Organic chemistry background I

Organic compounds

- **Definition**
  - Any member of compounds containing carbon
  - Exception: carbonates (HCO_3^- and CO_3^{2-}), simple carbon oxides (CO and CO_2), carbides*, cyanides (CN^-)

    ** carbides: compound composed of carbon and a less electronegative element*

    (ex: CaC_2, CSi, WC)

- **Makeup of organic molecules**
  - Millions of organic compounds exist due to the ability of carbon to form up to four stable carbon-carbon bonds
  - Unlimited kinds of *carbon skeletons* can be made
  - Elemental composition: C, H, O, N, S, P, halogens
  - Heteroatoms: elements in an organic molecule other than C and H

Description of a compound

- **Elemental composition**: which elements the compound contains
- **Molecular formula**: how many atoms of each of the elements are present in one molecule
- **Molecular mass**: sum of the masses of all atoms present in the molecule
- **Molecular structure (constitution)**: the exact connection of the atoms constituting the molecule
- **Molecular geometry**: the 3-D arrangement of the atoms

Isomers

- **Isomers**: the set of compounds whose molecular formula is identical, but the molecular structures are different

- **Stereoisomers**: the set of compounds whose molecular structure is identical, but the spatial arrangements are different

Electron shells of elements

- Atoms containing **“filled shells”** are stable
  - Noble gases: He, Ne, Ar, Kr, Xe, Rn

- Atoms in organic molecules have **tendencies to attain filled-shell conditions** by gaining, losing, or most importantly, **sharing electrons**
  - 1^{st} shell (K-shell): holds 2 electrons ($1s^2$)
  - 2^{nd} shell (L-shell): holds 8 electrons ($1s^2\ 2s^2\ 2p^6$)
  - 3^{rd} shell (M-shell): holds 18 electrons ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$), but a stable configuration is reached when the shell is filled with 8 electrons ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$)

Electron shells of elements

ref: EOC text

Table 2.1 Atomic Mass, Electronic Configuration, and Typical Number of Covalent Bonds of the Most Important Elements Present in Organic Molecules

	Element[a]			Number of Electrons in Shell						
Name	Symbol	Number	Mass[b] (u)	K	L	M	N	O	Net Charge of Kernel	Number of Covalent Bonds Commonly Occurring in Organic Molecules
Hydrogen	H	1	1.008	1					1+	1
Helium	He	2		2					0	
Carbon	C	6	12.011	2	4				4+	4
Nitrogen	N	7	14.007	2	5				5+	3,(4)[c]
Oxygen	O	8	15.999	2	6				6+	2,(1)[d]
Fluorine	F	9	18.998	2	7				7+	1
Neon	Ne	10		2	8				0	
Phosphorus	P	15	30.974	2	8	5			5+	3,5
Sulfur	S	16	32.06	2	8	6			6+	2,4,6(1)[d]
Chlorine	Cl	17	35.453	2	8	7			7+	1
Argon	Ar	18		2	8	8			0	
Bromine	Br	35	79.904	2	8	18	7		7+	1
Krypton	Kr	36		2	8	18	8		0	
Iodine	I	53	126.905	2	8	18	18	7	7+	1
Xenon	Xe	54		2	8	18	18	8	0	

[a] The underlined elements are the noble gases. [b] Based on the assigned atomic mass constant of u = atomic mass of $^{12}C/12$; abundance-averaged values of the naturally occurring isotopes.
[c] Positively charged atom. [d] Negatively charged atom.

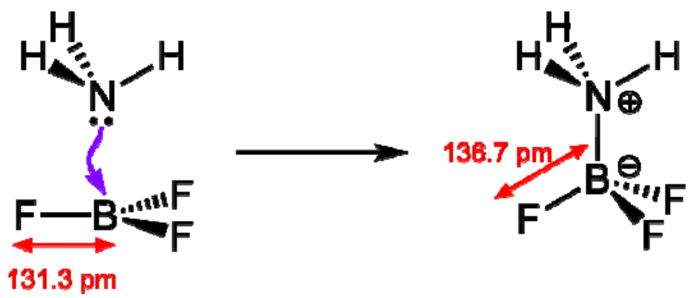
Covalent bond

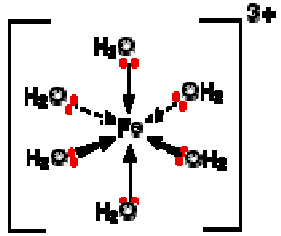
- Octet rule: atoms tend to combine in such a way that each atom has 8 electrons in its outer (valence) shell

- Covalent bond
  - Atoms complete their outer-shell octet by sharing a pair electrons, in most cases one electron contributed by each of the two bonded atoms
  - Each atom feels it has both of the shared electrons
  - The electron pairs are localized between the two positive atomic nuclei; the electrostatic attraction of these nuclei to these electrons holds the atoms together

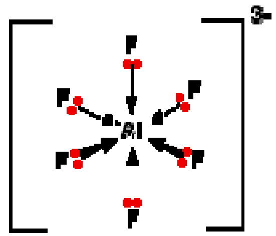
Covalent bond

- Coordinate bond
  - A kind of a covalent bond in which the two electrons derive from the same atom
  - One atom donates a lone pair of electrons (Lewis base) and the other atom accepts the electron pair (Lewis acid)

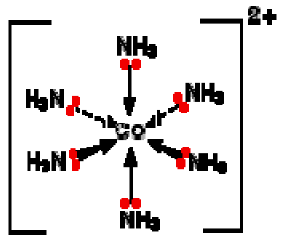




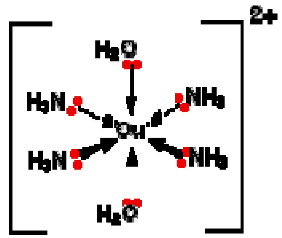
$[Fe(H_2O)_6]^{3+}$



$[AlF_6]^{3-}$

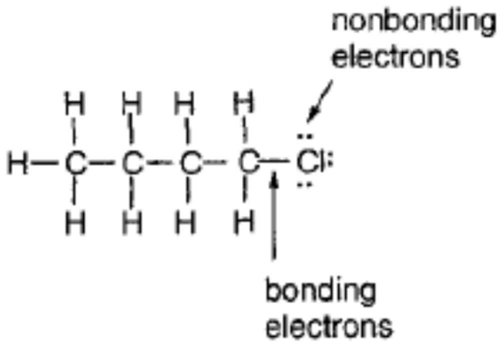


$[Co(NH_3)_6]^{2+}$



$[Cu(NH_3)_4(H_2O)_2]^{2+}$

Drawing molecular structures

(1) 

(3) $H_3CCH_2CH_2CH_2Cl$

(2) $H_3C-CH_2-CH_2-CH_2-Cl$

(4) 

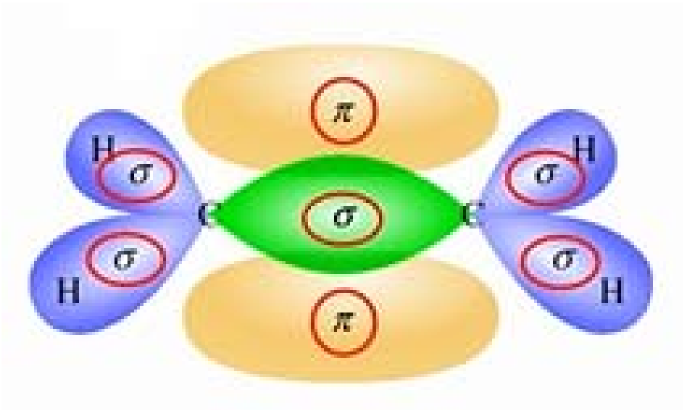
Covalent bonding

Q: How many (structural) isomers are there for monochlorinated butane (C_4H_9Cl)? Draw the chemical structures of all isomers.

Double and triple bonds

- Atoms with more than one missing electrons in their outer shells may form double or triple bonds

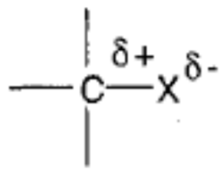
- Single covalent bond is a sigma (σ) bond; double and triple bonds contain one σ bond and π bond(s)
  - σ bond: a covalent bond in which orbital overlap of the bond is concentrated along the axis joining the two nuclei
  - π bond: a covalent bond formed by overlap of parallel p orbitals (generally weaker than the σ bonds)



http://chemistryistorture.blogspot.kr/2013/03/red-high-density-valence-bond-theory-so.html

Electronegativity

- The "electron cloud" or averaged electron position located between the two nuclei is, in general, distorted toward the atom that has the higher attraction for the electrons (the atom that is more ***electronegative***)
  - ex: carbon-halogen bond



- Electronegativity increases with increasing kernel size within a row in the Periodic Table and decreases with increasing kernel size within a column

Electronegativity

H 2.1																	He —
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne —
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar —
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr —
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe —
Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn —

ref: http://chemwiki.ucdavis.edu/Inorganic_Chemistry/Descriptive_Chemistry/ Periodic_Trends_of_Elemental_Properties/Periodic_Trends

Oxidation state

- For convenience, assign the possession of the electron pair in a covalent bond to the more electronegative atom

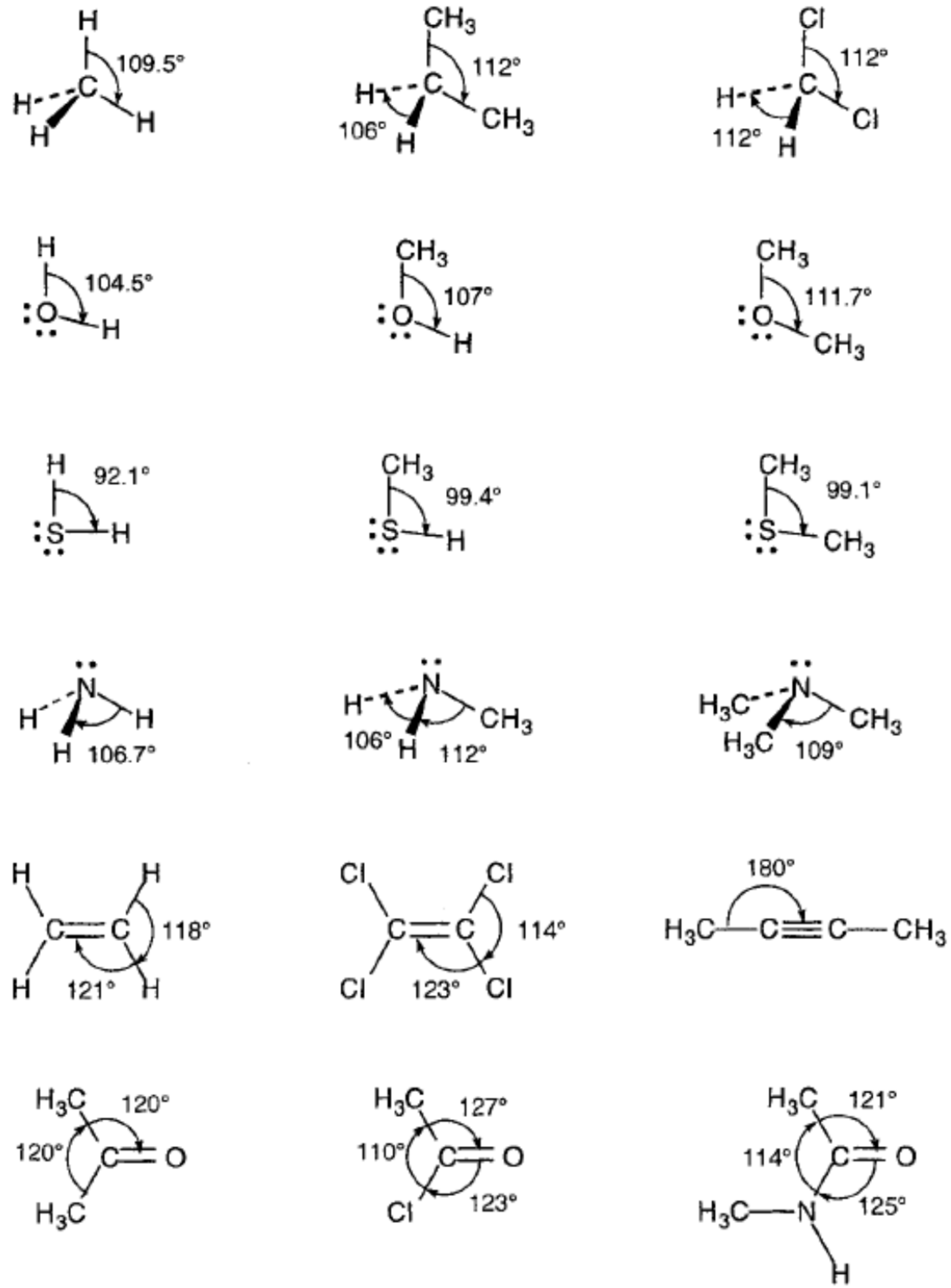
- Add 0 for each bond to an identical atom; -1 for each bond to a less electronegative atom or for each negative charge on the atom; +1 for each bond to a more electronegative atom or for each positive charge on the atom

Oxidation state

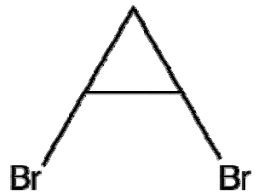
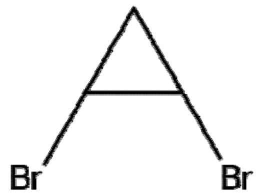
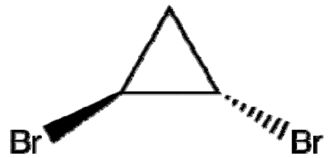
Q: Determine the oxidation state of each atom in acetate (CH_3COO^-).

Spatial arrangement of atoms

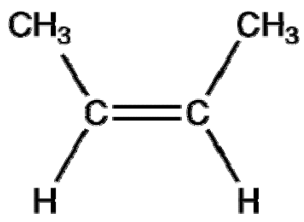
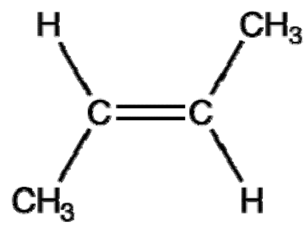
- Each pair of electrons, shared or unshared, wants to stay as far as possible from one another
  - For a carbon atom with four single bonds will form a tetrahedron
  - When carbon is bound to four identical atoms or groups (ex: CH_4), the bond angles should be 109.5°
  - The difference of the atoms or groups bound to a carbon leads to minor variations in the bond angles



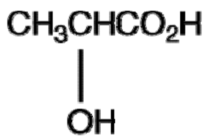
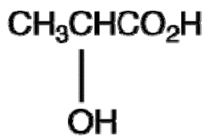
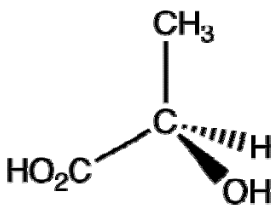
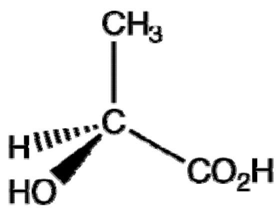
Stereoisomers

	cis–1,2–dibromo cyclopropane **(1)**	*trans*–1,2–dibromo cyclopropane **(2)**
molecular formula	$C_3H_4Br_2$	$C_3H_4Br_2$
structural formula		
configuration		

Stereoisomers

	cis–2–butene **(1)**	*trans*–2–butene **(2)**
molecular formula	C_4H_8	C_4H_8
structural formula	$CH_3CH{=}CHCH_3$	$CH_3CH{=}CHCH_3$
configuration		

Stereoisomers

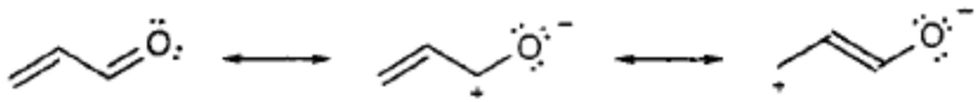
	(*R*)–lactic acid **(1)**	(*S*)–lactic acid **(2)**
molecular formula	$C_3H_6O_3$	$C_3H_6O_3$
structural formula		
configuration		

Delocalized electrons

- In some steric arrangements of organic molecules, electrons may move throughout a region covering more than two atoms
- Occurs in molecules exhibiting multiple π bonds spaced so that they can interact with one another
- Such series of π bonds are called “conjugated”
- The conjugated π bonds must be adjacent to each other and the σ bonds of all atoms involved must lie in one plane

Delocalized electrons

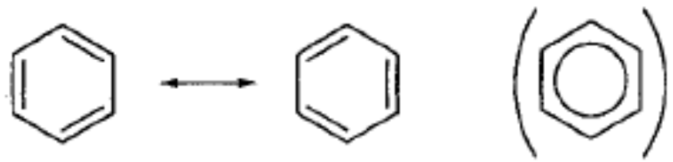
ex) acrolein (propenal): CH_2=CH-CHO



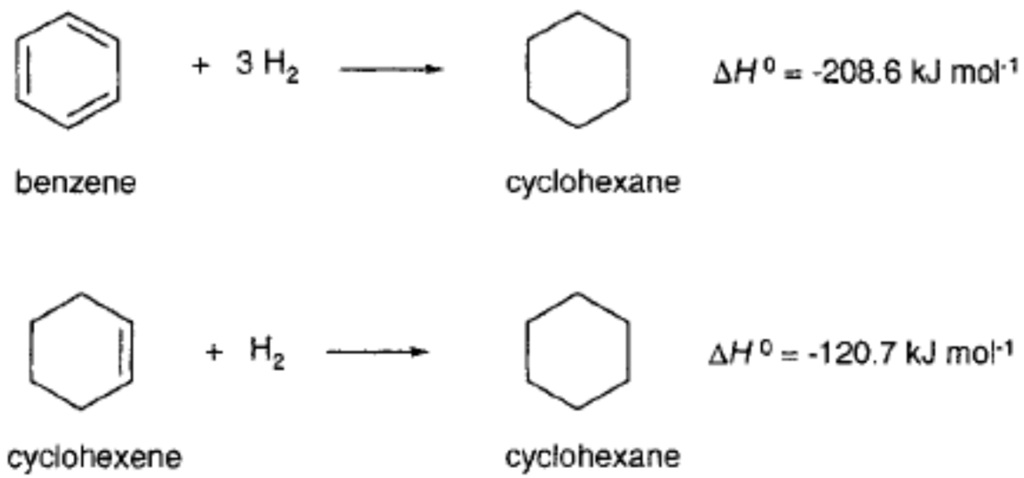
- The chemical structure is represented by extreme possibilities with back-and-forth arrows
- This does not mean the compound is in one of the extreme possibilities: the compound structure is somewhere in between
- This way of representing a chemical structure is called the ***resonance*** method

Delocalized electrons

ex) benzene: C_6H_6

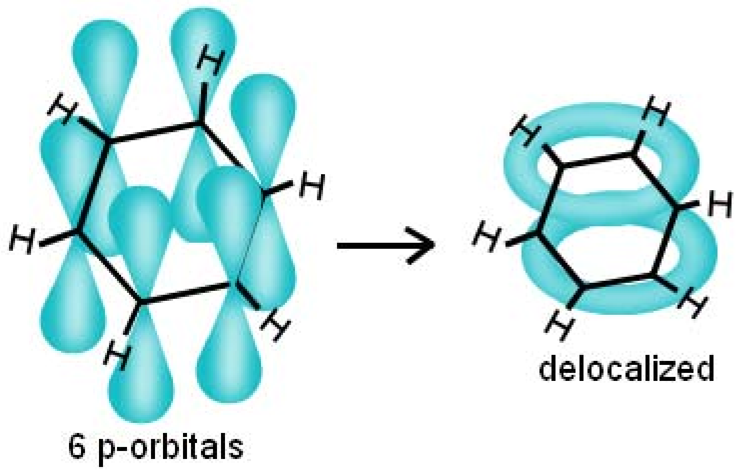


– The conjugation of the π bonds leads to greater stability of the chemical

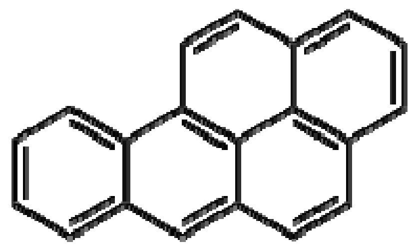


Aromatic compounds

- Aromaticity: the quality that renders a ring system especially stable by conjugated double bonds
- Aromatic rings: organic rings in which electrons are delocalized
- Polycyclic aromatic hydrocarbons: organic compounds containing only C and H, composed of multiple aromatic rings



ref: http://chemistry.tutorvista.com/organic-chemistry/benzene-reactions.html



Structure of benzo(a)pyrene

ref: http://http://en.wikipedia.org/wiki/Polycyclic_aromatic_hydrocarbon

Types of organic compounds

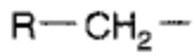
- **Volatile organic compounds (VOCs)**
- **Hydrophobic organic compounds (HOCs)**
- **Persistent organic pollutants (POPs)**
- **Endocrine disrupting compounds (EDCs)**
- **Pharmaceuticals and personal care products (PPCPs)**
- **Emerging contaminants**
- **Surfactants**
- **Solvents**
- **Plasticizers**
- **Pesticides (herbicides, insecticides, fungicides, …)**

Carbon skeleton

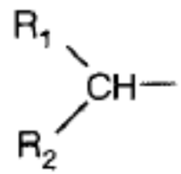
- Saturated vs. unsaturated
  - **Saturated**: no double or triple bond
  - **Unsaturated**: at least one double or triple bond
- Aliphatic / alicyclic / aromatic
  - **Aliphatic**: no ring structures
  - **Alicyclic**: contains at least one ring structure
  - **Aromatic**: contains at least one aromatic ring

Carbon skeleton

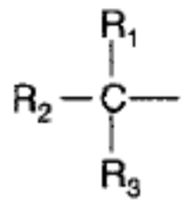
- Saturated aliphatic hydrocarbons
  - C_nH_{2n+2}
  - Called an **alkane** or a **paraffin**
  - Suffix: -ane
  - Prefix
    - ***n*** (normal)-: unbranched
    - ***iso-***: two methyl groups at the end
    - ***neo-***: three methyl groups at the end
  - Classification of alkyl (C_nH_{2n+1}) groups
    - *primary, secondary, tertiary*



primary



secondary

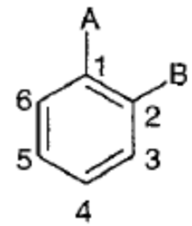


tertiary

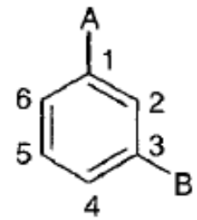
Carbon skeleton

- Unsaturated aliphatic hydrocarbons
  - **Alkenes** (or olefins): compounds containing one or several double bonds (ends with –ene)
  - **Alkynes**: compounds containing one or several triple bonds (ends with –yne)

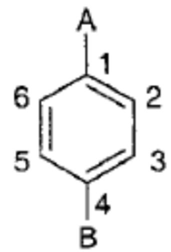
- Nomenclature in aromatic systems
  - Depending on the relative position of two substituents in a given ring system: *ortho-, meta-, para*



ortho or 1,2-



meta or 1,3-



para or 1,4-

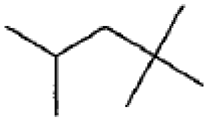
Carbon skeleton

- Examples of hydrocarbons

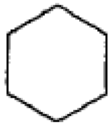
(a)

(b)

(c)



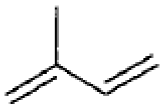
(d)



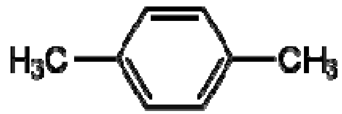
(e)

(f)

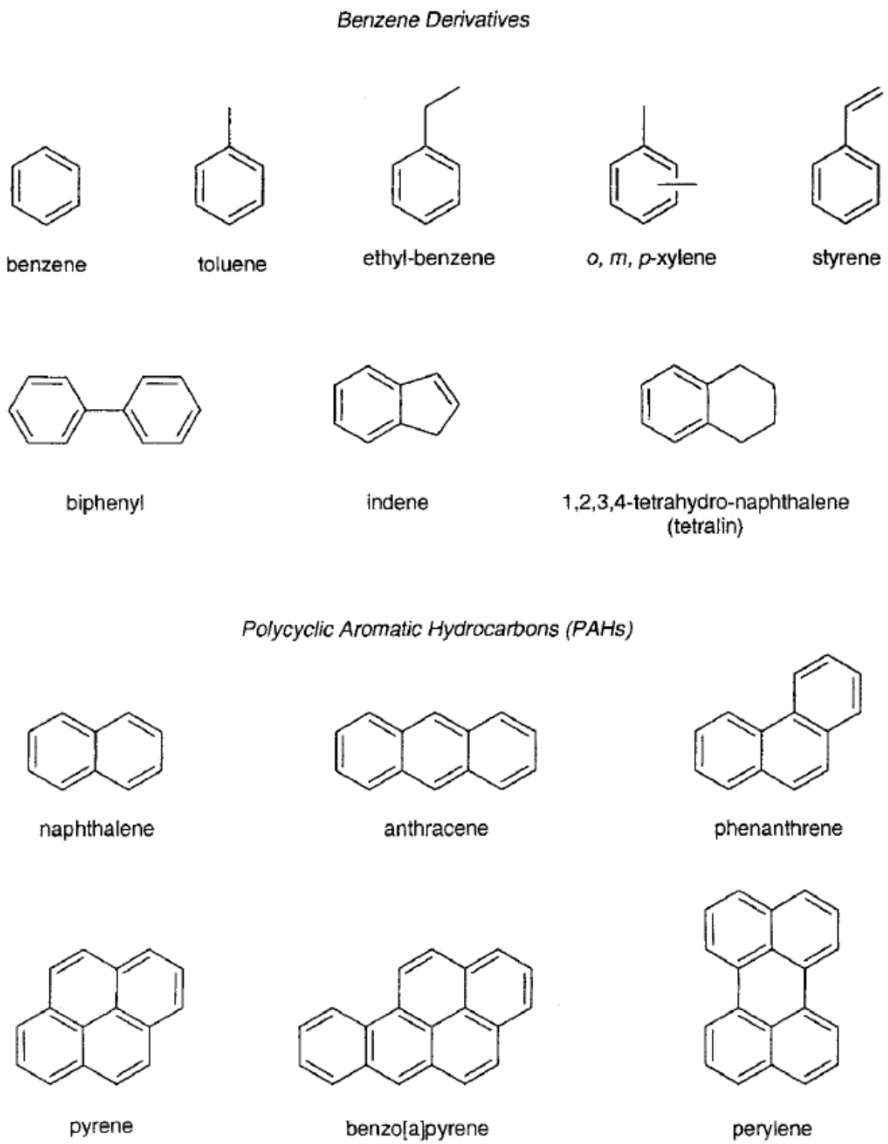
(g)



(h)



Aromatic hydrocarbons



- **BTEX**: **b**enzene, **t**oluene, **e**thyl-benzene, **x**ylenes; gasoline constituents

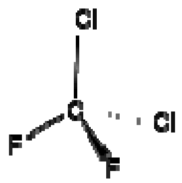
- **Polycyclic aromatic hydrocarbons (PAHs)**
  - Sources: combustion of fossil fuels, forest fires, mineral oils, creosotes, …
  - Some members are carcinogenic (ex: benzo[a]pyrene)
  - Planar structure
  - Bay region

Organohalogens

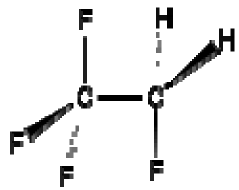
- Organic molecules containing one or several halogen (Cl, F, Br) atoms
- Vast production; significant environmental problem
- Characteristics
  - Strong C-X bonds (high electronegativity of halogens): Enhanced inertness of the molecule
  - **Very weak tendency to be engaged in hydrogen bonds**: Enhanced hydrophobicity, partitions into organic phases (accumulated in lipids)

Examples of organohalogens

- CFCs (chlorofluorocarbons): ozone-depletion and global warming potential



Dichlorodifluoromethane

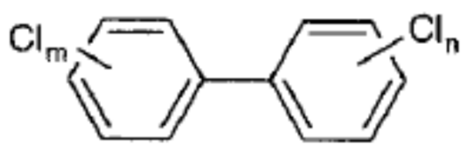


Tetrafluoroethane

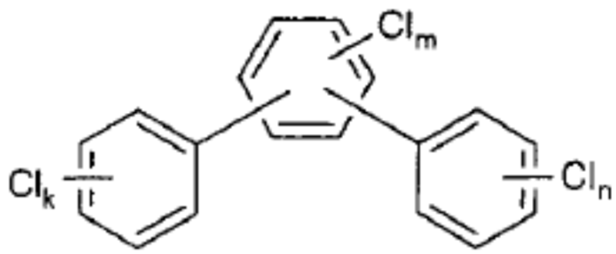
- Chlorinated solvents
  - Dichloromethane, trichloroethene, tetrachloroethene, 1,1,1-trichloroethane
  - One of the common groundwater pollutants

Examples of organohalogens

- Polychlorinated biphenyls (PCBs) and polychlorinated terphenyls (PCTs)
  - Congeners: isomers and compounds exhibiting different numbers of chlorine atoms but having the same source
  - 209 PCB congeners, 8149 PCT congeners
  - Uses: waxes, printing inks, paints, capacitor dielectric fluids, transformer coolants, etc.
  - Banned in many countries, but still ubiquitous in the environment



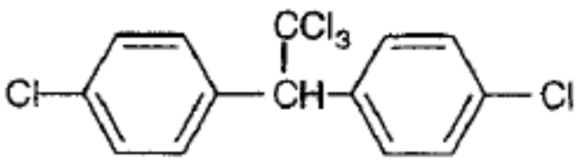
polychlorinated biphenyls
(PCBs, 209 possible congeners)



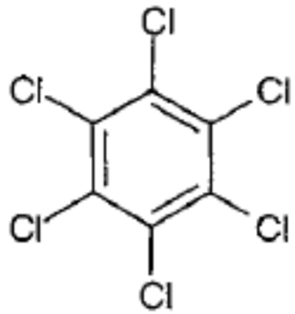
polychlorinated terphenyls
(PCTs, 8149 possible congeners)

Examples of organohalogens

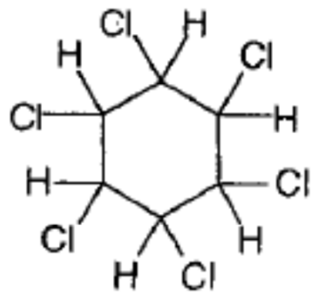
- Organochlorine pesticides
  - DDT, HCB, and HCH



p,p'-DDT



hexachlorobenzene
(HCB)



1,2,3,4,5,6-hexachlorocyclohexane
(HCH, 8 isomers,
one of them exists as a pair
of enantiomers)