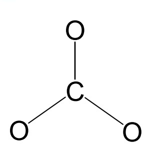


Molecules and ions that can be represented by more than one valid Lewis structure *which differ only in the position of non-bonding electrons and double bonds* exist as a hybrid of each contributing resonance structure.

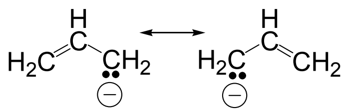
Resonance structures ("contributors")

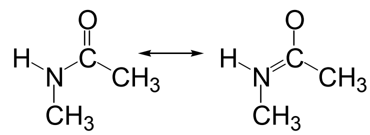


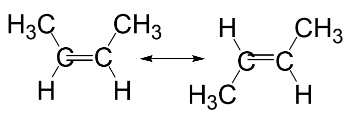
The hybrid is a combination (average) of all the contributing Lewis structures. It is more stable than the individual structures.

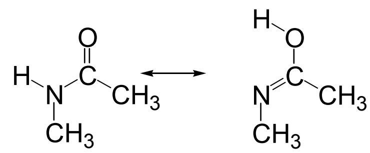


Problem: Which of the following are valid resonance structures?



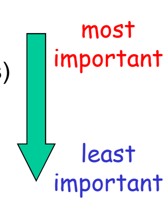




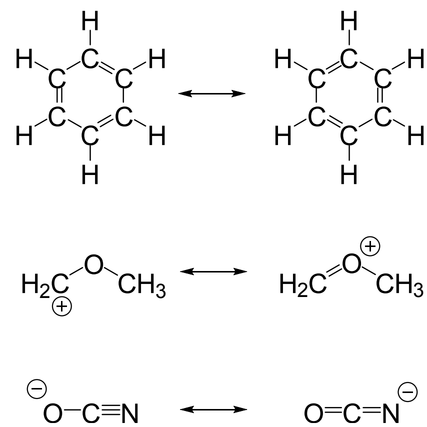


Guidelines for Recognizing and Drawing Resonance Structures

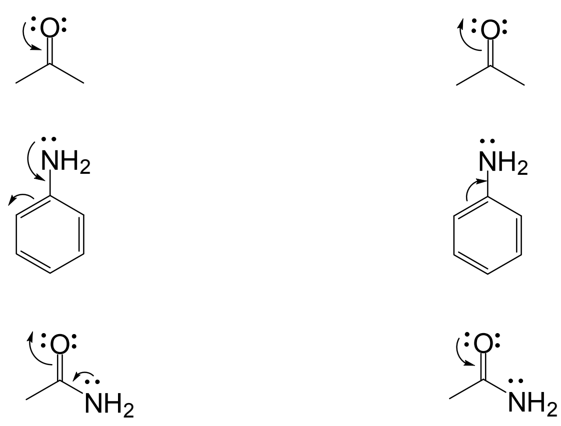
- Individual resonance structures *do not exist* - the *hybrid* does. The energy of the actual molecule is lower than what might be predicted for any of the contributing structures
- Resonance structures which possess features that impart stability contribute more to the hybrid structure. Stability is enhanced by:
  - Equivalent resonance structures contribute particular stability to the molecule
  - More bonds, stronger bonds
  - Complete valence shells (as opposed to incomplete valence shells)
  - Little (no) charge separation (separating charges costs energy!)
  - Negative charge on electronegative atoms (and visa versa)



Which structure in each pair is the more stable major contributor to the resonance hybrid? *[Consider the factors that contribute to the stability/instability of each resonance structure]*

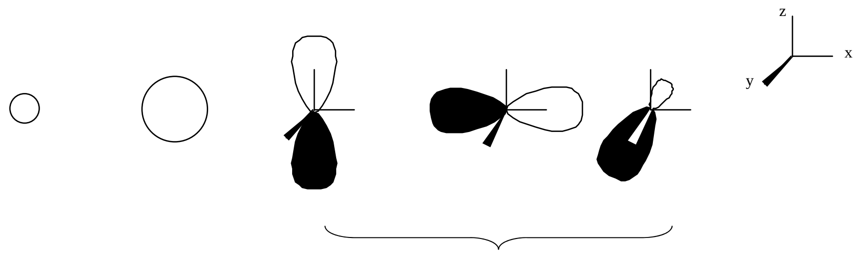


Problem: Which of the following sets of curved arrows accurately represents resonance? *[Draw the structures implied by the movement of electrons shown by the arrows, which of the species is a valid Lewis structure?]*



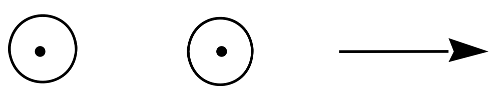
QUANTUM MECHANICS, ATOMIC ORBITALS AND MOLECULAR ORBITALS

Electrons are contained in atomic orbitals

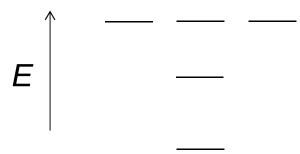


1s 2s 2p

Atomic orbitals overlap to form molecular orbitals



Carbon:

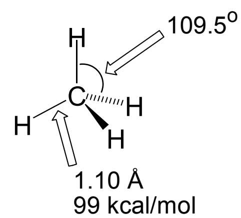


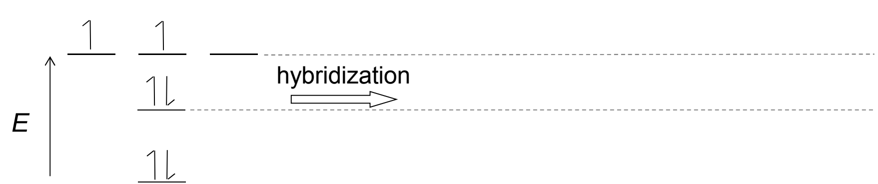
Filling Orbitals

maximum of two e⁻ per orbital
Aufbau Principle: e⁻ fill lower energy orbitals
Pauli Principle: e⁻ in same orbitals have different spins
Hund's rule: degenerate orbitals are filled equally

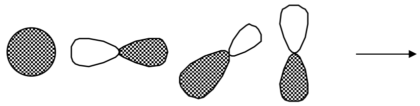
METHANE AND ETHANE: sp³ HYBRIDIZATION

e.g., methane, CH_4

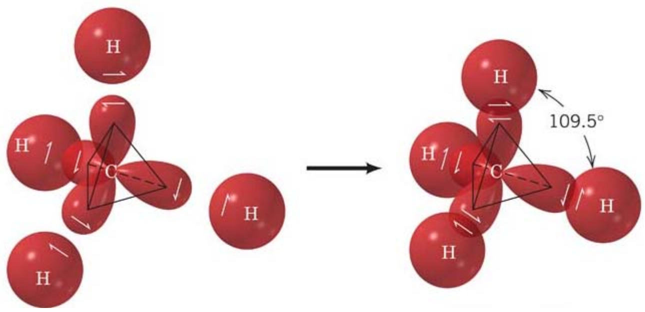




Hybridization

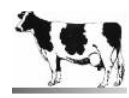


Orbital overlap



***s* + *sp*^{3} orbital overlap**

methane, CH_4: gas (bp=-161 °C). Used as natural gas, for synthesis of other compounds



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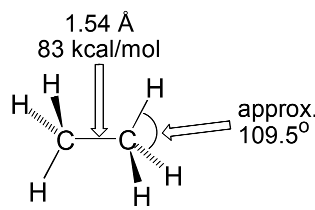
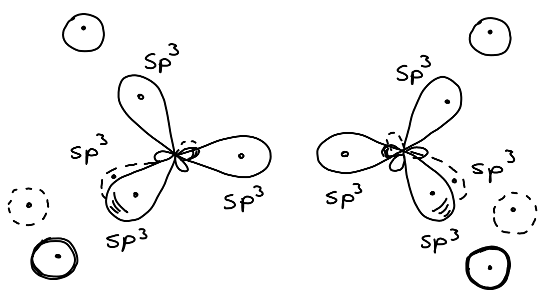
e.g., ethane, C_2H_6



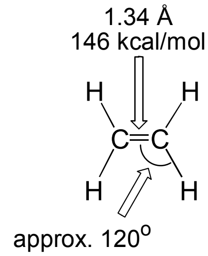


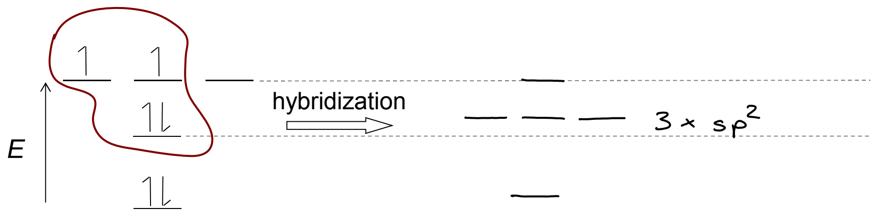
***sp*^{3} + *sp*^{3} orbital overlap**

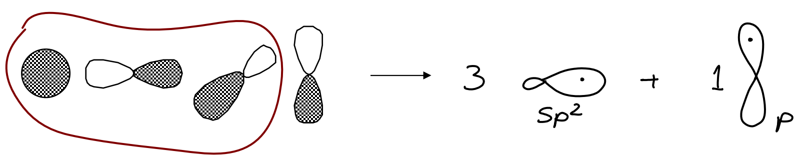
ethane, C_2H_6: gas (bp= -88 °C). Used in manufacture of C2 derivatives;
Minor constituent of natural gas.

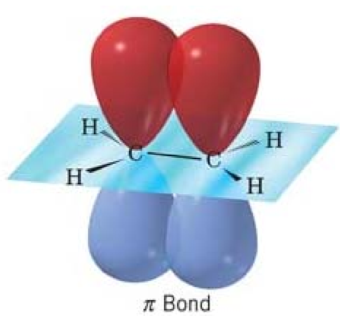
ALKENES:
sp^2 HYBRIDIZATION

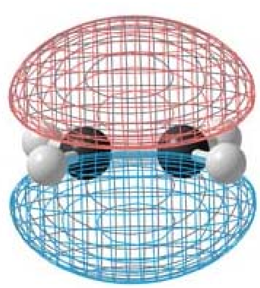
e.g., ethene (ethylene)









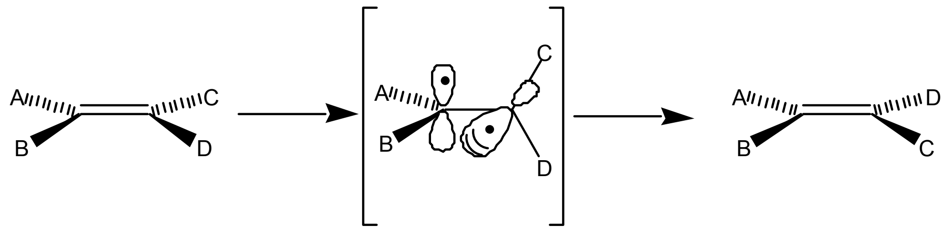


***p* + *p* orbital overlap**

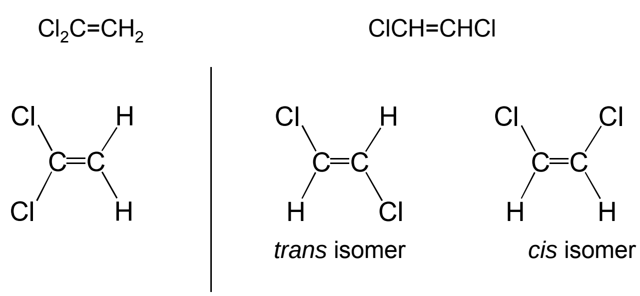
ethene (ethylene), C_2H_4: gas (bp= -102 °C). Monomer for preparation of polyethylene, used for synthesis of ethylene oxide.

LDPE HDPE

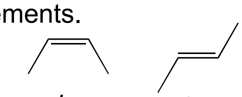
Alkenes are thermally stable and do not undergo rotation around the C=C bond.



Constitutional and Geometric Isomers of Alkenes



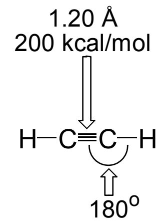
Geometric isomers have the same connectivity of atoms, but different spatial arrangements.

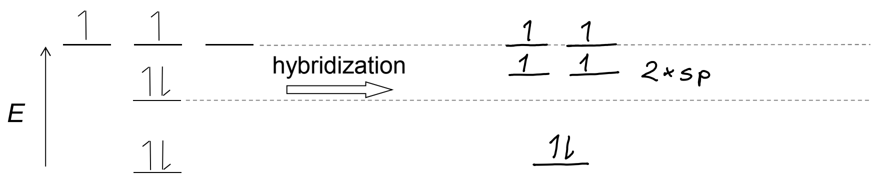


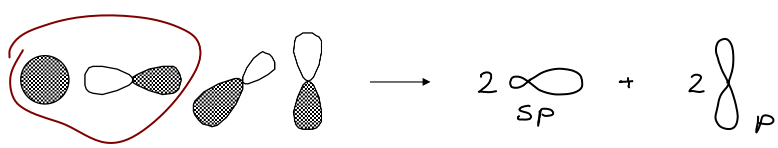
	cis	*trans*
bp/^{o}C	4	1
mp/^{o}C	-139	-104

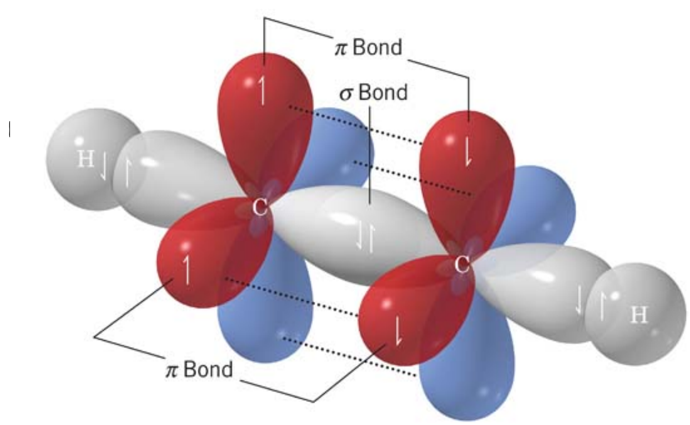
ALKYNES:
sp HYBRIDIZATION

e.g., ethyne (acetylene)



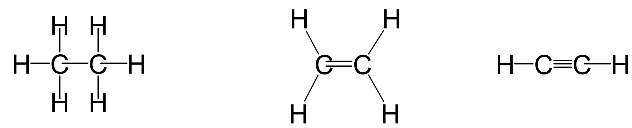






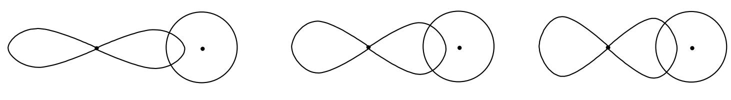
ethyne (acetylene), C_2H_2: gas (bp= -81 °C). Used in oxy-acetylene welding torches, for manufacturing of acetic acid.

Comparing C-H Bond Lengths in Alkanes, Alkenes and Alkynes



C-H bond lengths

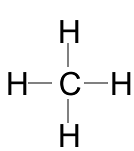
1.10 Å	1.08 Å	1.06 Å
Csp^3 + H1s	Csp^2 + H1s	Csp + H1s

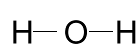


VALENCE SHELL ELECTRON PAIR REPULSION THEORY

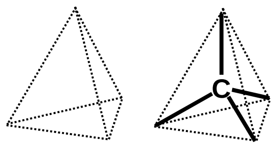
VSEPR Theory – *use to predict shape of molecules*

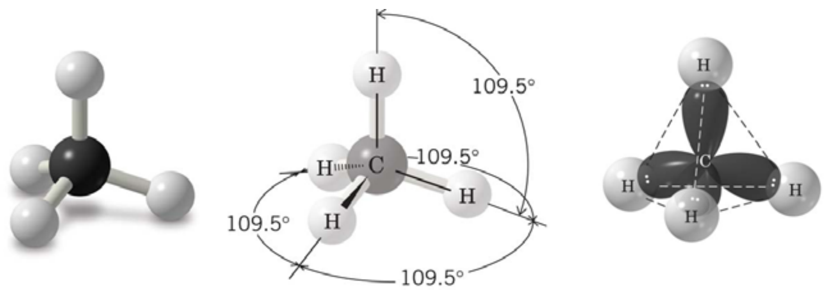
Pairs of valence e^- (in bonds and lone pairs) repel each other





sp^3 carbon atoms are tetrahedral: Practice drawing tetrahedra!





Using VSEPR theory, what are the approximate geometries of the following molecules?

1 A, trigonal planar; B, trigonal planar; C, trigonal planar

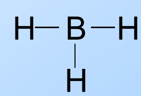
2 A, tetrahedral; B, tetrahedral; C, trigonal planar

3 A, trigonal planar; B, tetrahedral; C, linear

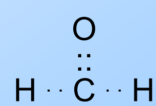
4 A, tetrahedral; B, trigonal planar; C, linear

5 A, trigonal planar; B, trigonal planar; C, linear

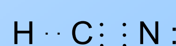
A



B

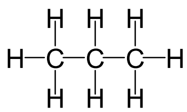


C



REPRESENTING ORGANIC MOLECULES IN 2D AND 3D

e.g., Propane (C_3H_8)



dash structure	condensed structure	bond-line structure	3-D structure

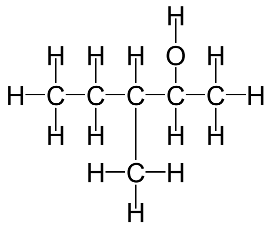
line = bond

bond end, angles, nodes = carbon

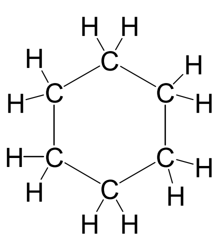
Do not show H on C; do show H on other atoms

Assume C is tetravalent unless charges/electrons are shown

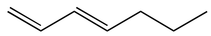
Remember you must *always show heteroatoms and hydrogen atoms on heteroatoms.* It is recommended that you always show lone pairs, however sometimes lone pairs are not shown. *Even if lone pairs are not shown, you need to be able to identify when they are present (consider octet rule and presence of charges)*

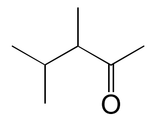


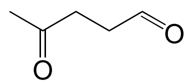
dash structure	condensed structure	bond-line structure

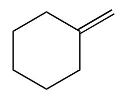


Problem. What is the molecular formula of each of the following compounds shown as bond-line structures?



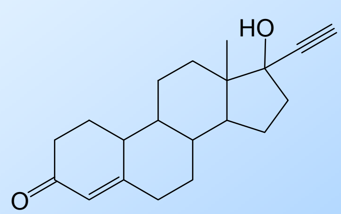






How many hydrogen atoms are there in norethindrone?

1 22
2 24
3 25
4 26
5 28

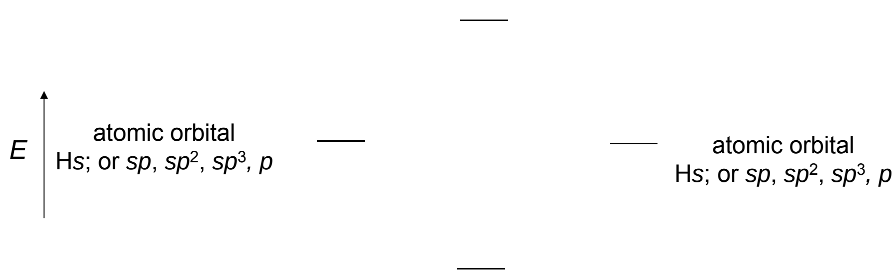


Constitutional Isomers

Given the common valencies of atoms (C=4, H=1), there might be a number of possible arrangements. These different structures are called *constitutional isomers*. Draw all the constitutional isomers with molecular formula C_4H_{10}.

BOND STRENGTHS

Orbital Energy Diagrams



Strong bonds are formed between atoms with similar size.
Long bonds are often weak.

Representative Bond Lengths and Strengths

	bond length	bond strength	
	Å	kcal/mol	kJ/mol
H-H	0.74	104	435
H-F	0.92	136	571
H-Cl	1.27	103	432
H-Br	1.41	87	366
H-I	1.61	71	289
H-O	0.97	110	460
H-C	1.10	99	414
C-C	1.55	88	368
C=C	1.33	152	636
C≡C	1.20	200	837
C-O	1.43	80	355
C=O	1.21	191	799
C-F	1.38	110	461
C-Cl	1.77	79	330
C-Br	1.95	67	280
C-I	2.14	57	240

1 Å = 10^{-10} m = 100 pm   1 kcal = 4.18 kJ

Structure ⇒ **Function**

Physical Properties of C_3H_8O

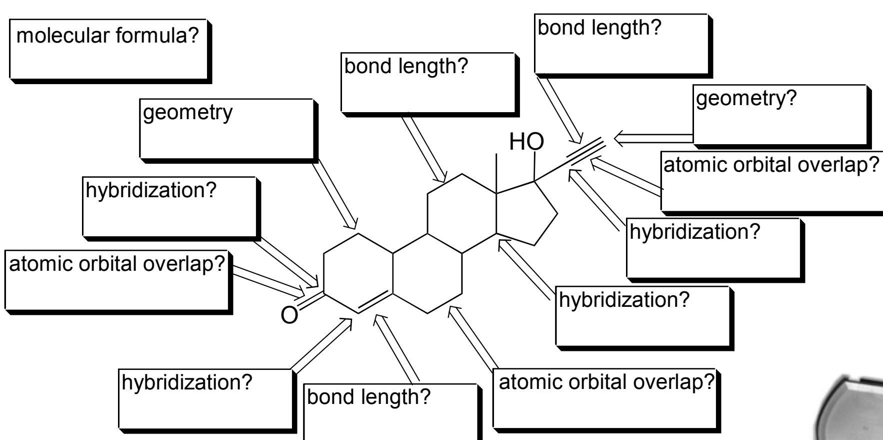
isopropyl alcohol	ethyl methyl ether
$(CH_3)_2CHOH$	$CH_3CH_2OCH_3$
water-miscible	water-insoluble
bp = 82 °C	bp = 8 °C

Reactivity of C_6H_{12}

1-hexene	cyclohexane
↓ Br_2	↓ Br_2
$C_6H_{13}Br$	no reaction

You know a lot about organic structures!

Problem. Norethindrone, is a steroidal oral contraceptive. Identify the hybridization and geometry of each atom, and the length and overlap of atomic orbitals for each bond.



What is the empirical formula?
What is the molecular formula?
What is the molecular weight?

SUMMARY: MOLECULAR STRUCTURE
CONCEPTS, MODELS, RULES AND THEORIES

Concept	*Prediction*
Valency/ Octet rule	Presence of lone pairs Formal charges
Bonding	Covalent bonds between atoms of similar electronegativity
	Ionic bonds between atoms of different electronegativity
VSEPR	Molecular geometry
Hybridization	Molecular geometry
Resonance	Charge distribution

TOPIC 1 ON EXAM 1

Types of Questions

- Identify formal charges, geometry (bond lengths, angles), hybridization.
- Draw and recognize resonance structures, constitutional isomers, atomic and molecular orbitals.

Preparing for Exam 1

- Get up-to-date *NOW!*
- Work as many problems as possible. Do the problems first, then consult the solutions manual.
- Work in groups, discuss chemistry, teach and test each other.

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