

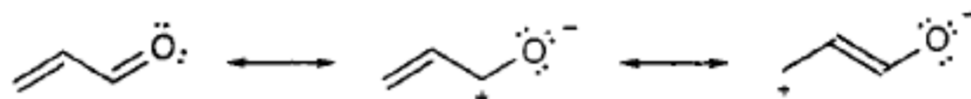
Organic chemistry background II

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

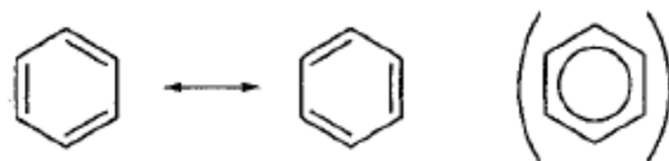
ex) acrolein (propenal): $\text{CH}_2=\text{CH}-\text{CHO}$



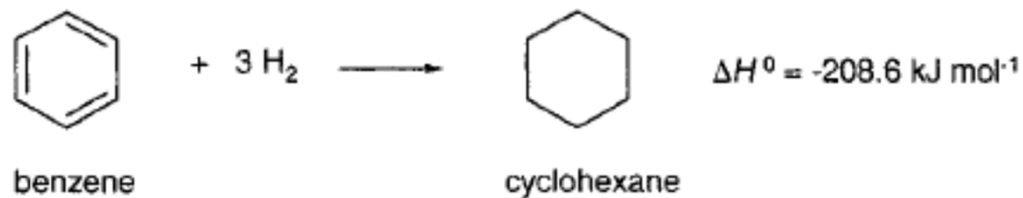
- The chemical structure is represented by extreme possibilities with back-and-forth arrows
- This does not mean the compound is in one of the extreme possibilities: the compound structure is somewhere in between
- This way of representing a chemical structure is called the **resonance** method

Delocalized electrons

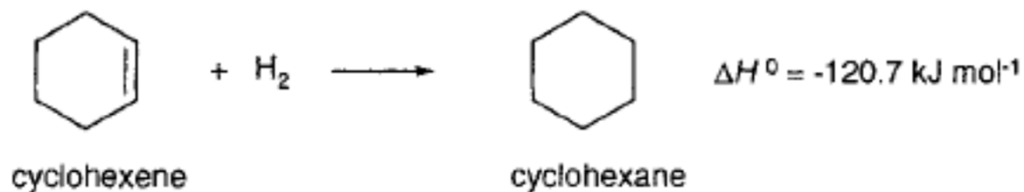
ex) benzene: C_6H_6



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

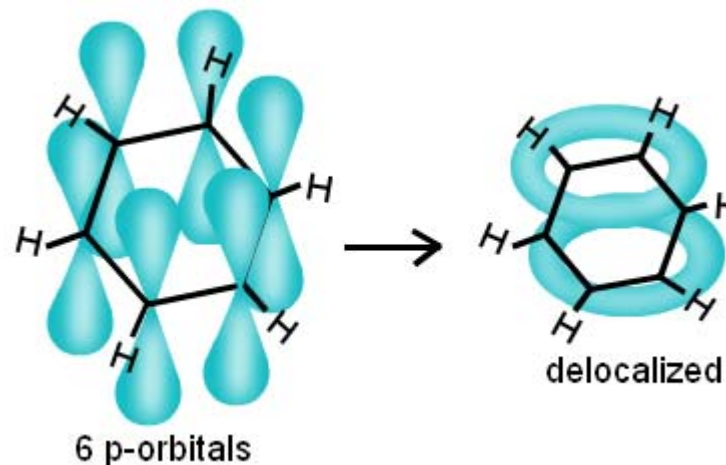


cf) $-120.7 \times 3 = -362.1$

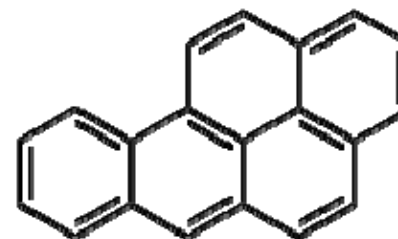


Aromatic compounds

- **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 (PAHs):** 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

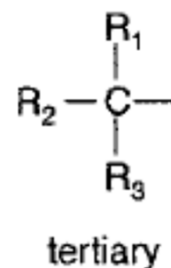
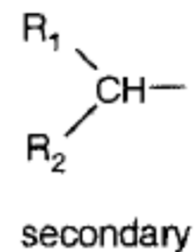
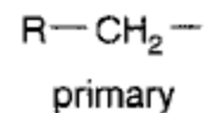
- **Volatile organic compounds (VOCs)**
- **Hydrophobic organic compounds (HOCs)**
- **Persistent organic pollutants (POPs)**
- **Endocrine disrupting compounds (EDCs)**
- **Pharmaceuticals and personal care products (PPCPs)**
- **Emerging contaminants**
- **Surfactants**
- **Solvents**
- **Plasticizers**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

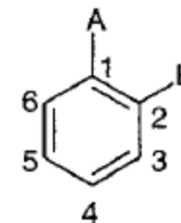
Carbon skeleton

- 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*

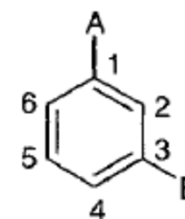


Carbon skeleton

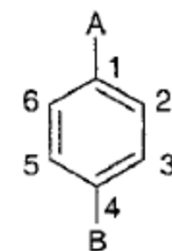
- Unsaturated aliphatic hydrocarbons
 - **Alkenes** (or olefins): compounds containing one or several double bonds (ends with –ene)
 - **Alkynes**: compounds containing one or several triple bonds (ends with –yne)
- Nomenclature in aromatic systems
 - Depending on the relative position of two substituents in a given ring system: *ortho-*, *meta-*, *para*



ortho or 1,2-



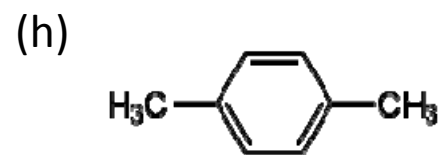
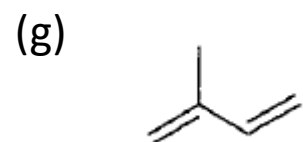
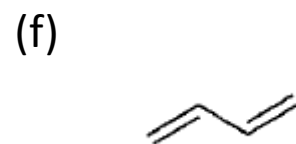
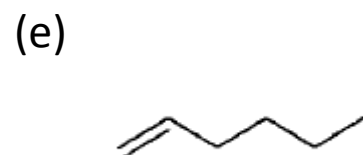
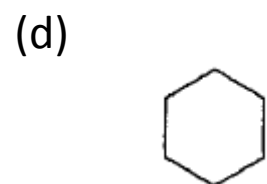
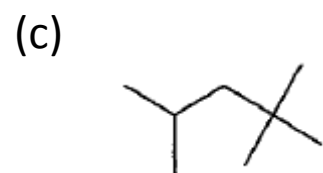
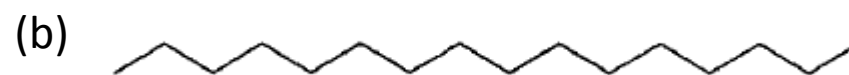
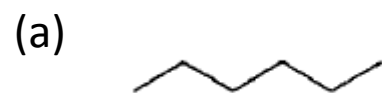
meta or 1,3-



para or 1,4-

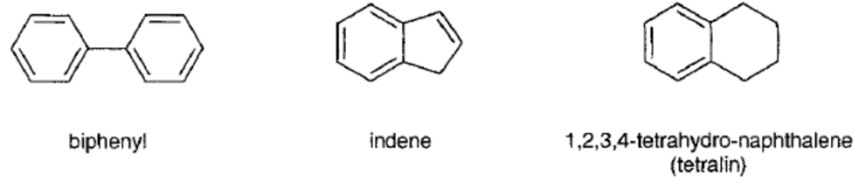
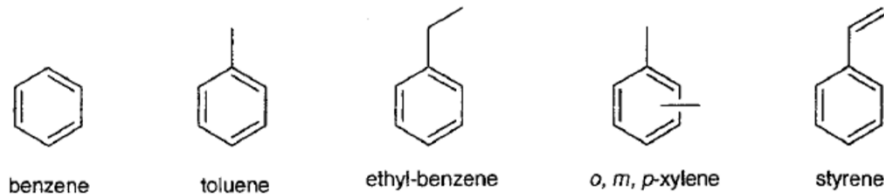
Carbon skeleton

- Examples of hydrocarbons

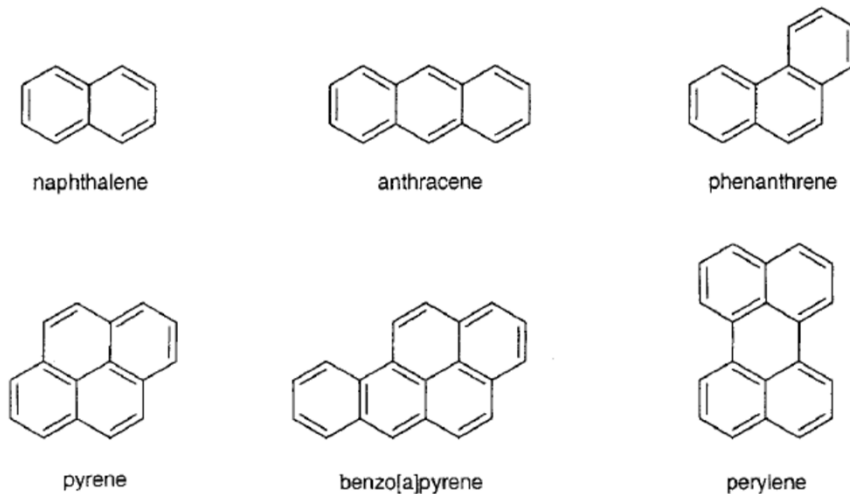


Aromatic hydrocarbons

Benzene Derivatives



Polycyclic Aromatic Hydrocarbons (PAHs)



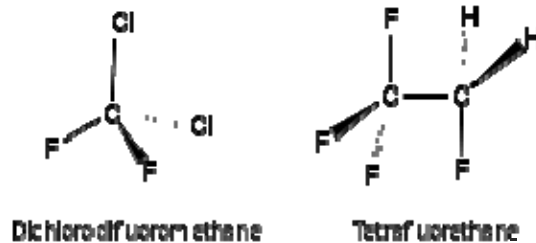
- **BTEX: benzene, toluene, ethyl-benzene, xylenes; gasoline constituents**
- **Polycyclic aromatic hydrocarbons (PAHs)**
 - Sources: combustion of fossil fuels, forest fires, mineral oils, creosotes, ...
 - Some members are carcinogenic (ex: benzo[a]pyrene)
 - Planar structure
 - Bay region

Organohalogenes

- 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 organohalogenes

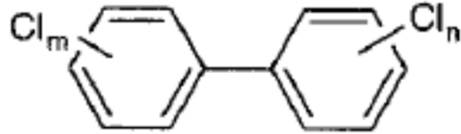
- **CFCs** (chlorofluorocarbons): ozone-depletion and global warming potential



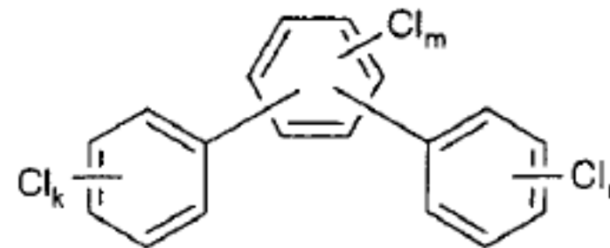
- **Chlorinated solvents**
 - Dichloromethane, trichloroethene (TCE), tetrachloroethene (PCE), 1,1,1-trichloroethane
 - One of the common groundwater pollutants

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



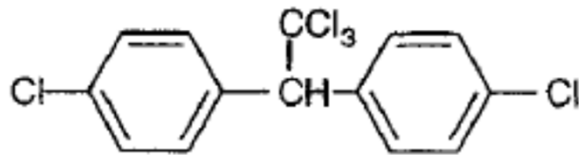
polychlorinated biphenyls
(PCBs, 209 possible congeners)



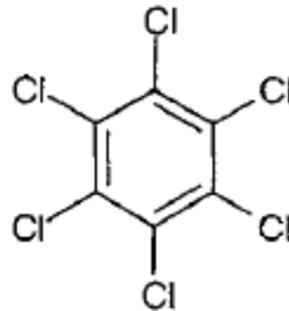
polychlorinated terphenyls
(PCTs, 8149 possible congeners)

Examples of organohalogens

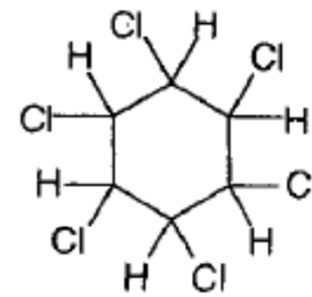
- **Organochlorine pesticides**
 - DDT, HCB, and HCH



p,p'-DDT



hexachlorobenzene
(HCB)

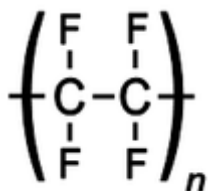


1,2,3,4,5,6-hexachlorocyclohexane
(HCH, 8 isomers,
one of them exists as a pair
of enantiomers)

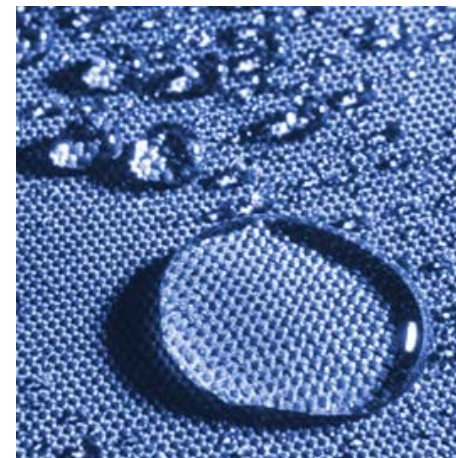
Examples of organohalogens

prefix "per-" denotes thorough or utterly

- **Perfluorinated compounds (PFCs)**
 - Organofluorine compounds containing only C-F and C-C bonds in their backbone structure with functional groups containing other heteroatoms
 - Highly stable, non-wetting, very slippery, fire resistant
 - Teflon production, fire-fighting foam, used in metal plating, photographic, fabric and semiconductor industry
 - PFOS (perfluorooctane sulfonate) and PFOA (perfluorooctanoic acid): major emerging contaminants in concern



Teflon



Examples of organohalogens

- **Brominated flame retardants**

- Emerging contaminants of current concern
- Inhibitory effect on combustion processes → reduce the flammability of products they are applied to
- Widely used in plastics and textile applications
- Major groups: polybrominated biphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs)

