Organic chemistry background IV

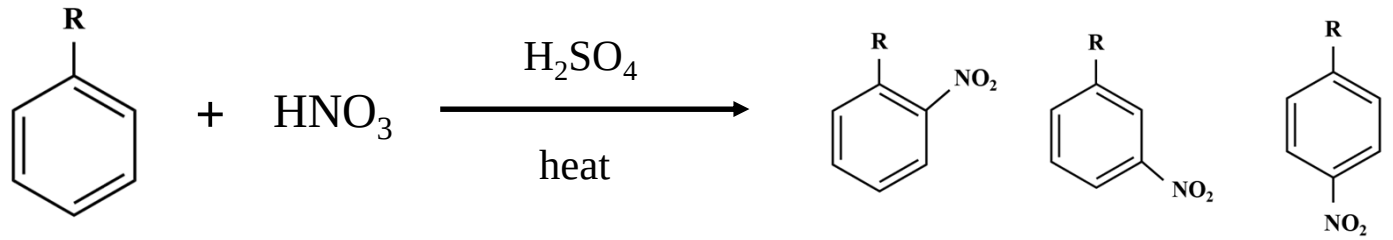
Organic chemistry background IV

- **Electron donating & withdrawing groups**
- **Hydrogen bond donor & acceptors**
- **Functional groups with heteroatoms**
  - O-containing functional groups
  - N-containing functional groups
  - S-containing functional groups

Electron donating and withdrawing groups

- A functional group attached to a carbon atom in an organic molecule may affect the reactivity of the molecule

ex) Nitration of a substituted benzene



ortho meta para

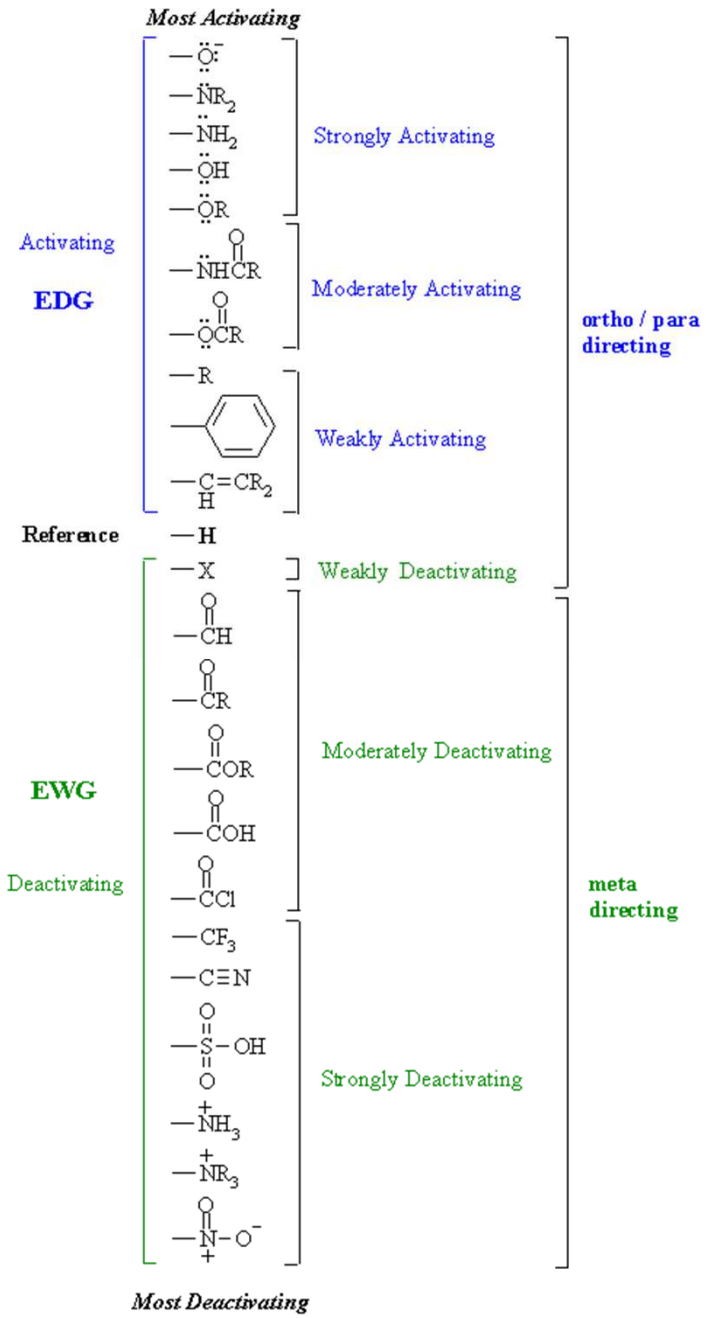
R	Reaction rate relative to benzene	Product ratio			Comments
		ortho	meta	para	
CH_3	25	63%	3%	34%	**Activated** (ortho/para directed)
CF_3	2.5×10^{-5}	6%	91%	3%	**Deactivated** (meta directed)

EDGs & EWGs

- Electron donating groups (EDGs)
  - Increase the electron density of the aromatic ring
  - Make the molecule more nucleophilic (activated)
  - The molecule tends to react with electrophiles at ortho- & para-sites

VS.

- Electron withdrawing groups (EWGs)
  - Decrease the electron density of the aromatic ring
  - Make the molecule less nucleophilic (deactivated)
  - The molecule tends to react with electrophiles at meta-sites


Most Activating
Activating
EDG
Strongly Activating
Moderately Activating
Weakly Activating
ortho / para directing
Reference
—H
Weakly Deactivating
EWG
Deactivating
Moderately Deactivating
Strongly Deactivating
meta directing
Most Deactivating

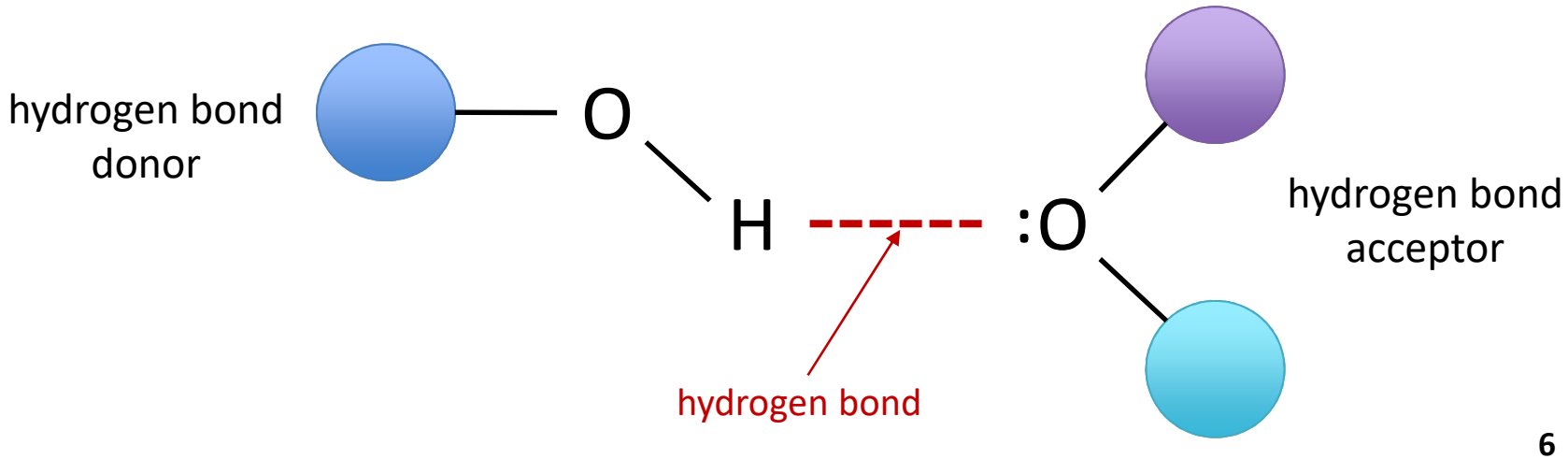
Hydrogen (bond) donors and acceptors

- **Hydrogen (bond) donors**

  An ion or molecule which possesses a hydrogen atom attached to a relatively electronegative atom such that the hydrogen can participate in a hydrogen bond

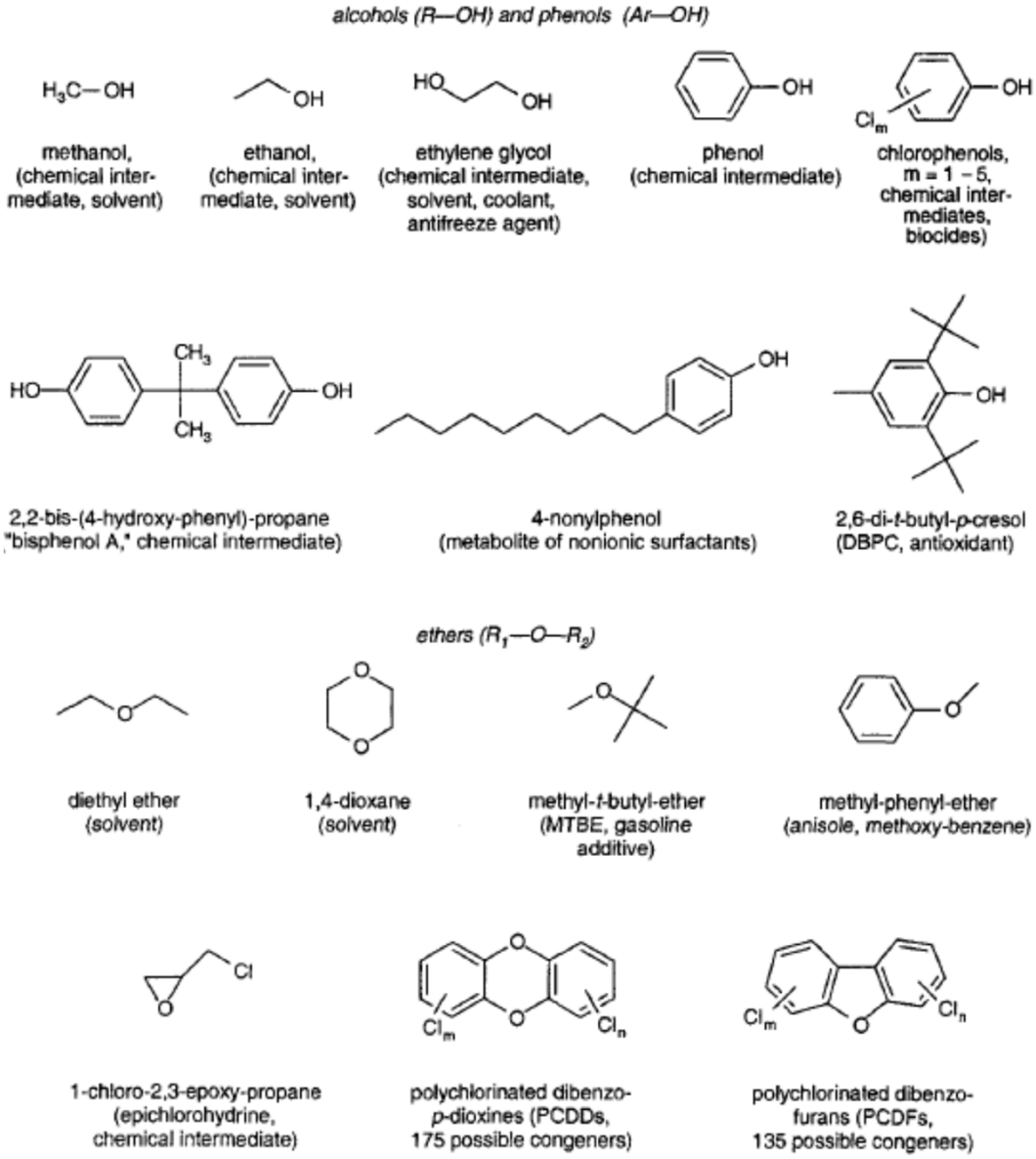
- **Hydrogen (bond) acceptors**

  An electronegative ion or molecule which possesses a lone electron pair in order to form a hydrogen bond



Oxygen-containing functional groups

- **Alcohols, phenols and ethers**
  - Alcohols: R-OH (R: alkyl group)
  - Phenols: R-OH (R: aromatic group)
  - Ethers: R_1-O-R_2

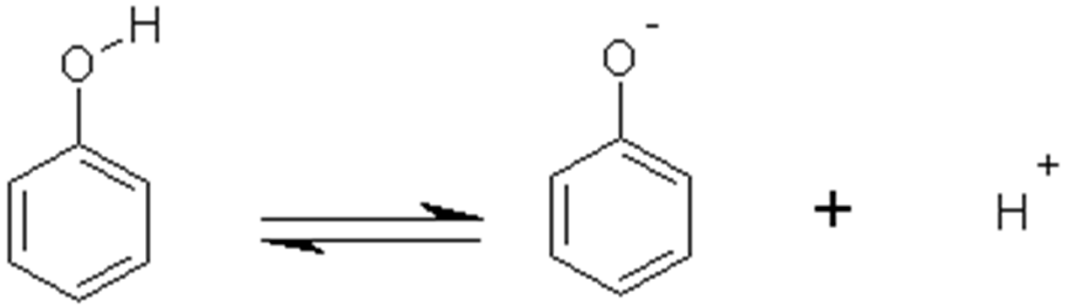


Oxygen-containing functional groups

- **Alcohols, phenols and ethers**
  - Oxygen atoms participate in hydrogen bonds: significant changes in physicochemical properties of the molecule
  - R-OH: may act as both H-donor and H-acceptor
  - R_1-O-R_2: acts only as an H-acceptor
  - Dissociation of a R-OH group
    - R-OH group may dissociate in water (renders H^+) → act as a weak acid
    - Especially for phenols
    - Greater dissociation tendency for phenols substituted with electron-withdrawing substituents

Dissociation of phenols

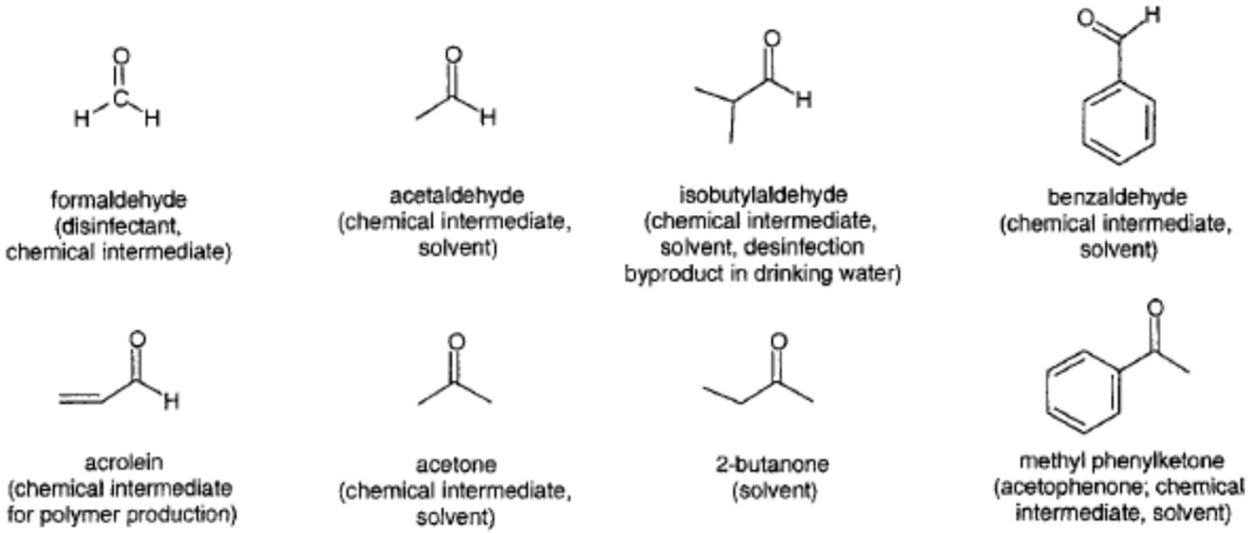
Compound	pK_a	Dominant species at pH=7.0
phenol	9.95	protonated (>99.9%)
2,4-dichlorophenol	7.90	protonated (~89%)
pentachlorophenol	4.90	deprotonated (>99.9%)



protonated deprotonated

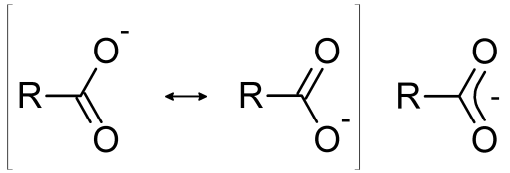
Oxygen-containing functional groups

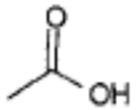
- **Aldehyde and keto groups**
  - C=O bonds
  - Aldehyde: C-CHO; keto: R_1-CO-R_2
  - H-acceptors
  - Quite reactive



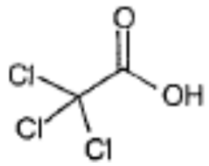
Oxygen-containing functional groups

- **Carboxylic groups**
  - R-COOH
  - May dissociate in aqueous solution (pK_a in the range of 0-6)
  - Both strong H-donors and acceptors

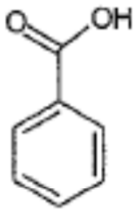




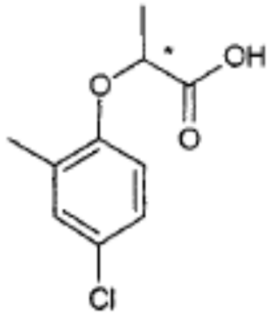
acetic acid



trichloroacetic acid (herbicide, atmospheric breakdown product of chlorinated solvents)



benzoic acid (food preservative, additive, chemical intermediate)

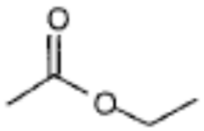


(R,S)-2-(4-chloro-2-methyl phenyl) - propionic acid ((R,S)-mecoprop; herbicide)

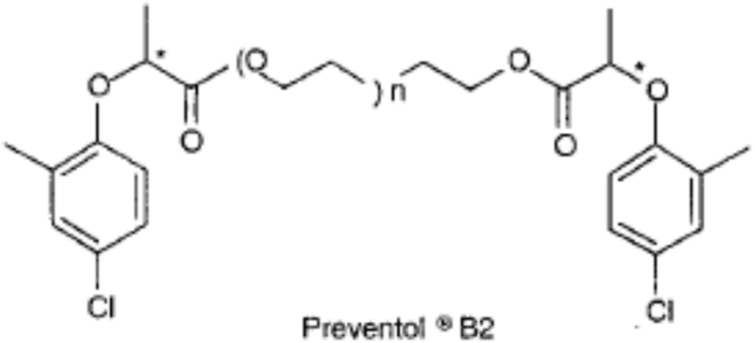
Oxygen-containing functional groups

- **Ester groups**
  - R_1-COO-R_2; -OH of a carboxylic acid is replaced by a –OR group
  - Act only as a H-acceptor (smaller impact on a compound's water solubility)

  ex) phthalates: often used as plasticizers

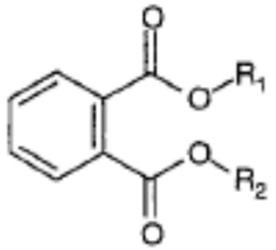


ethylacetate
(acetic acid ethyl ester; solvent)



Preventol ® B2

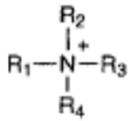
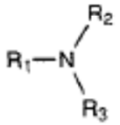
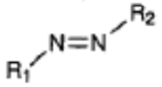
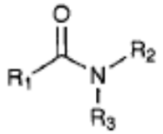
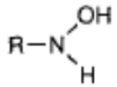
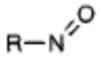
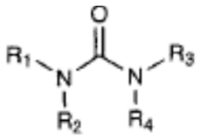
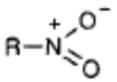
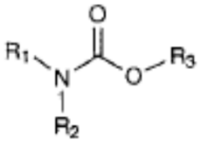
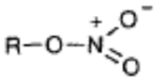
(roof protection agent)



phthalates
(R_1, R_2 = C_1, to C_{10}; plasticizers)

Nitrogen-containing functional groups

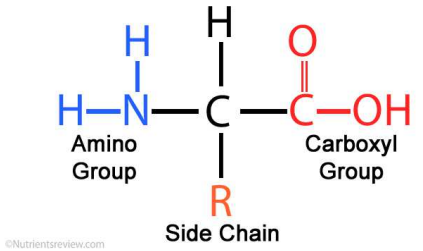
Table 2.5 Some Important Nitrogen-Containing Functional Groups Present in Anthropogenic Organic Compounds

Group	Name (oxidation state of nitrogen)	Group	Name (oxidation state of nitrogen)
	ammonium (-III)	$R_1-NH-NH-R_2$	hydrazo (-II)
	amino[a] (-III) (amine)		azo (-I)
	carboxylic acid amide[a] (-III)		hydroxyl-amine (-I)
$R-C\equiv N$	cyano, nitrilo (-III)		nitroso (+I)
	urea (-III)		nitro (+III)
	carbamate (-III)		nitrato (+V) (nitrate)

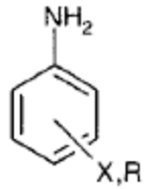
[a]Primary if $R_2 = R_3 = H$; secondary if $R_2 = H$ and $R_3 \neq H$; tertiary if $R_2 \neq H$ and $R_3 \neq H$.

Nitrogen-containing functional groups

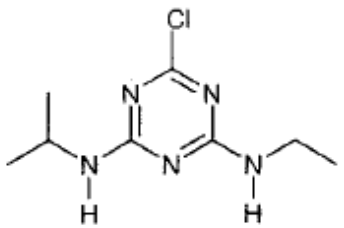
Amino Acid Structure



- **Amine groups**
  - Types: primary/secondary/tertiary
  - Natural/synthetic compounds
    - Natural example: amino acids
    - Synthetic example: anilines (intermediate for synthesis of dyes, pharmaceuticals, pesticides, antioxidants, …), atrazine (pesticide)
  - Acts as both H-acceptors and donors
    - H-acceptors: to a lesser extent
    - H-donors: only for primary and secondary amines
  - Slightly basic: acquire a proton in an aqueous solution to form a cationic ammonium species



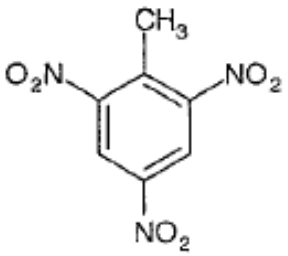
aniline and substituted anilines (chemical intermediates)



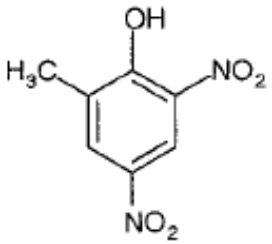
atrazine (a triazine herbicide)

Nitrogen-containing functional groups

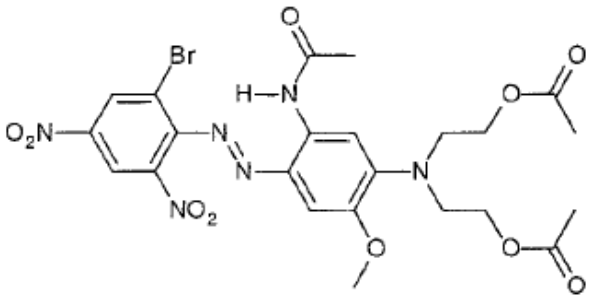
- **Nitro groups**
  - Widely used in the chemical industry
    - Explosives (ex: TNT), agrochemicals (ex: DNOC), dyes (ex: Dispersive Blue 79)
  - Strong electron-withdrawing characteristics
    - Significantly affect the electron distribution in a molecule
    - Significantly affect the chemical properties of the compound
  - Explosives: multiple nitro groups in the molecules
    - Nitro group as built-in oxidant
    - Very fast oxidation of the molecule



2,4,6-trinitrotoluene
(TNT, explosive)



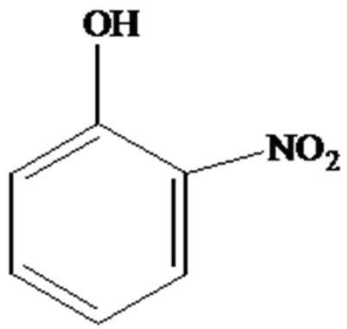
2,4-dinitro-*o*-cresol
(DNOC, herbicide)



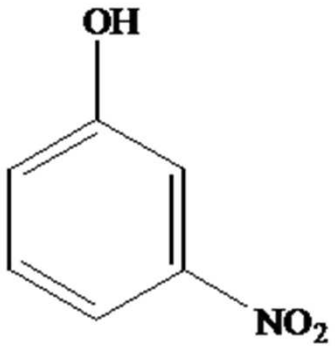
Dispersive Blue 79
(textile dye)

Dissociation of nitrophenols

Compound	pK_a
phenol	9.95
2-nitrophenol (ortho)	7.17
3-nitrophenol (meta)	8.28

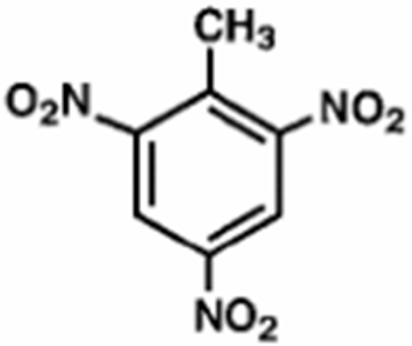


ortho-Nitrophenol or
2-Nitrophenol

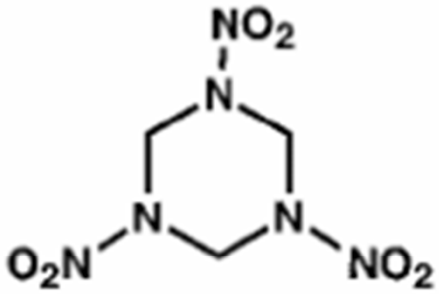


meta-Nitrophenol or
3-Nitrophenol

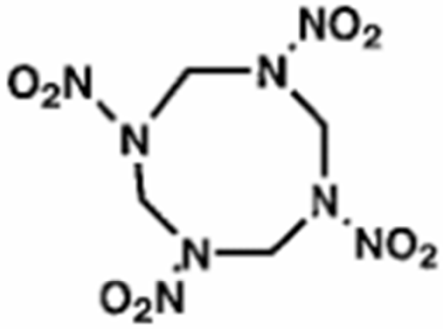
Examples of explosives containing nitro groups



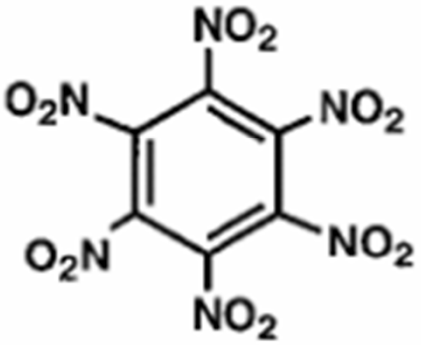
TNT



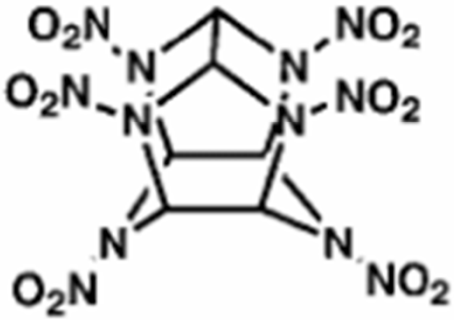
RDX



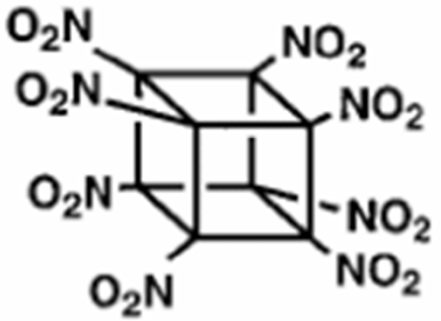
HMX



HNB



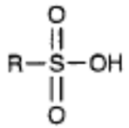
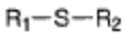
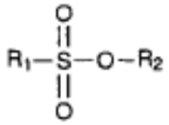
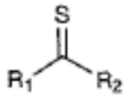
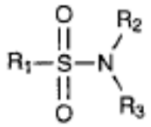
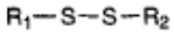
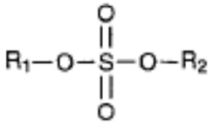
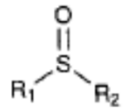
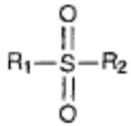
CL-20



ONC

Sulfur-containing functional groups

Table 2.6 Some Important Sulfur-Containing Functional groups Present in Anthropogenic Organic Compounds

Group	Name (oxidation state of sulfur)	Group	Name (oxidation state of sulfur)
	thiol, mercaptan (-II)		sulfonic acid (+IV)
	thioether, sulfide (-II)		sulfonic acid ester (+IV)
	thiocarbonyl (-II)		sulfonic acid amide, sulfonamide (+IV)
	disulfide (-I)		sulfuric acid ester, sulfate (+VI)
	sulfoxide (0)		
	sulfone (+II)		

Organic chemistry background III

Organic chemistry background III

- **Hydrocarbons**
  - Carbon skeleton
  - Examples of aromatic hydrocarbons

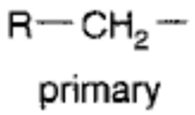
- **Organohalogens**
  - General characteristics
  - Some examples

Carbon skeleton

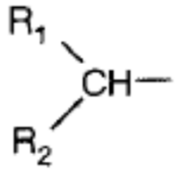
- Saturated vs. unsaturated
  - **Saturated**: no double or triple bond
  - **Unsaturated**: at least one double or triple bond
- Aliphatic / alicyclic / aromatic
  - **Aliphatic**: no ring structures
  - **Alicyclic**: contains at least one ring structure
  - **Aromatic**: contains at least one aromatic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

Carbon skeleton

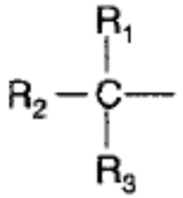
- Saturated aliphatic hydrocarbons
  - **C_nH_{2n+2}**
  - Called an **alkane** or a **paraffin**
  - Suffix: -ane
  - Prefix
    - ***n*** (normal)-: unbranched
    - ***iso-***: two methyl groups at the end
    - ***neo-***: three methyl groups at the end
  - Classification of alkyl (C_nH_{2n+1}) groups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



primary



secondary

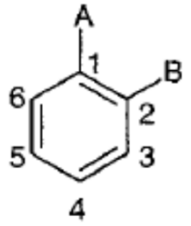


tertiary

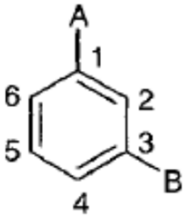
Carbon skeleton

- 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)

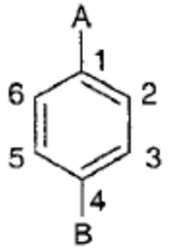
- Nomenclature in aromatic systems
  - Depending on the relative position of two substituents in a given ring system: *ortho-, meta-, para*



ortho or 1,2-



meta or 1,3-



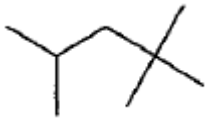
para or 1,4-

Carbon skeleton

- Examples of hydrocarbons

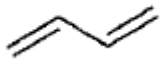
(a) 

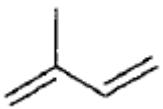
(b) 

(c) 

(d) 

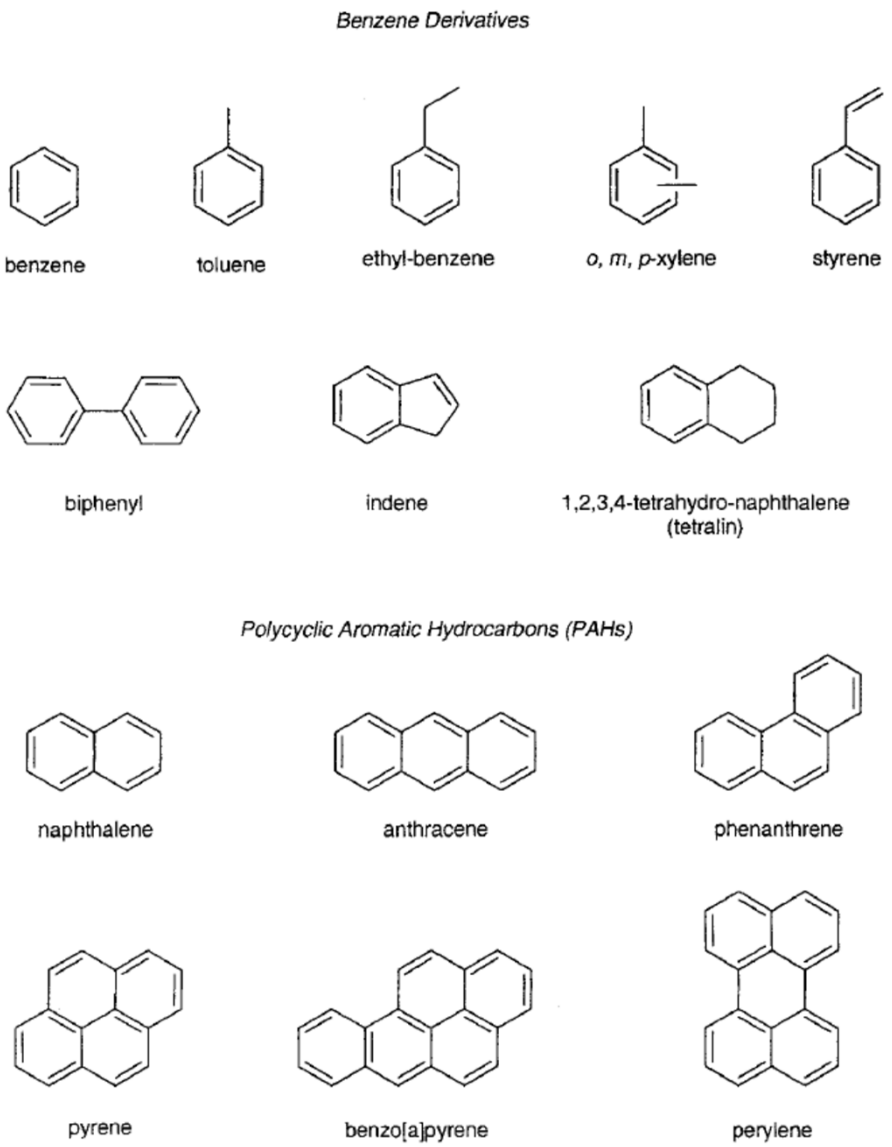
(e) 

(f) 

(g) 

(h) 

Examples of aromatic hydrocarbons



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

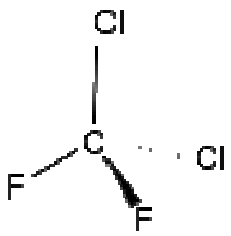
- **Polycyclic aromatic hydrocarbons (PAHs)**
  - Sources: combustion of fossil fuels, forest fires, mineral oils, creosotes, …
  - Some members are carcinogenic (ex: benzo[a]pyrene)
  - Planar structure
  - Bay region

Organohalogens

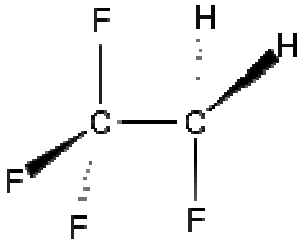
- Organic molecules containing one or several halogen (Cl, F, Br) atoms
- Vast production; significant environmental problem
- Characteristics
  - Strong C-X bonds (high electronegativity of halogens): Enhanced inertness of the molecule
  - **Very weak tendency to be engaged in hydrogen bonds**: Enhanced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

Examples of organohalogens

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



Dichlorodifluoromethane

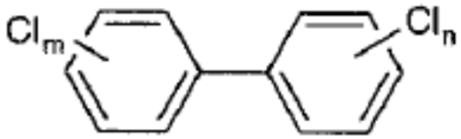


Tetrafluoroethane

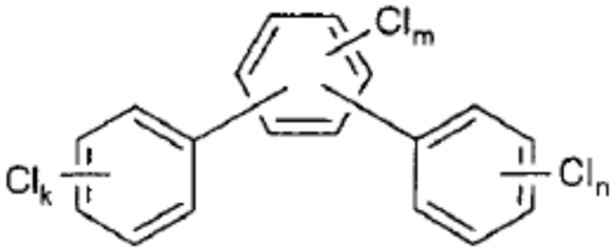
- **Chlorinated solvents**
  - Dichloromethane, trichloroethene (TCE), tetrachloroethene (PCE), 1,1,1-trichloroethane
  - One of the common groundwater pollutants

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)

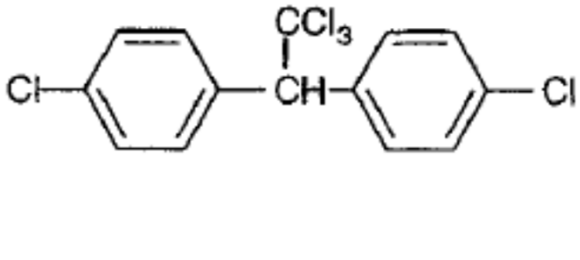


polychlorinated terphenyls
(PCTs, 8149 possible congeners)

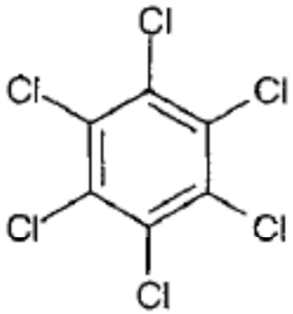
EOC p37

Examples of organohalogens

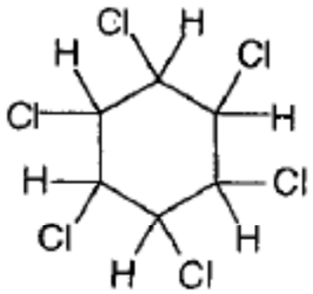
- **Organochlorine pesticides**
  - DDT, HCB, and HCH



p,p'-DDT



hexachlorobenzene
(HCB)

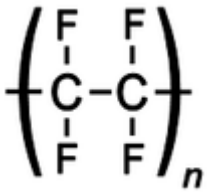


1,2,3,4,5,6-hexachlorocyclohexane
(HCH, 8 isomers,
one of them exists as a pair
of enantiomers)

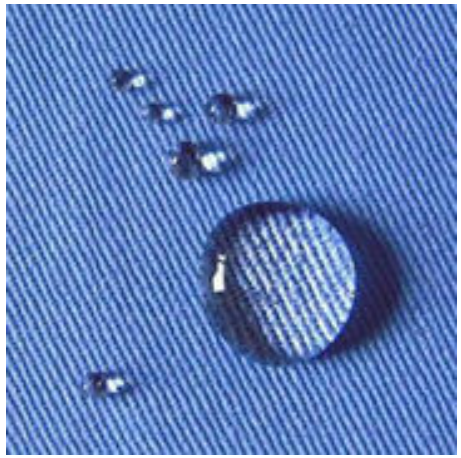
Examples of organohalogens

prefix "per-" denotes thorough or utterly

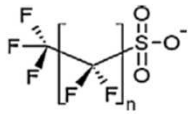
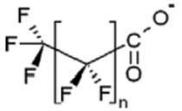
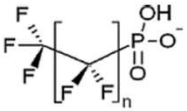
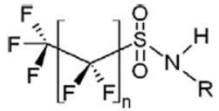
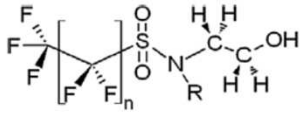
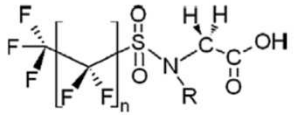
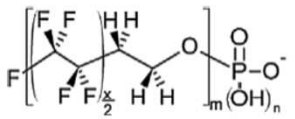
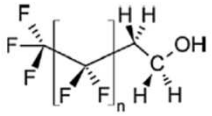
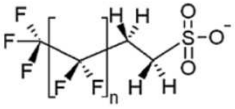
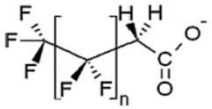
- **Per- and poly-fluoroalkyl substances** (PFASs)
  - Organofluorine compounds rich in C-F bonds in their alkyl moiety
  - Highly stable, non-wetting, very slippery, fire resistant
  - Teflon production, fire-fighting foam, used in metal plating, photographic, fabric and semiconductor industry
  - PFSAs (perfluoroalkyl sulfonates) and PFCAs (perfluoroalkyl carboxylates): major PFASs sub-classes in concern



Teflon



PFAS examples

Perfluoroalkyl substances Perfluroalkyl sulfonates	PFSAs	$C_nF_{2n+1}SO_3^-$		n = 3–9
Perfluoroalkyl carboxylates	PFCAs	$C_nF_{2n+1}COO^-$		n = 1–17
Perfluoroalkyl phosphonates	PFPAs	$C_nF_{2n+1}(O)P(OH)O^-$		n = 4, 6, 8
Perfluoroalkyl sulfonamides	FASAs	$C_nF_{2n+1}SO_2NH_2$		n = 8, R = H n = 8, R = CH_3 n = 8, R = C_2H_5 n = 4, R = CH_3
Perfluoroalkyl sulfonamidoethanols	FASEs	$C_nF_{2n+1}SO_2NHCH_2CH_2OH$		n = 8, R = CH_3 n = 8, R = C_2H_5 n = 4, R = CH_3
Perfluoroalkyl sulfonamidoacetic acids	FASAAs	$C_nF_{2n+1}SO_2NHCH_2COOH$		n = 8, R = H n = 8, R = CH_3 n = 8, R = C_2H_5
Polyfluoroalkyl substances Polyfluoroalkyl phosphoric acid esters	PAPs	$(O)P(OH)_{3-x}\ (OCH_2CH_2C_nF_{2n+1})_x$		m = 1, n = 2, x:2 monoPAP m = 2, n = 1, x:2 diPAP
n:2 Fluorotelomer alcohols	n:2 FTOHs	$C_nF_{2n+1}CH_2CH_2OH$		n = 4, 6, 8, 10
x:2 Fluorotelomer sulfonates	x:2 FTSAs	$C_nF_{2n+1}CH_2CH_2SO_3^-$		n = 4, 6, 8, 10
n:2 Fluorotelomer carboxylates	x:2 FTCA	$C_nF_{2n+1}CH_2COO^-$		n = 4, 6, 8, 10

Environmental Science & Technology

pubs.acs.org/est

Viewpoint

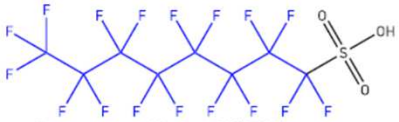
A New OECD Definition for Per- and Polyfluoroalkyl Substances

Zhanyun Wang,* Andreas M. Buser, Ian T. Cousins, Silvia Dematttio, Wiebke Drost, Olof Johansson, Koichi Ohno, Grace Patlewicz, Ann M. Richard, Glen W. Walker, Graham S. White, and Eeva Leinala

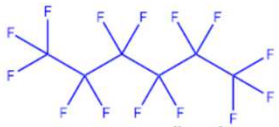
■ A REVISED PFAS DEFINITION

To address these concerns, the report presents a revised, broadly inclusive PFAS definition: "*PFASs are defined as fluorinated substances that contain at least one***fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it)**, *i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group* ($-CF_3$) *or a perfluorinated methylene group* ($-CF_2-$) *is a PFAS*". The "noted exceptions" refer to a carbon atom with a H/Cl/Br/I atom attached to it.

Examples of PFASs that already meet the definition by Buck et al. (2011)*

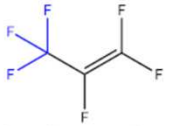


perfluorooctanesulfonic acid (PFOS)
Chemical Abstracts Service Registry Number (CASRN) 1763-23-1

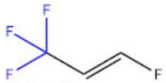


perfluorohexane
CASRN 355-42-0

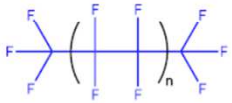
perfluoromethane
CASRN 75-73-0



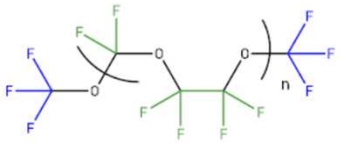
hexafluoropropylene (HFP)
CASRN 116-15-4



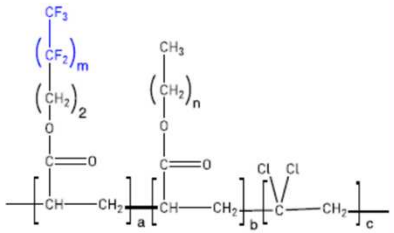
HFO-1234ze
CASRN 29118-24-9



an example of
polytetrafluoroethylene (PTFE)
CASRN 9002-84-0



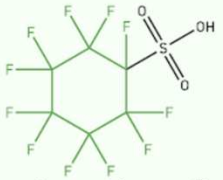
an example of perfluoropolyethers (PFPEs)



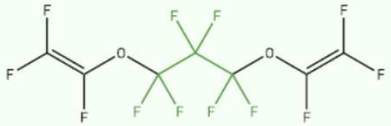
an example of side-chain
fluorinated polymers (SCFPs)

* **Blue** moieties = fully fluorinated alkyl moieties that already meet the definition by Buck et al. (2011); **green** moieties = fully fluorinated alkanediyl moieties that are added under the new OECD definition; **orange** moieties = aromatic rings

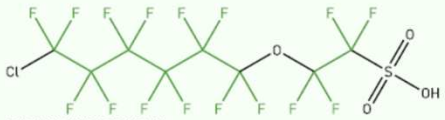
Examples of PFASs that are added under the new OECD definition*



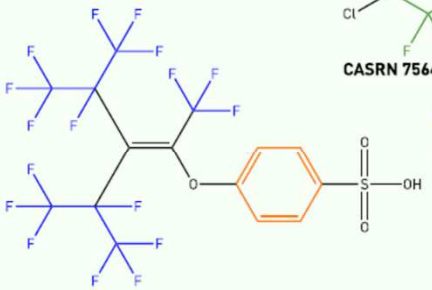
perfluorocyclohexanesulfonic acid
CASRN 2106-55-0



CASRN 13846-22-5

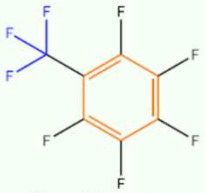


CASRN 756426-58-1

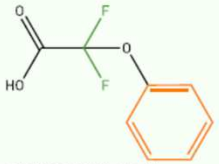


CASRN 271794-15-1

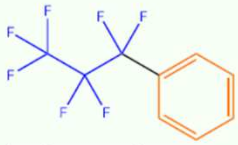
Fipronil
CASRN 120068-37-3



perfluorotoluene
CASRN 434-64-0



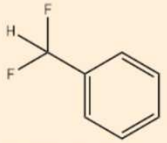
CASRN 24210-45-5



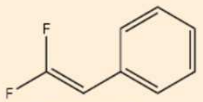
(perfluoropropyl)benzene
CASRN 378-98-3

Examples of substances that are NOT PFASs

CASRN 771-56-2



CASRN 455-31-2



CASRN 405-42-5

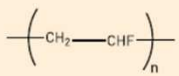
trifluoromethane
CASRN 75-46-7

CASRN 75-72-9

CASRN 75-63-8

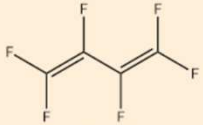
CASRN 2314-97-8

difluoromethane
CASRN 75-10-5

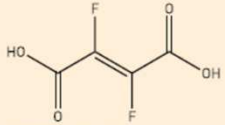


polyvinyl fluoride (PVF)

tetrafluoroethylene (TFE)
CASRN 116-14-3



hexafluorobutadiene
CASRN 685-63-2



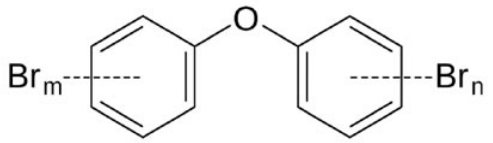
CASRN 685-64-3

Examples of organohalogens

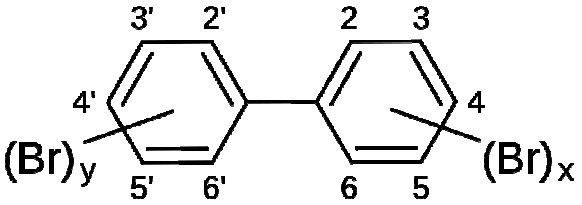
- **Brominated flame retardants**
  - Emerging contaminants of current concern
  - Inhibitory effect on combustion processes → reduce the flammability of products they are applied to
  - Widely used in plastics and textile applications
  - Major groups: polybrominated biphenyl ethers (PBDEs) and polybrominated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

#10

#11



#12



#13