Organic chemistry background III:
Delocalization of electrons

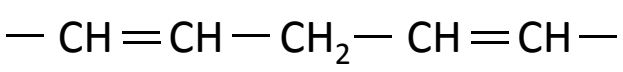
Delocalized electrons

- 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"**

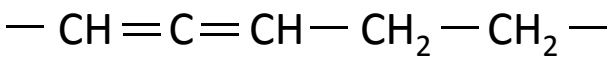
Conjugated double bonds occur when

- Two double bonds originates at adjacent atoms

cf1) isolated → non-conjugated

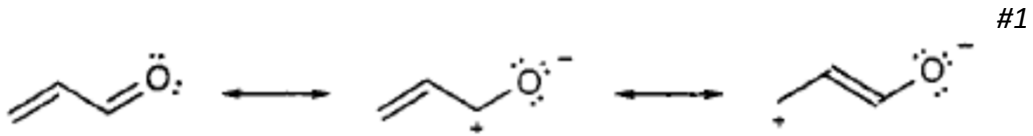


cf2) cumulated



Resonance method

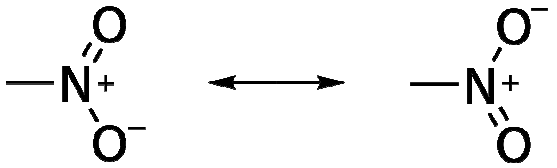
ex) acrolein (propenal): CH_2=CH-CHO



- 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

Conjugate bond examples

#2



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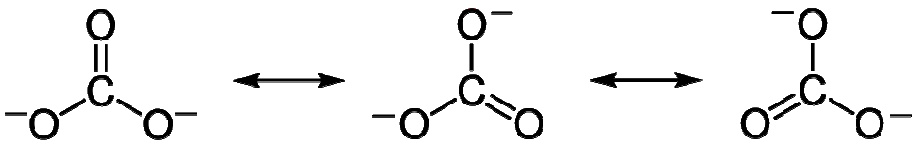

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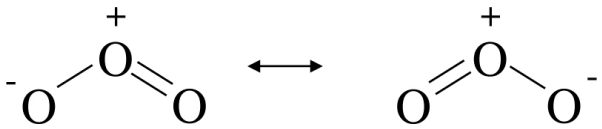

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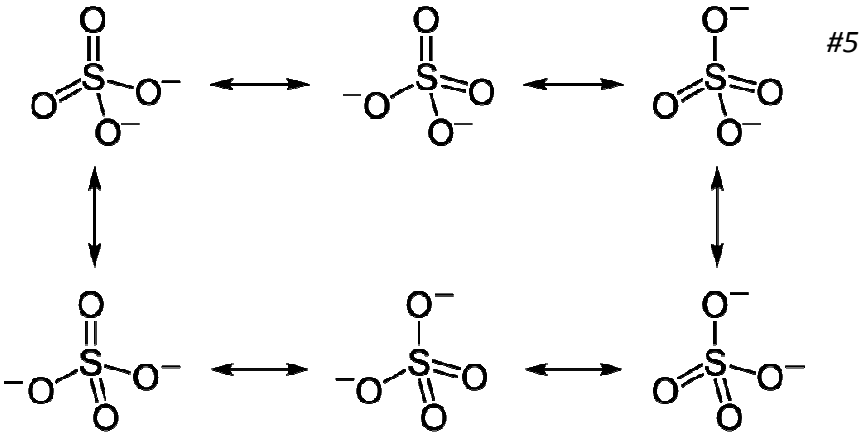


Electron shifts

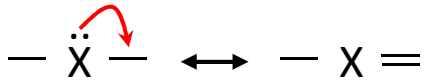
- Useful when writing resonance structures

- Draw electron-shift arrows for the followings:

  – From a π bond to an adjacent bond position:

  – From a π bond to an adjacent atom:

  – From an atom to an adjacent bond position:



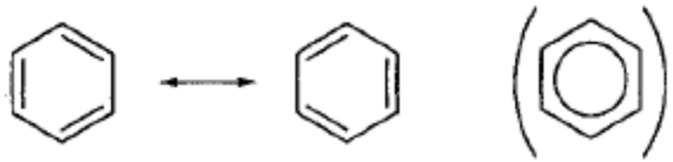
Representing resonance structures

Q: Use electron shifts to identify and represent the resonance structure for acetate (CH_3COO^-).

Delocalized electrons in a ring structure

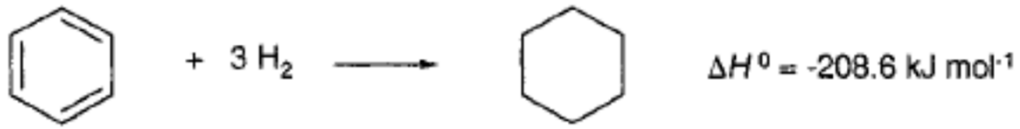
ex) benzene: C_6H_6

#1



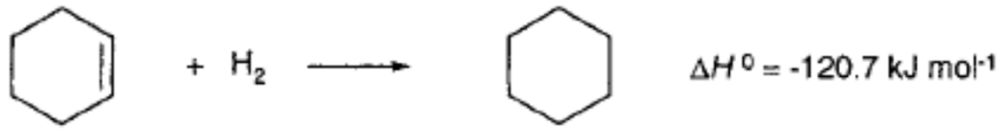
– The conjugation of the π bonds leads to greater stability of the chemical

#1



benzene cyclohexane

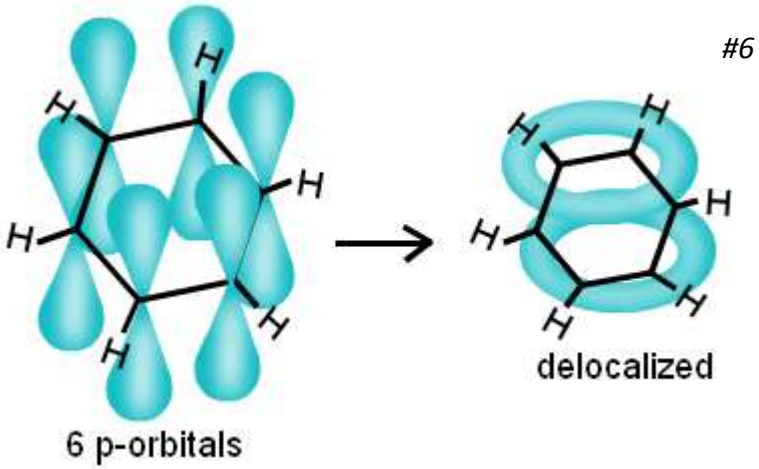
cf) -120.7 × 3 = -362.1



cyclohexene cyclohexane

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



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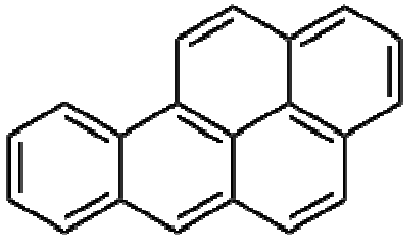


#7

Structure of benzo(a)pyrene

References

#1) Schwarzenbach, R., Gschwend, P. M., Imboden, D. M. (2003) Environmental Organic Chemistry, 2nd ed., John Wiley & Sons, p. 29.

#2) https://commons.wikimedia.org/wiki/File:Nitro_group_resonance_structure.svg

#3) https://en.wikipedia.org/wiki/File:Carbonate-ion-resonance-2D.png

#4) https://commons.wikimedia.org/wiki/File:Ozone_resonance_structures.jpg

#5) https://commons.wikimedia.org/wiki/File:Sulfate-resonance-2D.png

#6) http://chemistry.tutorvista.com/organic-chemistry/benzene-reactions.html

#7) http://en.wikipedia.org/wiki/Polycyclic_aromatic_hydrocarbon

Organic chemistry background IV:

Hydrocarbons and organohalogens

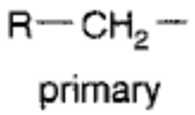
Carbon skeleton

- 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

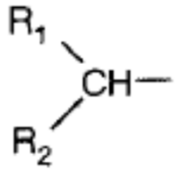
Carbon skeleton

- 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*

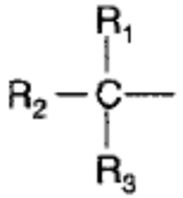
#1



primary



secondary

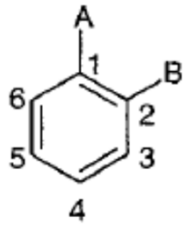


tertiary

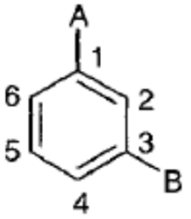
Carbon skeleton

- 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)

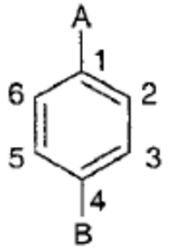
- Nomenclature in aromatic systems
  - Depending on the relative position of two substituents in a given ring system: *ortho-, meta-, para*



ortho or 1,2-



meta or 1,3-



para or 1,4-

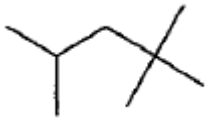
Carbon skeleton

- Examples of hydrocarbons

#2

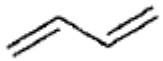
(a) 

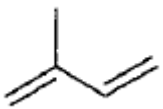
(b) 

(c) 

(d) 

(e) 

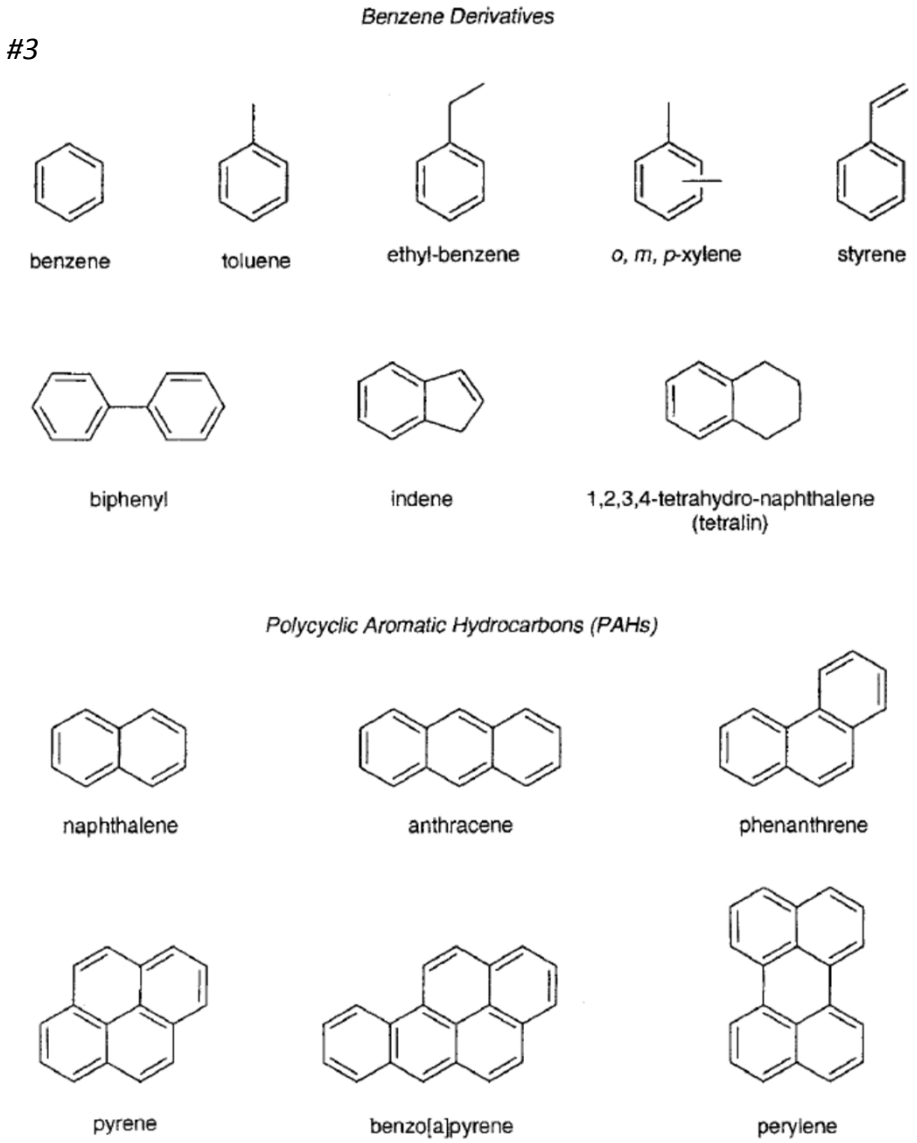
(f) 

(g) 

(h) 

Aromatic hydrocarbons

#3



- **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

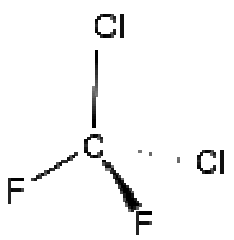
Organohalogens

- 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)

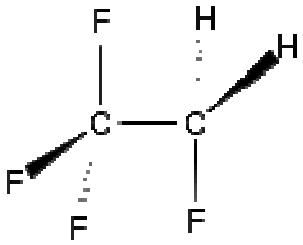
Examples of organohalogens

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

#4



Dichlorodifluoromethane



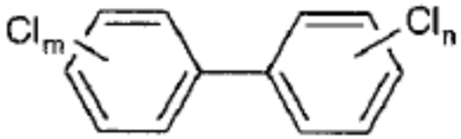
Tetrafluoroethane

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

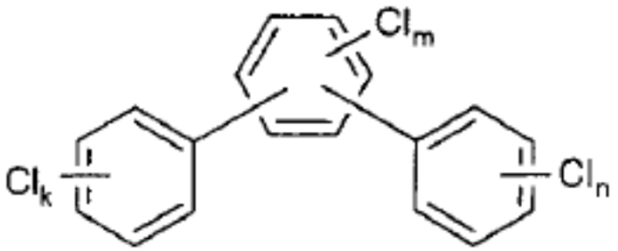
Examples of organohalogens

- **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

#5



polychlorinated biphenyls
(PCBs, 209 possible congeners)

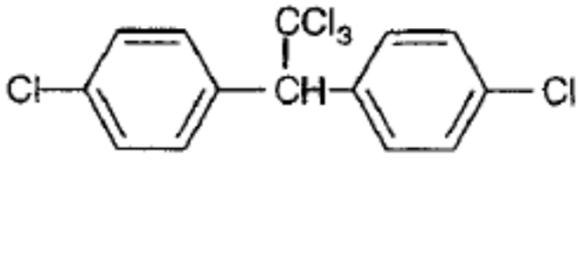


polychlorinated terphenyls
(PCTs, 8149 possible congeners)

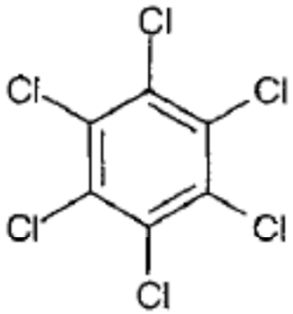
EOC p37

Examples of organohalogens

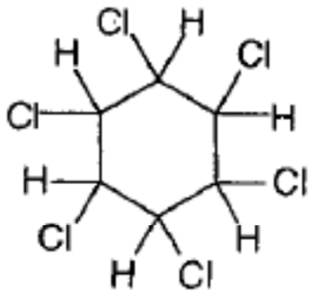
- **Organochlorine pesticides**
  - DDT, HCB, and HCH



p,p'-DDT



hexachlorobenzene
(HCB)



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

#5

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

#6

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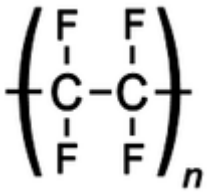

Teflon

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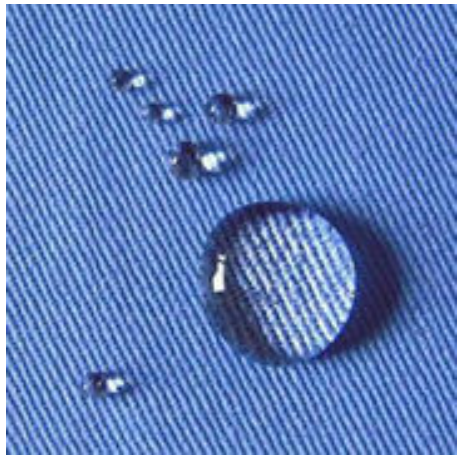

Examples of organohalogens

- **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)

#10

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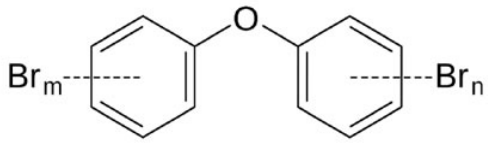

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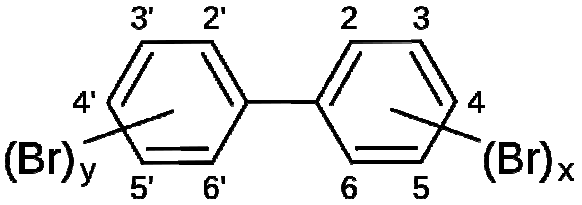

#13

References

#1, #2, #3, #5) Schwarzenbach, R., Gschwend, P. M., Imboden, D. M. (2003) Environmental Organic Chemistry, 2nd ed., John Wiley & Sons, p. 32, p. 33, p. 34, p. 37.

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#11) https://www.polymers.co.uk/carpet-and-tile-backing-coatings

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#13) https://en.wikipedia.org/wiki/Polybrominated_biphenyl