

# Organic chemistry background II

# Delocalized electrons

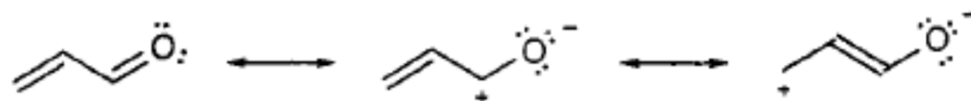
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- In some steric arrangements of organic molecules, electrons may move throughout a region covering more than two atoms
- Occurs in molecules exhibiting multiple  $\pi$  bonds spaced so that they can interact with one another
- Such series of  $\pi$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

# Delocalized electrons

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

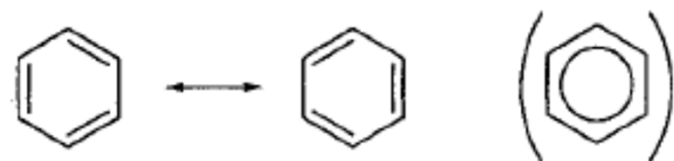


- The chemical structure is represented by extreme possibilities with back-and-forth arrows
- This does not mean the compound is in one of the extreme possibilities: the compound structure is somewhere in between
- This way of representing a chemical structure is called the **resonance** method

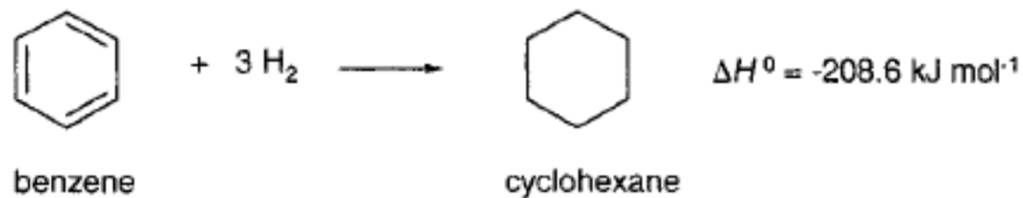
# Delocalized electrons

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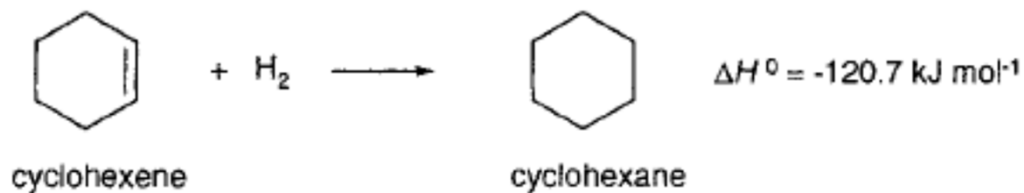
ex) benzene: C<sub>6</sub>H<sub>6</sub>



- The conjugation of the  $\pi$  bonds leads to greater stability of the chemical



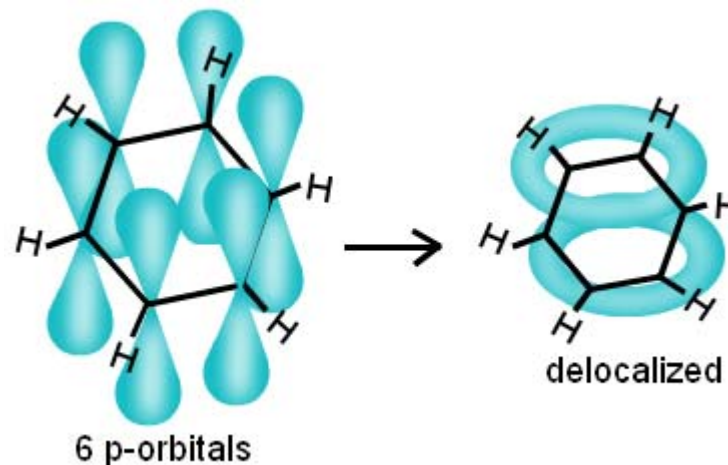
*cf)  $-120.7 \times 3 = -362.1$*



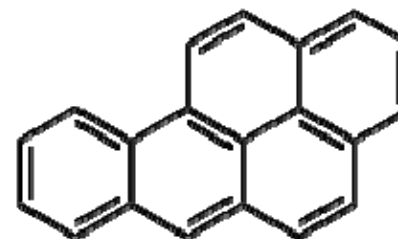
# Aromatic compounds

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- **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](http://http://en.wikipedia.org/wiki/Polycyclic_aromatic_hydrocarbon)

# Types of organic compounds

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- **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

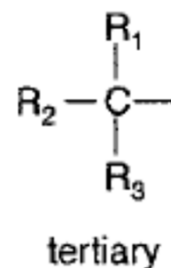
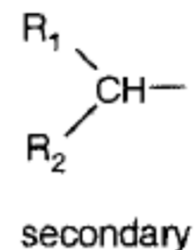
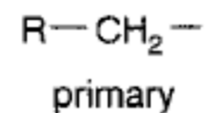
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- Saturated vs. unsaturated
  - **Saturated:** no double or triple bond
  - **Unsaturated:** at least one double or triple bond
- Aliphatic / alicyclic / aromatic
  - **Aliphatic:** no ring structures
  - **Alicyclic:** contains at least one ring structure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

# Carbon skeleton

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- 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*

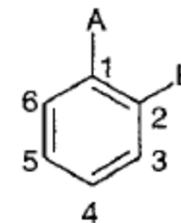




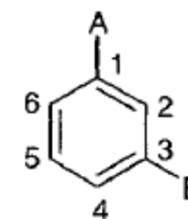
# Carbon skeleton

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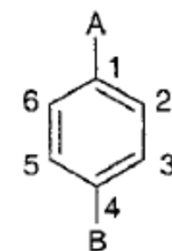
- Unsaturated aliphatic hydrocarbons
  - **Alkenes** (or olefins): compounds containing one or several double bonds (ends with –ene)
  - **Alkynes**: compounds containing one or several triple bonds (ends with –yne)
- Nomenclature in aromatic systems
  - Depending on the relative position of two substituents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



*ortho* or 1,2-



*meta* or 1,3-

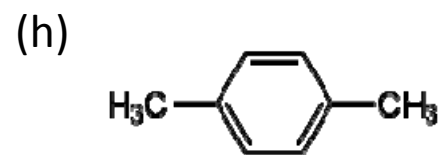
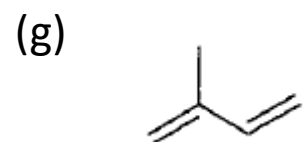
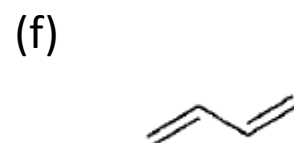
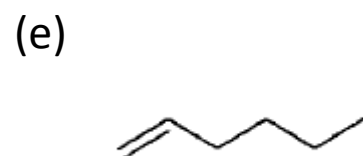
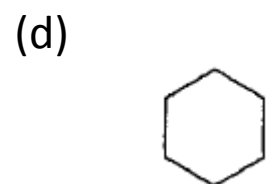
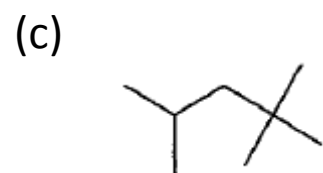
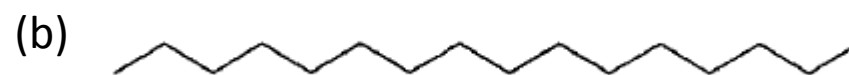
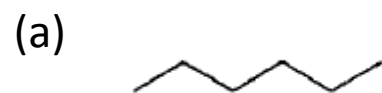


*para* or 1,4-

# Carbon skeleton

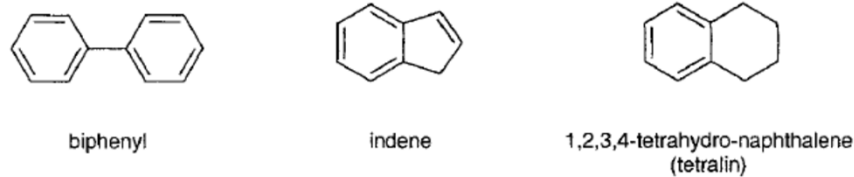
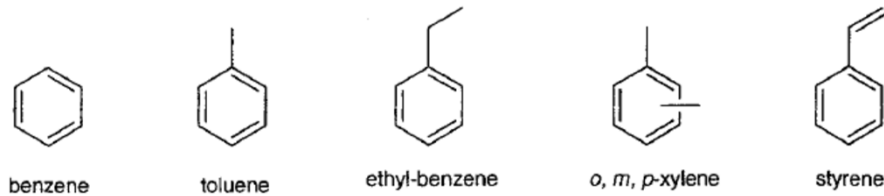
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- Examples of hydrocarbons

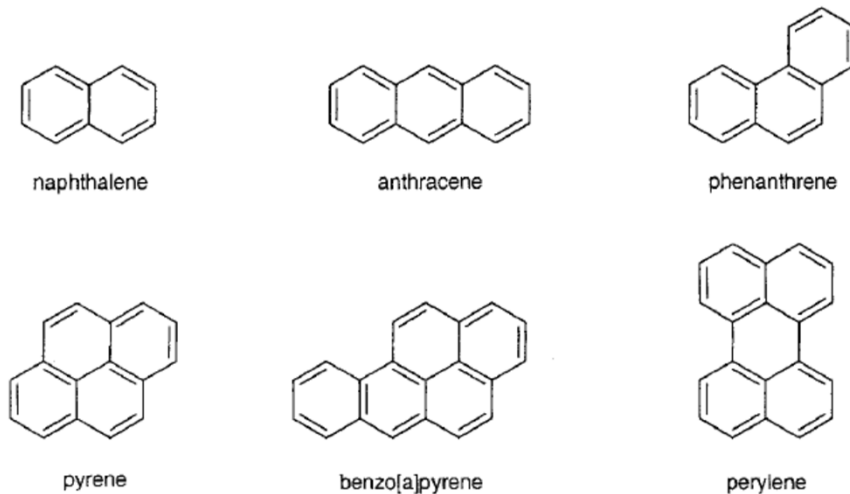


# Aromatic hydrocarbons

## 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

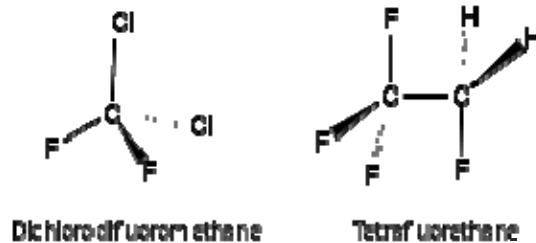
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- Organic molecules containing one or several halogen (Cl, F, Br) atoms
- Vast production; significant environmental problem
- Characteristics
  - Strong C-X bonds (high electronegativity of halogens): Enhanced inertness of the molecule
  - **Very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

# Examples of organohalogenes

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

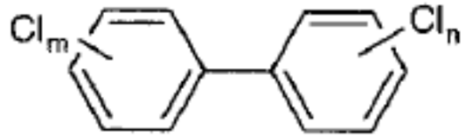


- **Chlorinated solvents**
  - Dichloromethane, trichloroethene (TCE), tetrachloroethene (PCE), 1,1,1-trichloroethane
  - One of the common groundwater pollutants

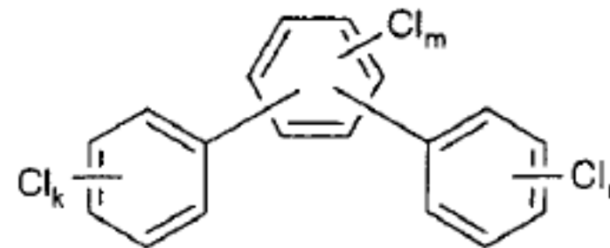
# Examples of organohalogens

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- **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)

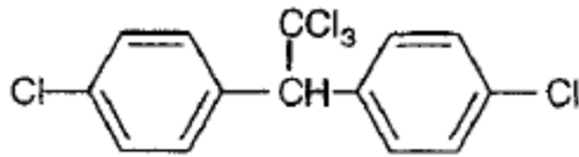


polychlorinated terphenyls  
(PCTs, 8149 possible congeners)

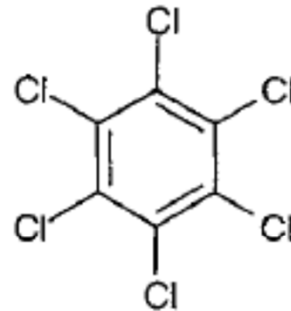
# Examples of organohalogenes

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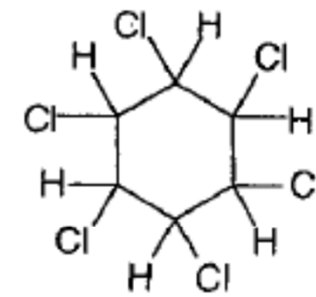
- **Organochlorine pesticides**
  - DDT, HCB, and HCH



p,p'-DDT



hexachlorobenzene  
(HCB)

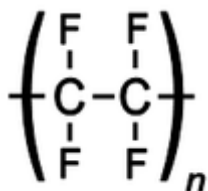


1,2,3,4,5,6-hexachlorocyclohexane  
(HCH, 8 isomers,  
one of them exists as a pair  
of enantiomers)

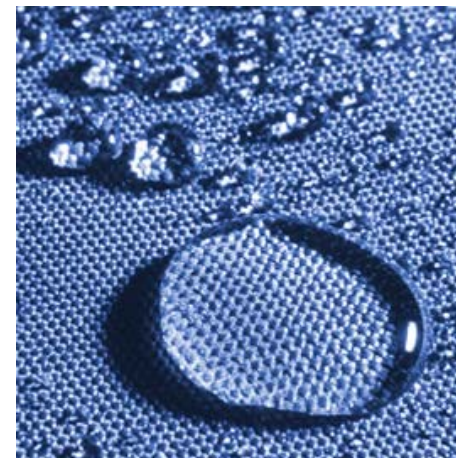
# Examples of organohalogens

*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

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- **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)

