Organic Molecules are Boring

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.

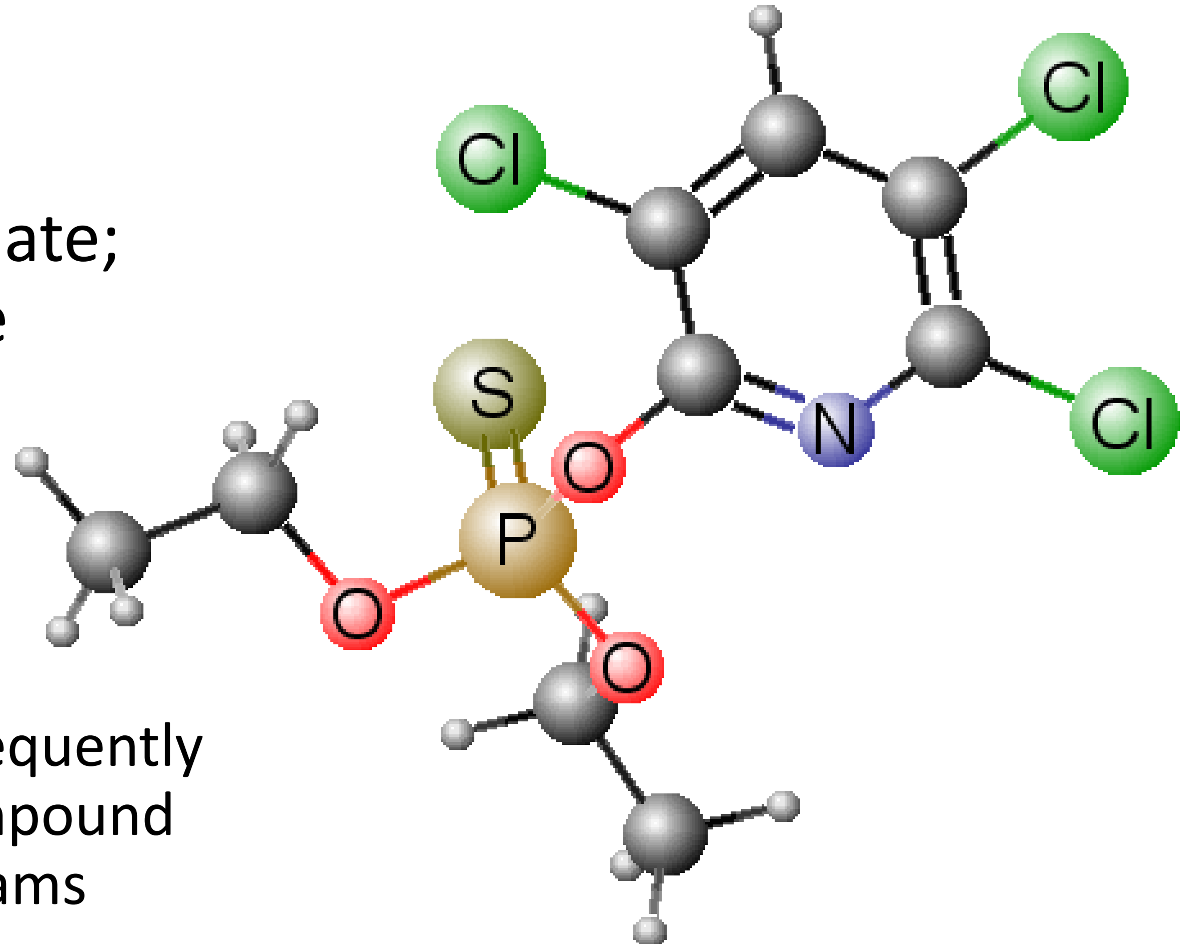
Organic chemistry is a discipline within chemistry which involves the scientific study of the structure, properties, composition, reactions, and preparation (by synthesis or by other means) of chemical compounds consisting primarily of carbon and hydrogen, which may contain any number of other elements, including nitrogen, oxygen, the halogens as well as phosphorus, silicon and sulfur

Organic Molecules are Boring

DOW CHEMICAL NIGHTMARE

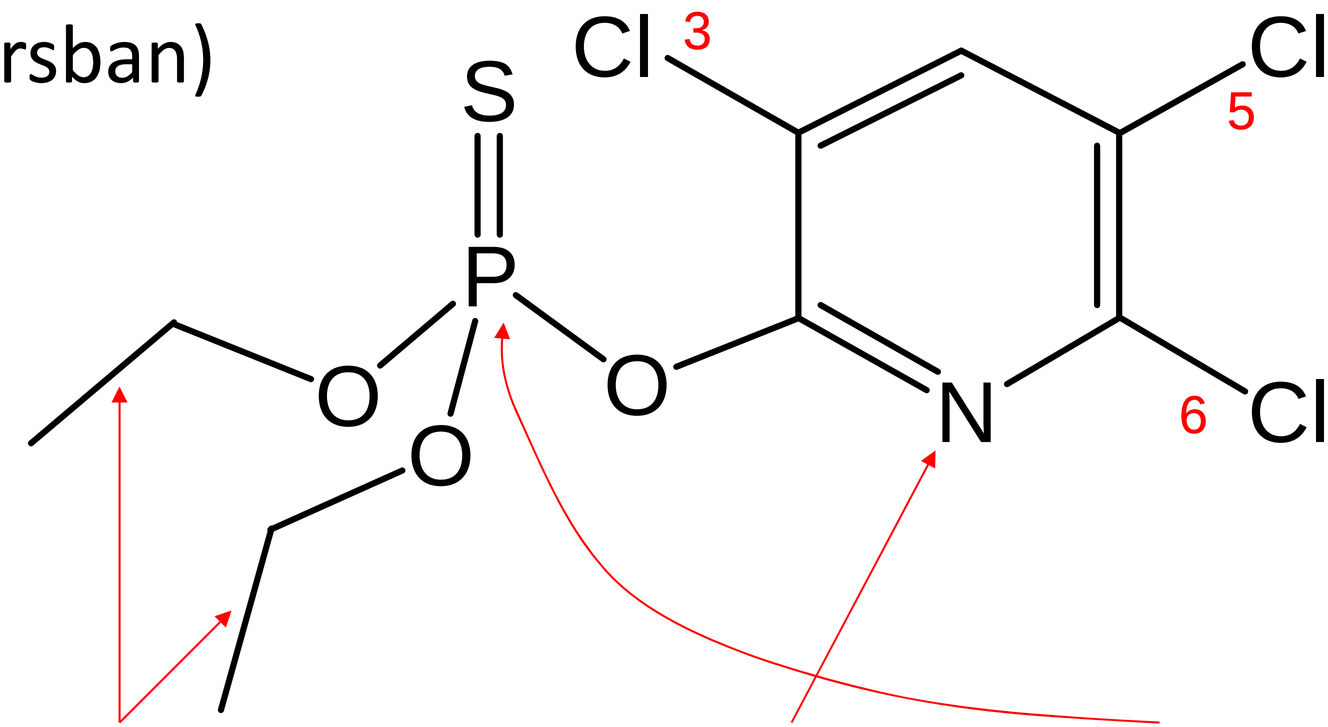
Interesting molecule of the day

- Chlorpyrifos (Dursban)
  - organophosphate; thiophosphate
  - uses
    - agricultural insecticide
    - termiticide
    - third most frequently detected compound in urban streams
    - BANNED FROM HOUSEHOLD USE



Interesting molecule of the day

- Chlorpyrifos (Dursban)



O,*O*-diethyl-*O*-(3,5,6-trichloro-2-pyridinyl)phosphorothioic acid

[ChemSpider](#)
[ChemID Plus](#)

Interesting molecule of the day

- Chlorpyrifos (Dursban)
  - may affect fetal brain development
    - Whitney et al., 1995. *Toxicol. Appl. Pharmacol.* 134, 53-62.

"Results indicate that low doses of chlorpyrifos target the developing brain during the critical period in which cell division is occurring..."

"Our finding of a much greater sensitivity to chlorpyrifos in the neonate, in terms of both systemic toxicity and targeting of DNA and protein synthesis within the brain, emphasize the need for caution in assigning safety standards."

Interesting molecule of the day

- Chlorpyrifos (Dursban)

Washington growers continue use of chemical tied to workers' cancer

Washington orchard owners last year applied more than 270,000 pounds of chlorpyrifos, a pesticide linked to lung cancer and nerve damage in farm workers…

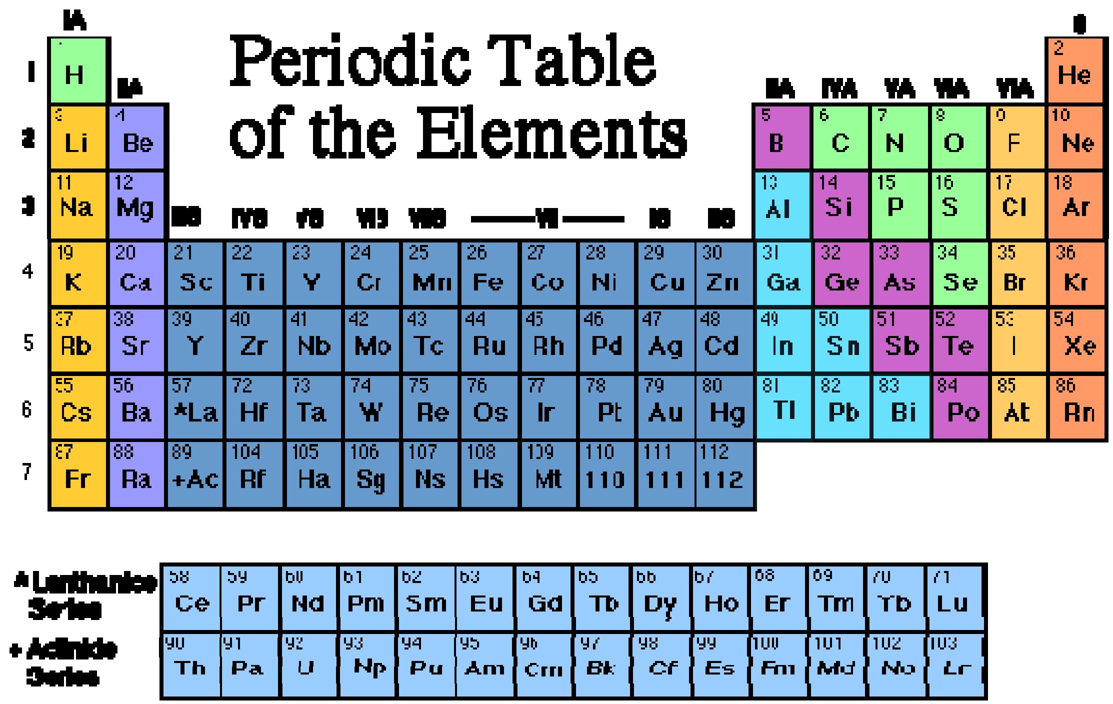
Spokane Spokesman-Review; August 24, 2004

Interesting molecule of the day

- Chlorpyrifos (Dursban)
  - EPA phase out/eliminate rule, June 2000
    - 10× safety factor to provide "adequate safety margin for children"
      - 1996 Food Quality Projection Act
    - not all agree;
      see *Agricultural and Environmental News*

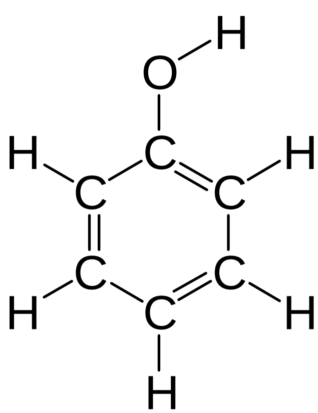
Organic Chemistry Review

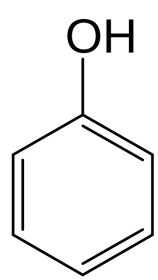
- What elements make up organic compounds?
  - C, H, O, N, S
  - Halogens: F, Cl, Br, I

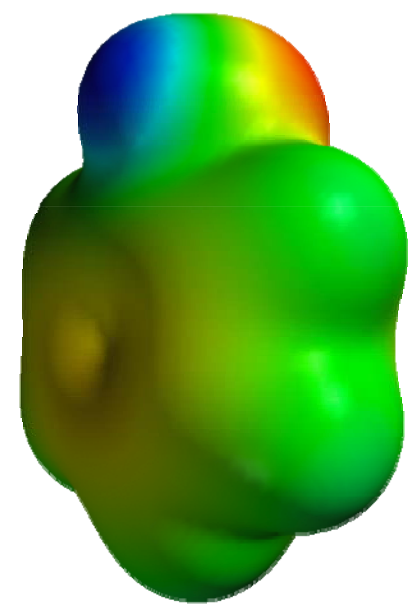


Formulae and Structure

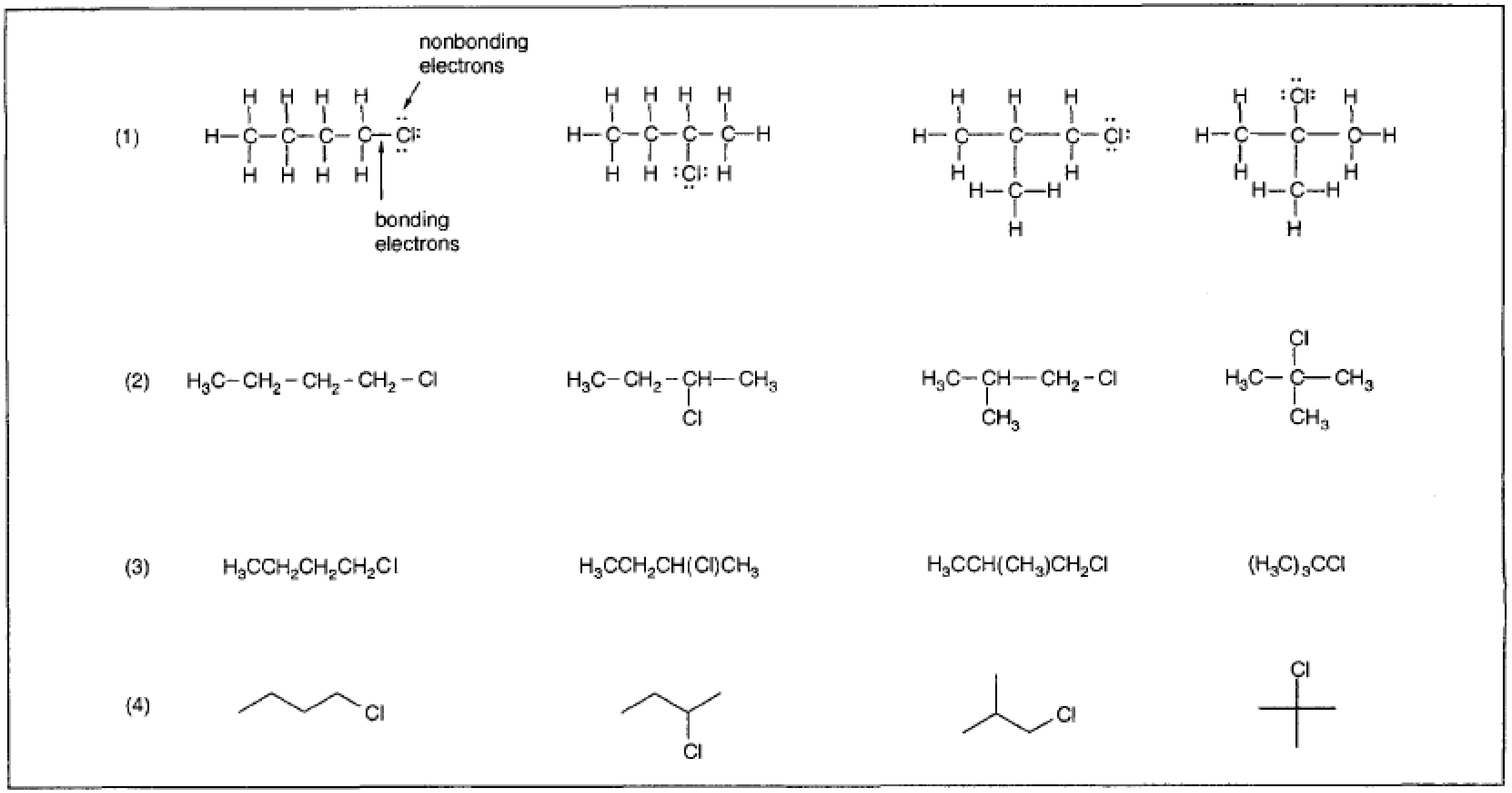
- What is the molecular formula of phenol?
  - C_6H_6O
- What is a structural formula of phenol?
  - C_6H_5OH
- What is the structure of phenol?







Formulae and Structure



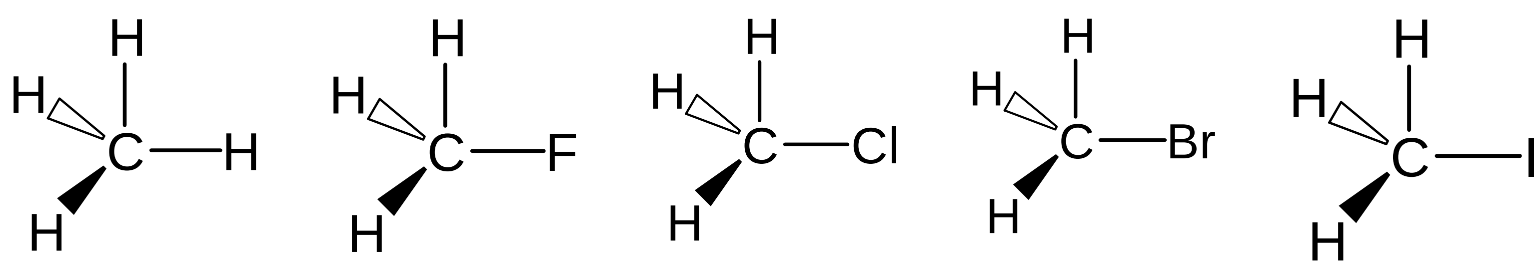
Covalent Bonds

- What is a covalent bond?

- Missing electrons in outer shell?

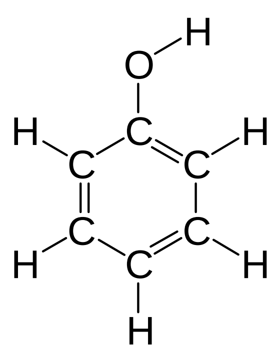
Covalent Bonds

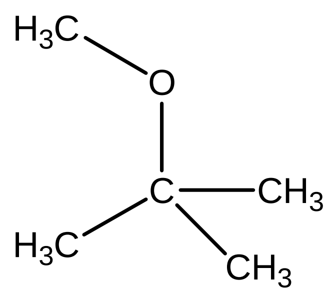
- Which element(s) form monovalent bonds?
  - H, F, Cl, Br, I
  - missing 1 electron in outer shell

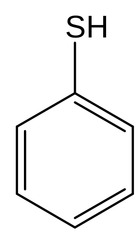


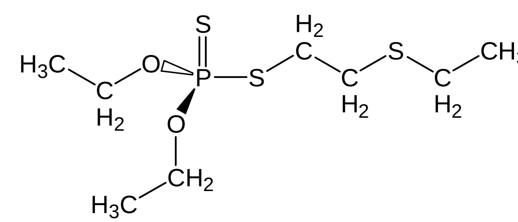
Covalent Bonds

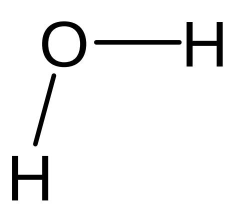
- Which element(s) form bivalent bonds?
  - O, S (in the –II oxidation state)
  - missing 2 electrons in outer shell

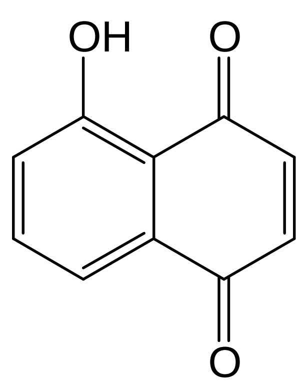


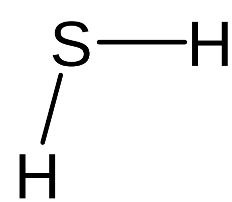


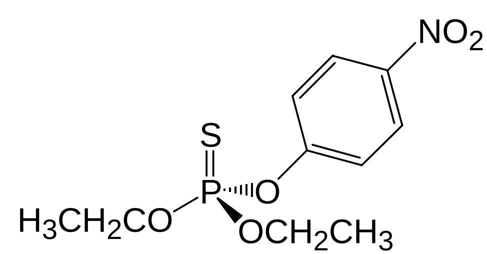






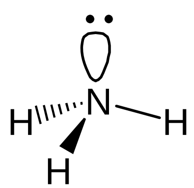


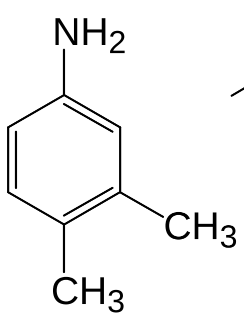


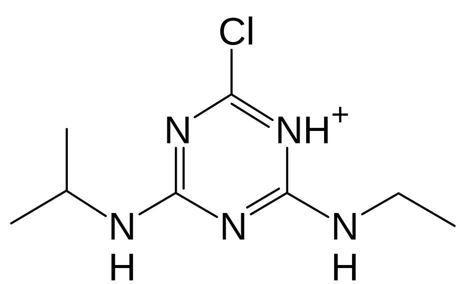


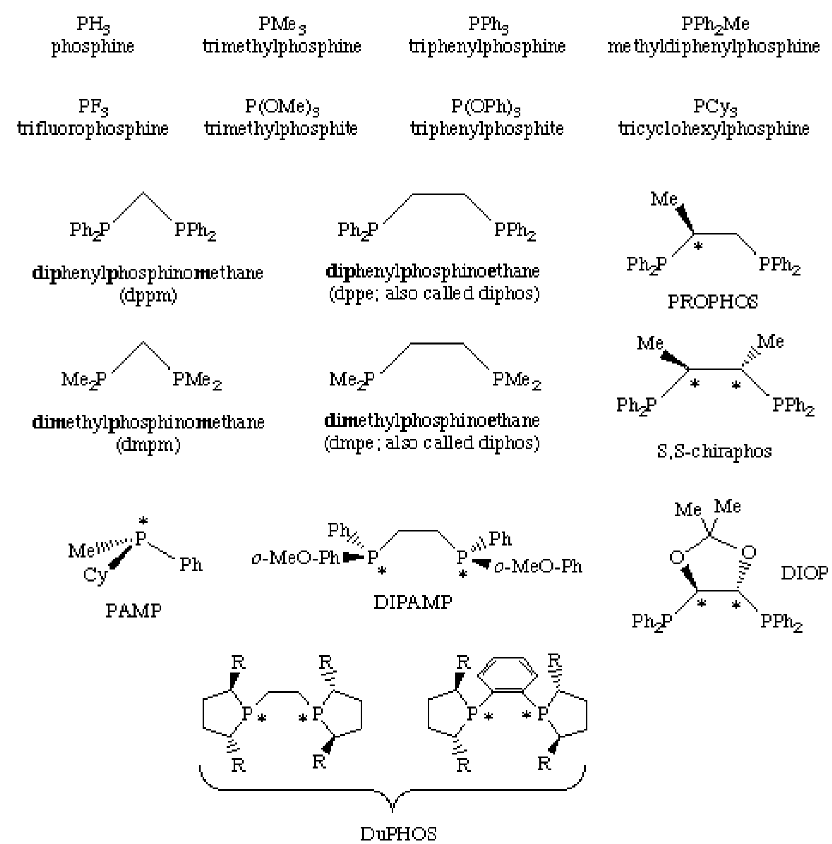
Covalent Bonds

- Which element(s) form trivalent bonds?
  - N, P (in the -III, -III oxidation state)
  - missing 3 electrons in outer shell



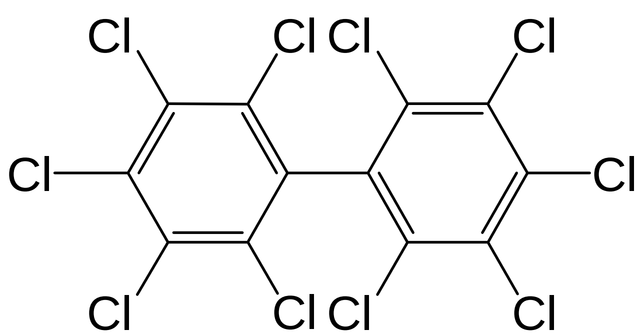


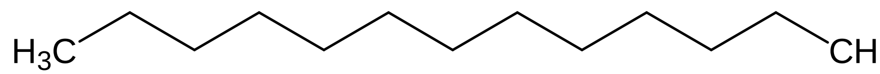


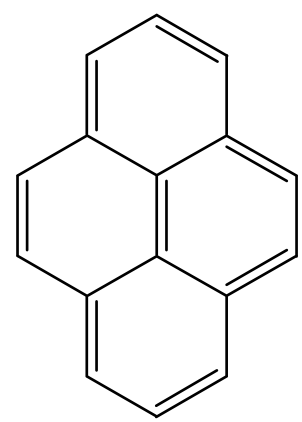


Covalent Bonds

- Which element(s) form tetravalent bonds?
  - C
  - missing 4 electrons in outer shell

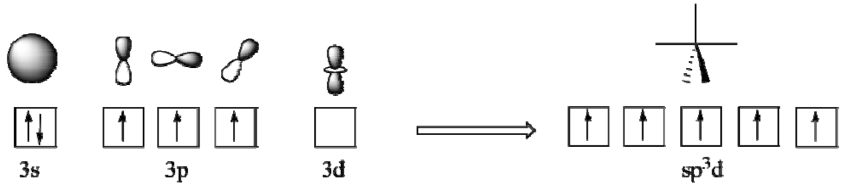


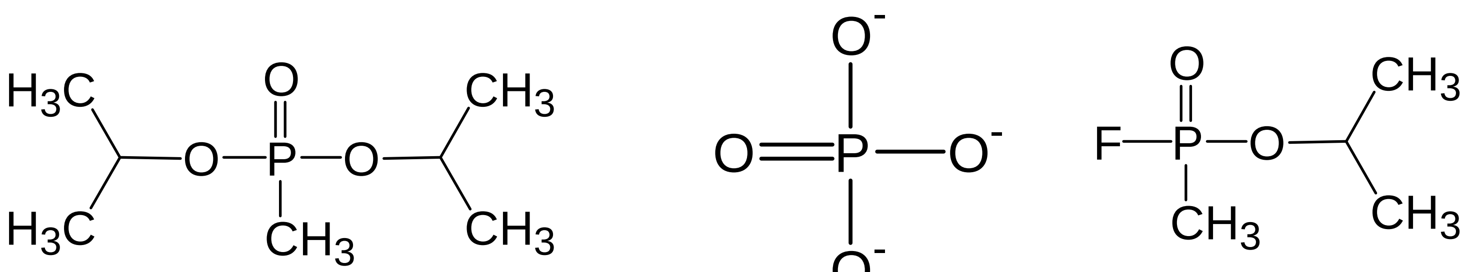




Covalent Bonds

- Which element(s) form pentavalent bonds?
  - P (in the +V oxidation state)
  - missing 5 electrons in the outer shell





Covalent bond strength $A-B \rightarrow A^{\bullet} + B^{\bullet};\ \Delta H^{0}_{AB}$

Table 2.2 Average Bond Lengths (Å) and Average Bond Enthalpies ($kJ \cdot mol^{-1}$) of Some Important Covalent Bonds[a]

Bond	Length/Enthalpy	Bond	Length/Enthalpy	Bond	Length/Enthalpy
		Diatomic Molecules			
H–H	0.74/436	F-F	1.42/155	O=O	1.21/498
H–F	0.92/566	Cl–Cl	1.99/243	N≡N	1.10/946
H–Cl	1.27/432	Br–Br	2.28/193		
H–Br	1.41/367	I–I	2.67/152		
H–I	1.60/298				
		Covalent Bonds in Organic Molecules			
Single bonds[b]					
H–C	1.11/415	C–C	1.54/348	C–F	1.38/486
H–N	1.00/390	C–N	1.47/306	C–Cl	1.78/339
H–O	0.96/465	C–O	1.41/360	C–Br	1.94/281
H–S	1.33/348	C–S	1.81/275	C–I	2.14/216
Double and triple bonds					
C=C	1.34/612	C=O[d]	1.20/737	C≡C	1.16/838
C=N	1.28/608	C=O[e]	1.20/750	C≡N	1.16/888
C=S[c]	1.56/536	C=O[f]	1.16/804		

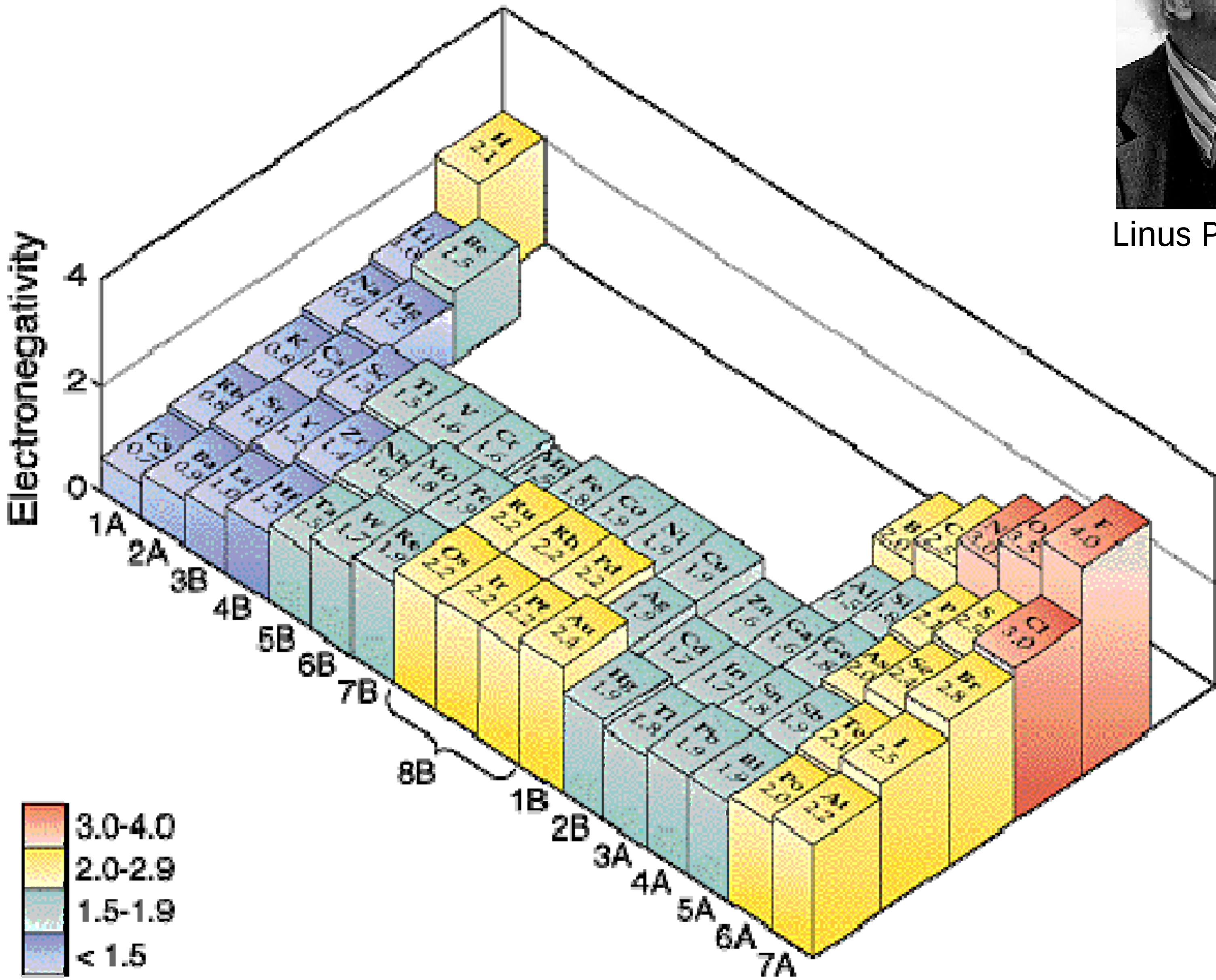
[a] Bond length/bond enthalpy. Note that 1 Å equals 0.1 nm. [b] Bond lengths are given for bonds in which none of the partner atoms is involved in a double or triple bond. In such cases bond lengths are somewhat shorter. [c] In carbon disulfide. [d] In aldehydes. [e] In ketones. [f] In carbon dioxide.

Energy savings or expenditures

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

- Break 4 C-H and 2 O=O → need +2656 KJ/mol
- Create 2 C-O and 4 H-O → produce -3468 KJ/mol

Electronegativity



Linus Pauling

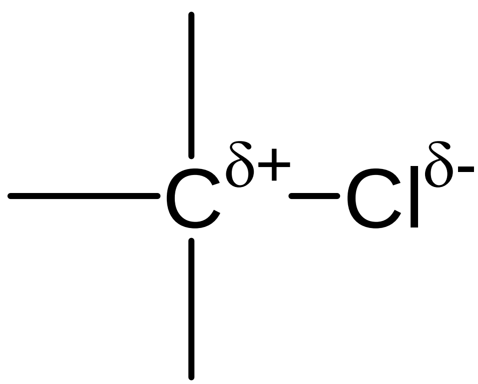
Electronegativity

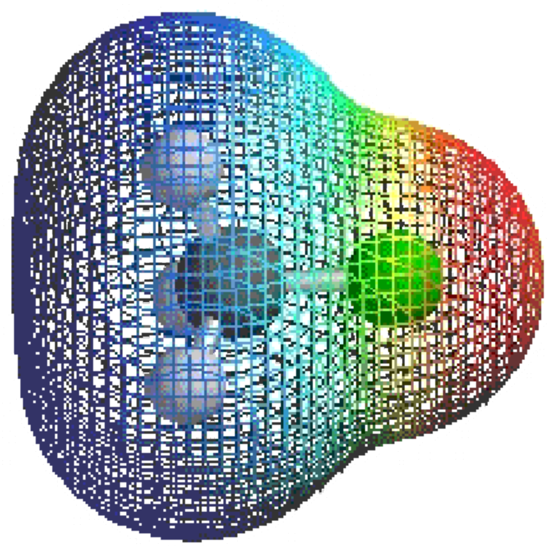
charge	+1	+4	+5	+6	+7
	H				
	2.2				
		C	N	O	F
		2.5	3.0	3.5	4.0
			P	S	Cl
			2.2	2.5	3.0
					Br
					2.8
					I
					2.5

a complete table

Electronegativity

- How does electronegativity affect covalent bonding?
  - The "electron cloud," or average electron position, between the two atoms is shifted toward the atom that more strongly attracts electrons





Bond Strength

- Which bond do you think is the strongest?

bond length (Å)

A. C $\overset{1.38}{—}$ F 486 kJ mol^{-1}

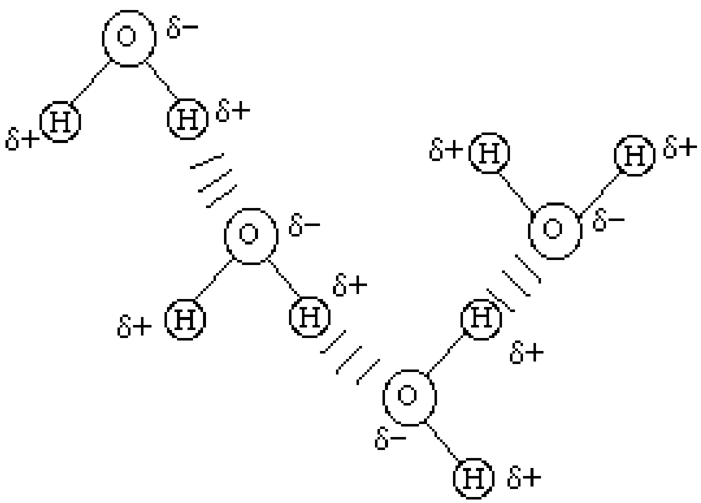
B. C $\overset{1.78}{—}$ Cl 339 kJ mol^{-1}

C. C $\overset{1.94}{—}$ Br 281 kJ mol^{-1}

D. C $\overset{2.14}{—}$ I 216 kJ mol^{-1}

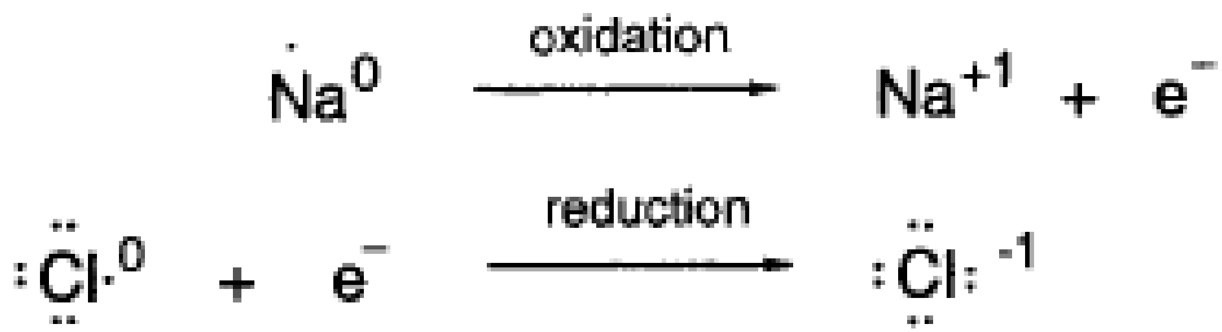
Hydrogen Bonding

- Why are hydrogen bonds formed?
  - hydrogen covalently bonds with an electronegative heteroatom (X) like O, S, N
  - H electron is pulled away and its proton (+) is left bare
    - acts like a proton
  - The bare "proton" attracts other electronegative atoms



bond strength
~ 20 kJ mol^{-1}

Oxidation & Reduction



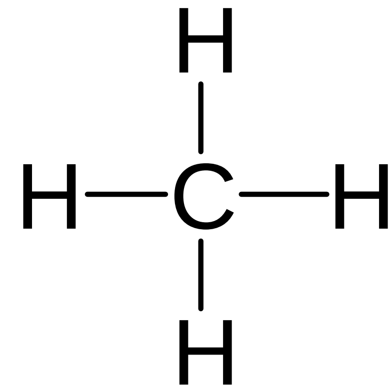
Oxidation State

- Status of electrons in bonds
  - gained or lost to neighboring atom or ion
  - depends on relative electronegativity of atoms or ions
    - similar electronegativity (e.g., C-S, C-I, C-P), electrons lost to heteroatom (i.e., S, I, P)
- Oxidation state value (Roman numerals)
  - negative if electrons are gained
  - positive if electrons are lost
  - for single atom or average for all atoms of that type in a molecule
    - average can be fractional

Oxidation State

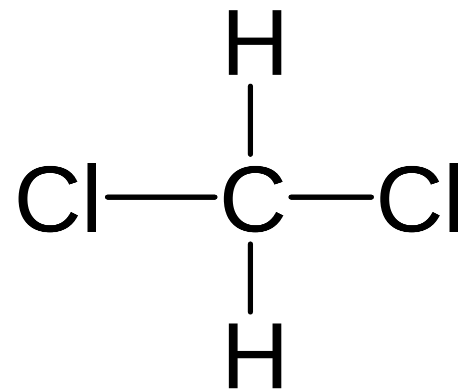
- What is the oxidation state of carbon in methane?

C(-IV)



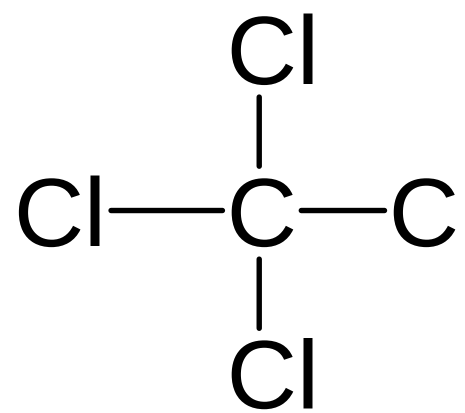
- What is the oxidation state of carbon in dichloromethane?

C(0)



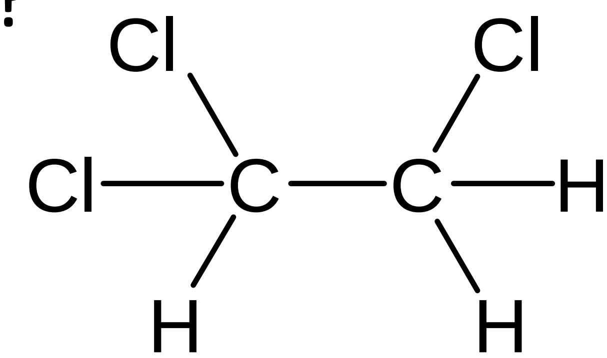
- What is the oxidation state of carbon in carbon tetrachloride?

C(+IV)



Oxidation State

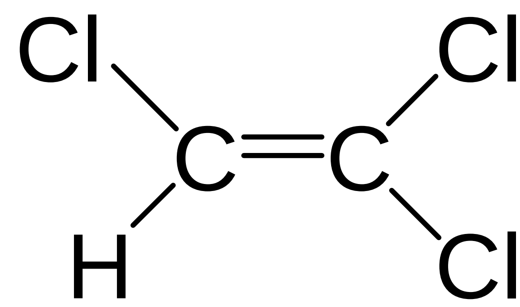
- What is the average oxidation stat of C in 1,1,2-trichloroethane?



first carbon: +1
second carbon: -1

C(0)

- What is the average oxidation state of C in trichloroethylene?



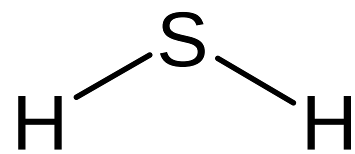
first carbon: 0
second carbon: +2

C(+I)

Oxidation State

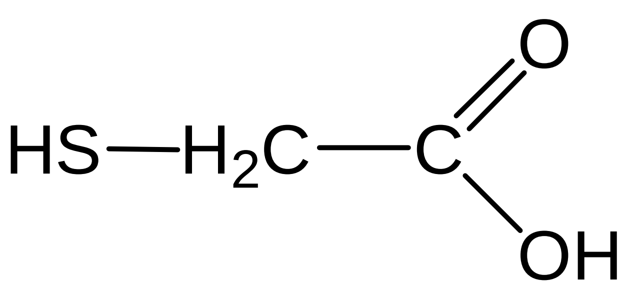
- What is the would oxidation state of sulfur in hydrogen sulfide?

S(-II)



- What is the oxidation state of S in mercaptoacetic acid?

S(-II)



Orientation and size

- Bond Angle

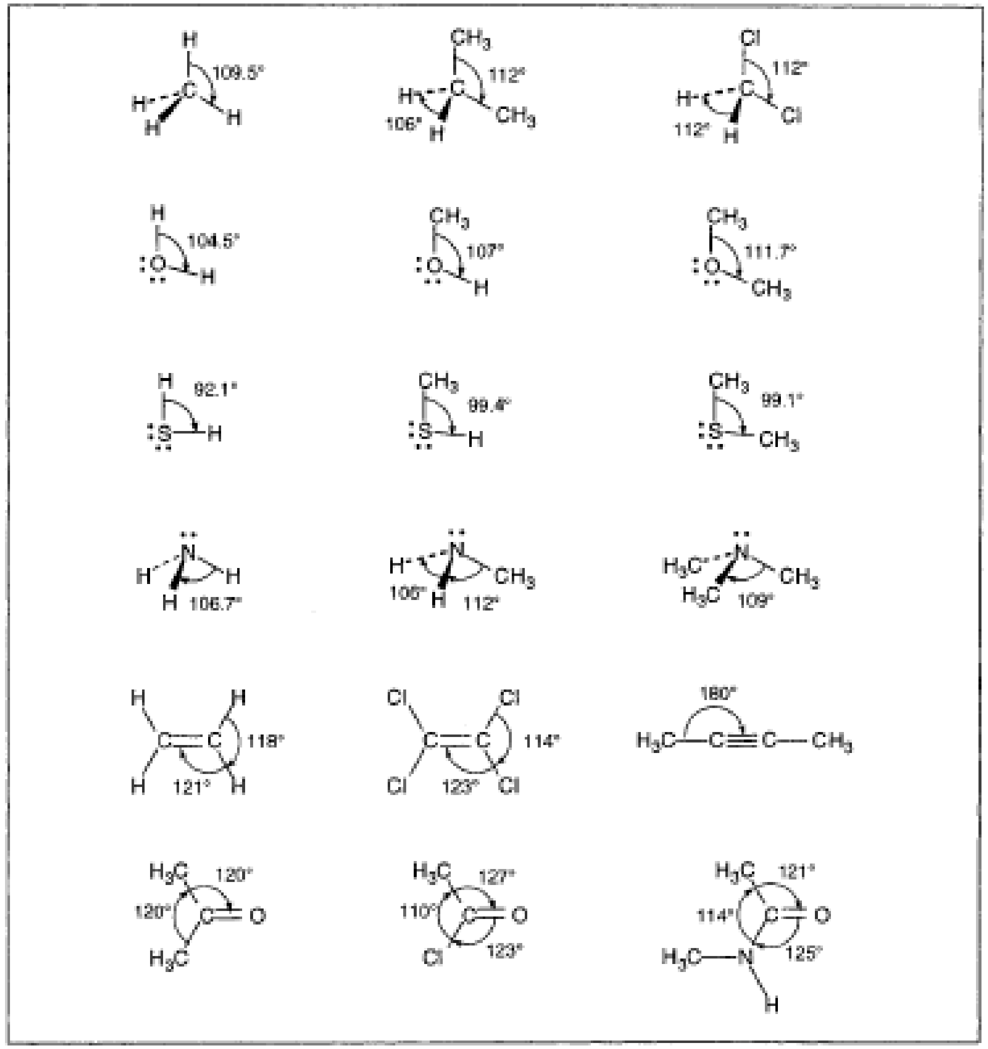


Figure 2.3 Examples of bond angles in some simple molecules (from Hendrickson et al., 1970, and March 1992).

Orientation and size

- Orientation

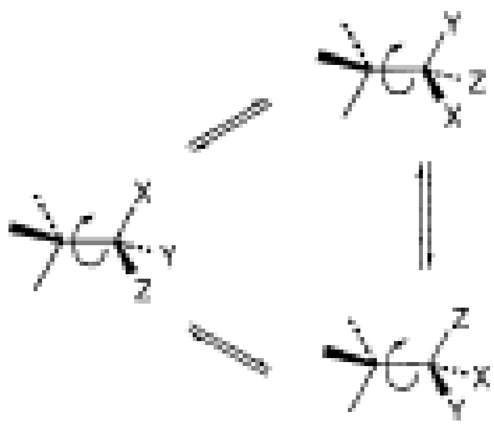


Figure 2.4 Rotation about a σ–bond leading to various spatial arrangements of the atoms in a molecule.

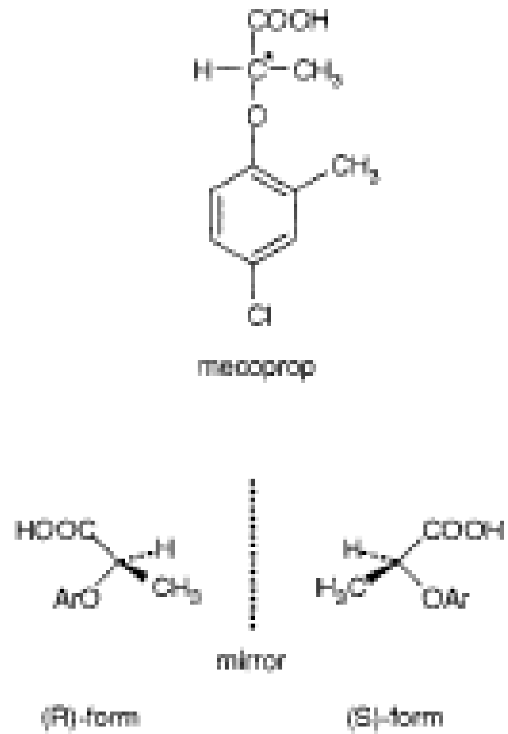


Figure 2.5 The two enantiomeric forms of the herbicide mecoprop. The * indicates the asymmetric carbon center. Ar denotes the aromatic substituent.

Orientation and size

- Restricted rotation

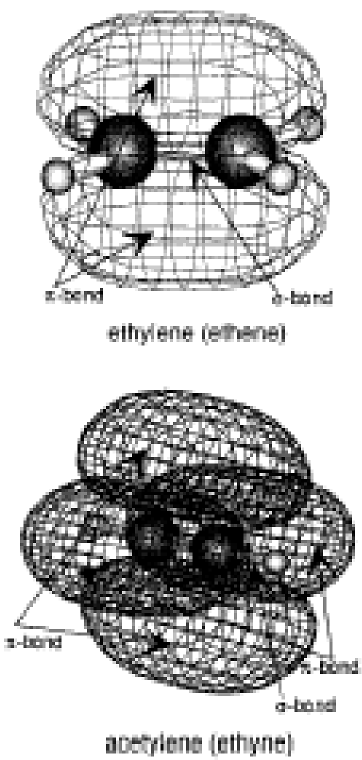


Figure 2.6 Simplified picture of a double (ethylene) and triple (acetylene) bond, respectively.

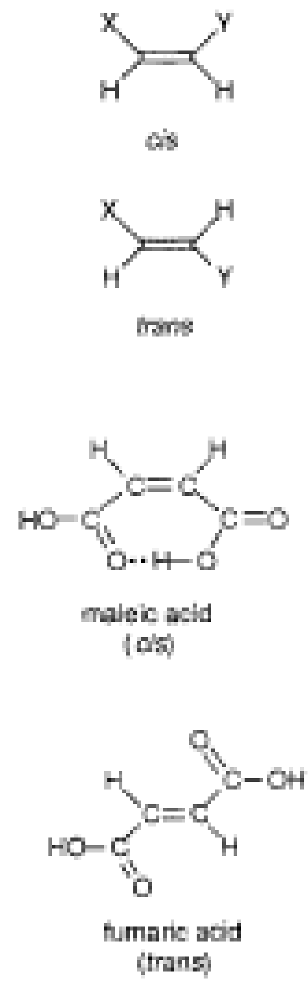
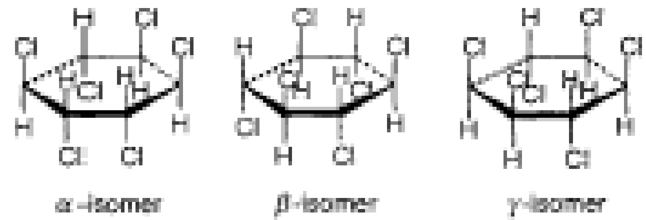


Figure 2.7 *Cis/trans* isomerism at double bonds exhibiting two substituents.

Orientation and size

- Rings



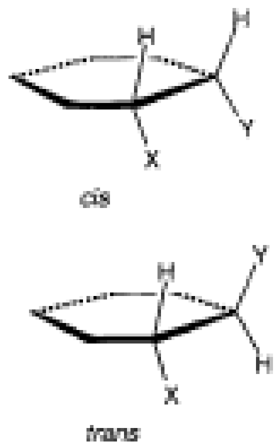
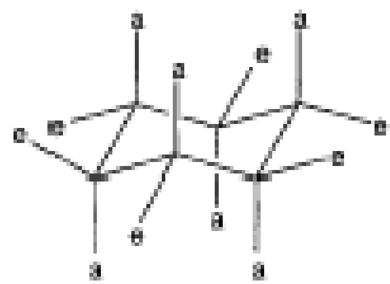
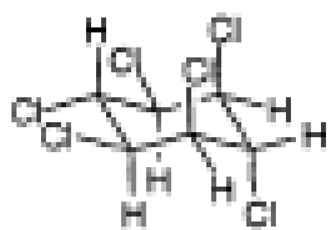


Figure 2.8 *Cis/trans* isomerism in ring systems, such as in cyclohexane.





lindane

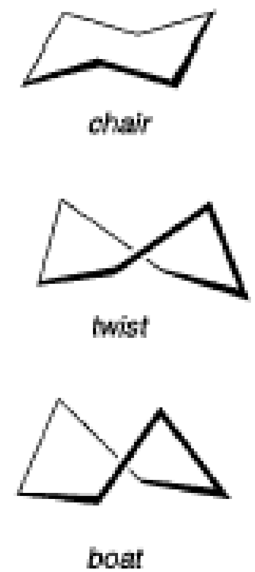
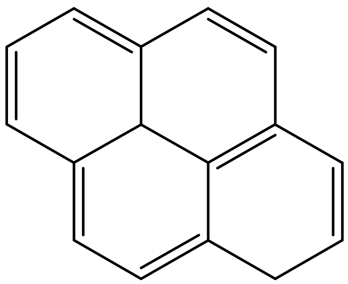


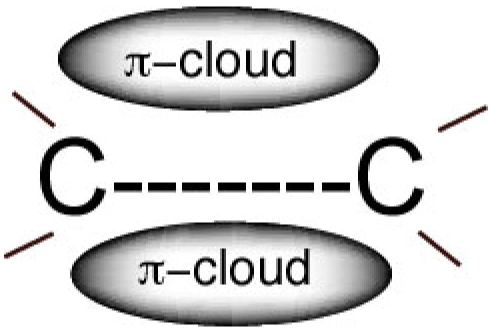
Figure 2.9 Different possible conformations of a six-membered ring (e.g., cyclohexane).

Delocalized Electrons

- Do delocalized electrons make a compound more or less stable?



  - The restraints on electron positions are diminished, their energy levels are lowered, and hence, the compound is more stable.
  - delocalized electrons = double, triple bonds = stronger bonds



Resonance and aromaticity

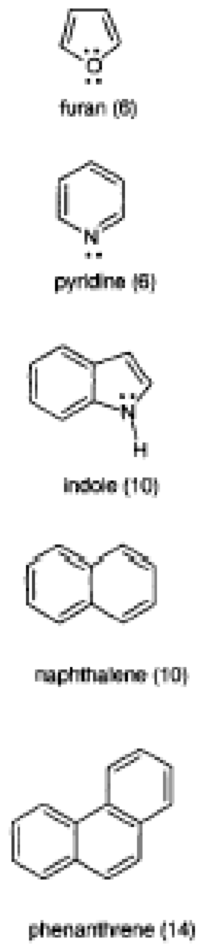
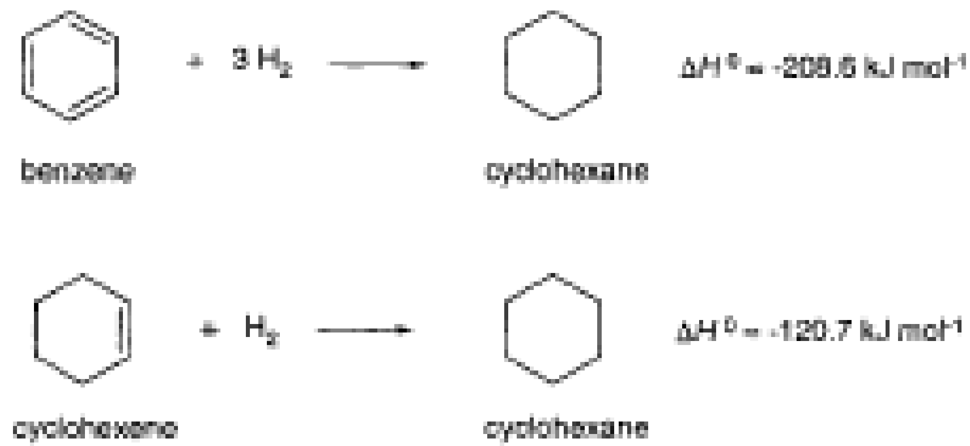
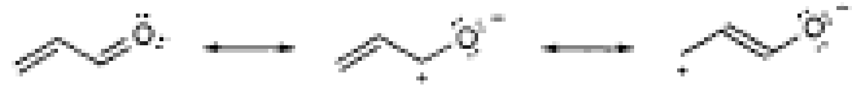
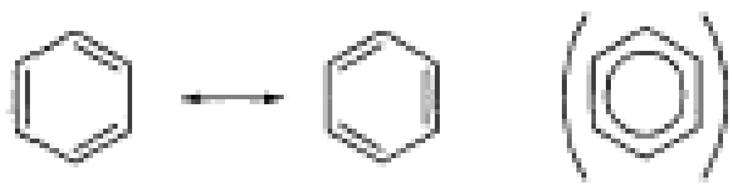


Figure 2.11 Some additional examples of organic compounds that are aromatic (in parentheses, number of π-electrons).

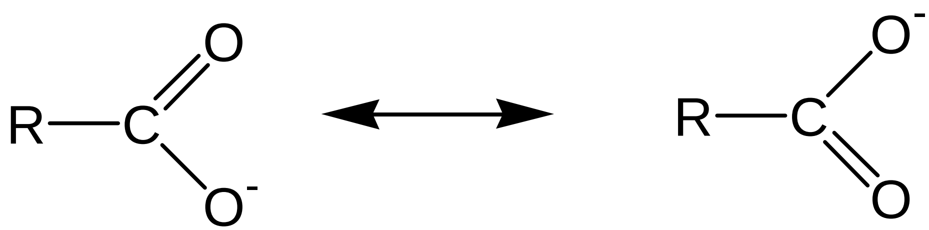




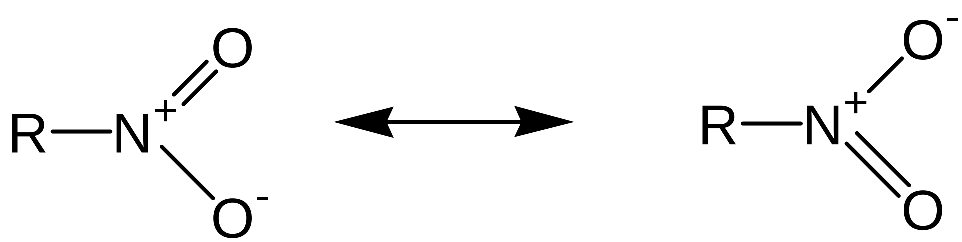


Delocalized Electrons

- What are two common functional groups that "resonate?"

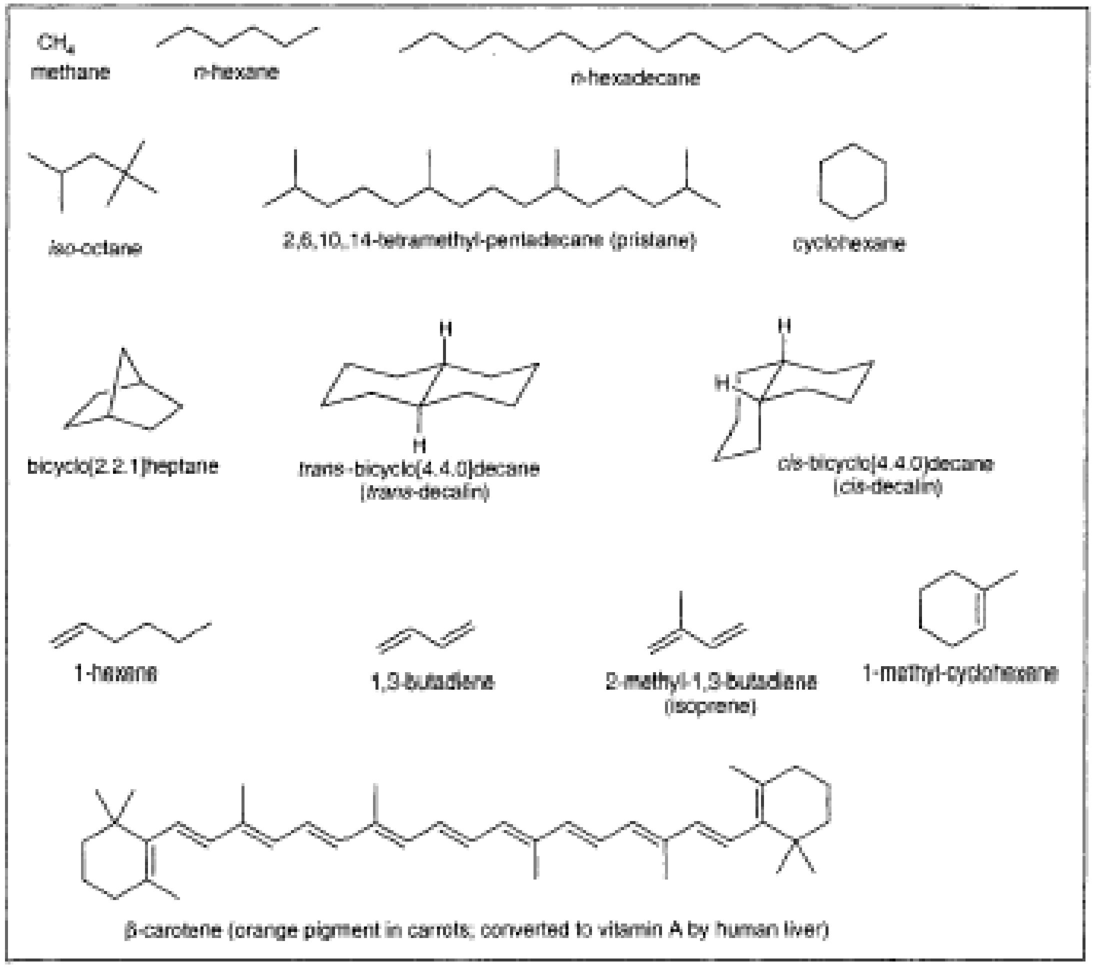


carboxyl

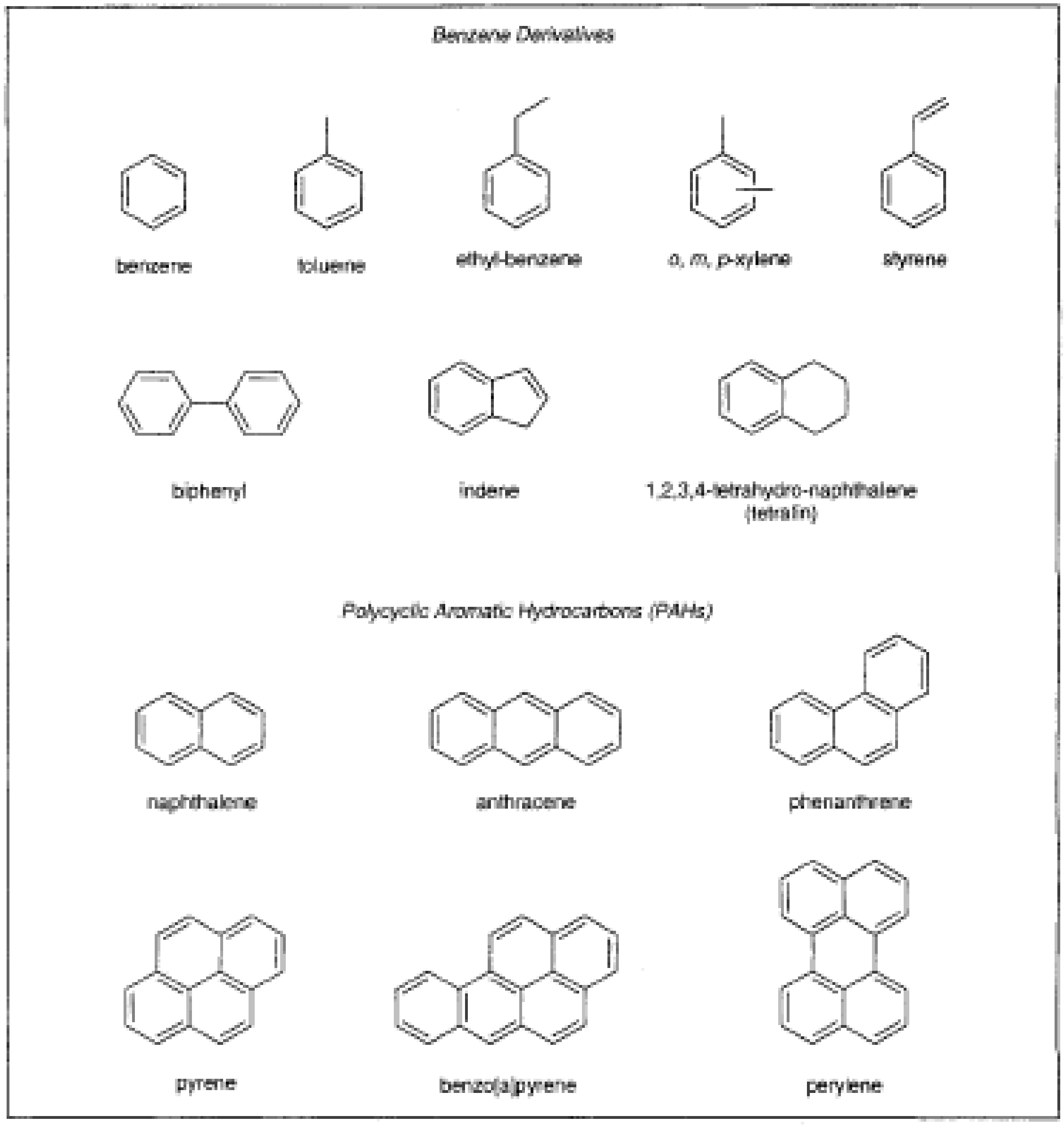


nitro

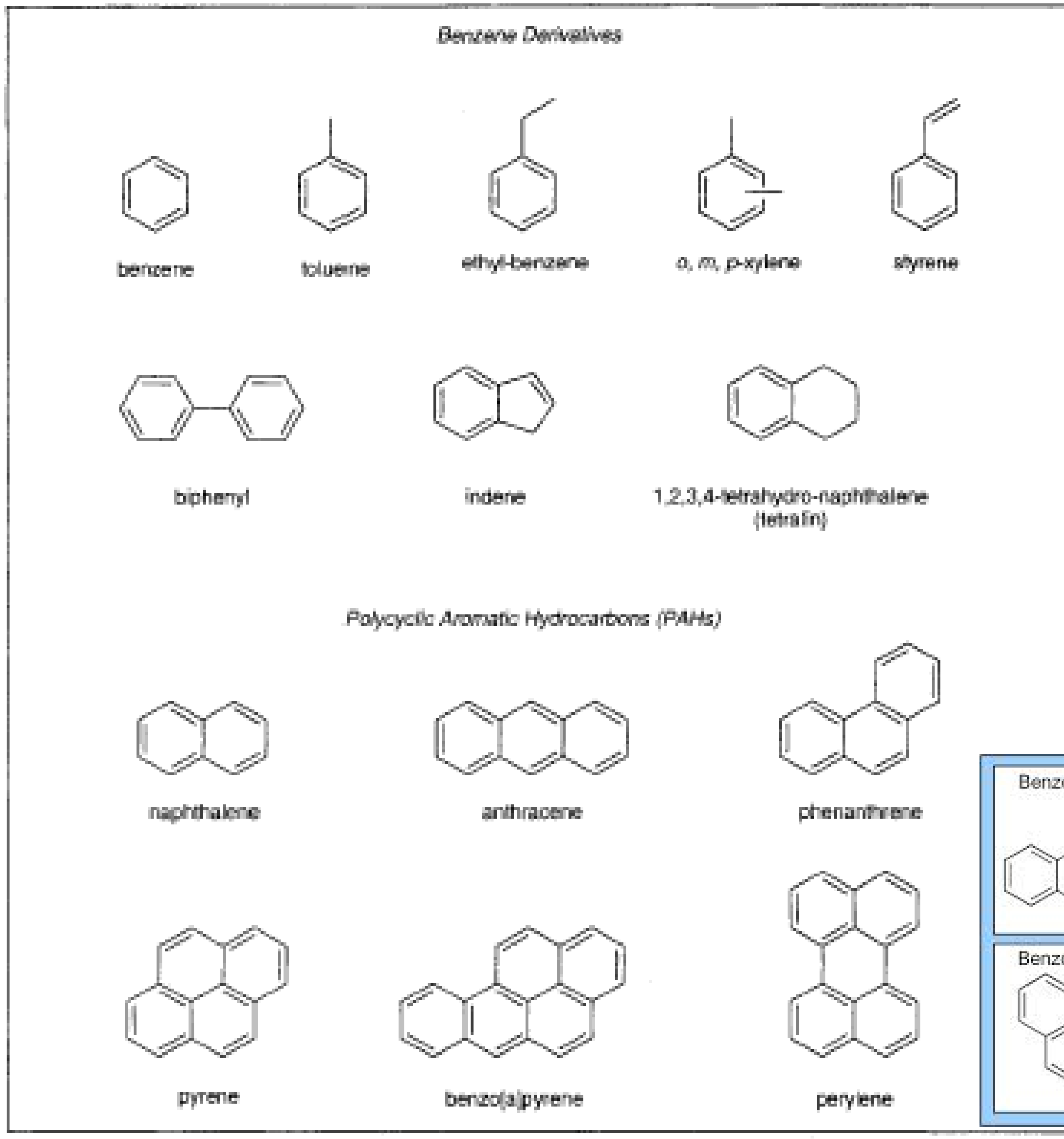
Structure and nomenclature

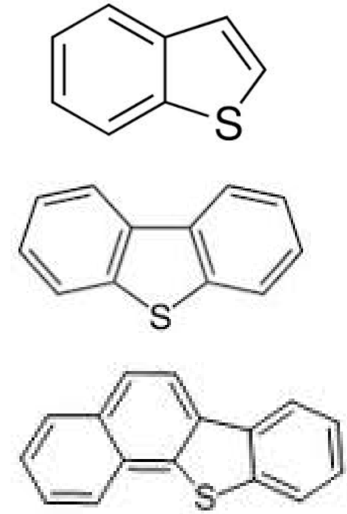


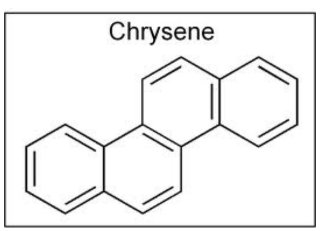
Structure and nomenclature

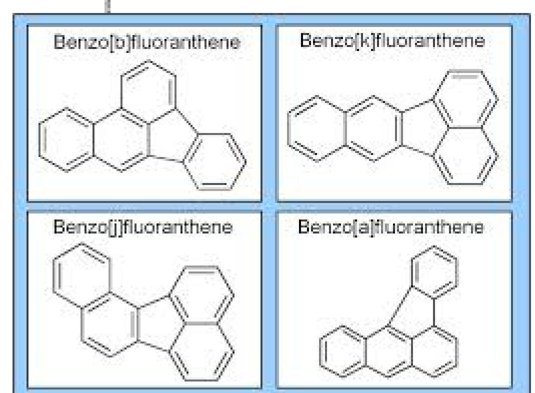


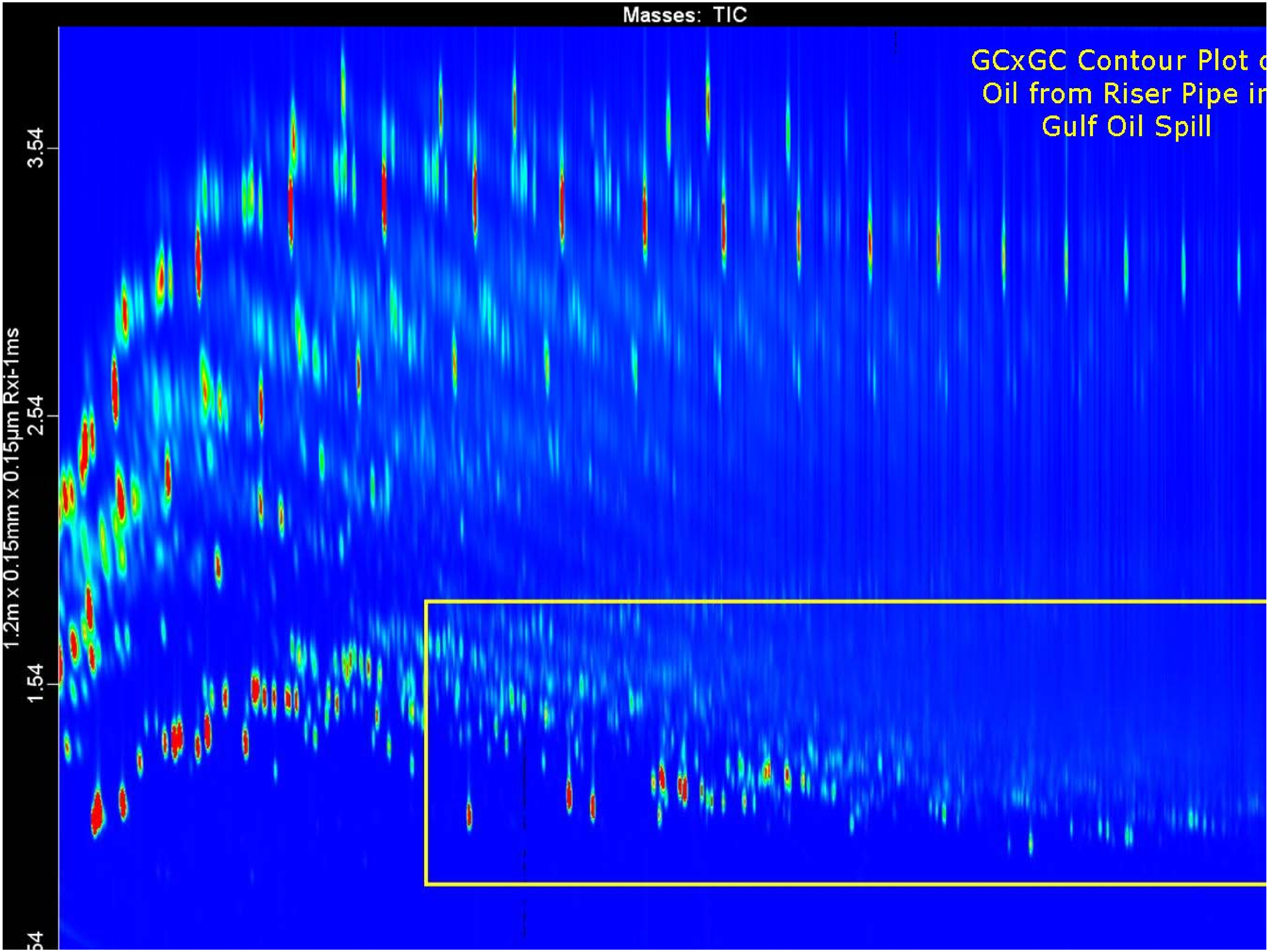
Structure and nomenclature

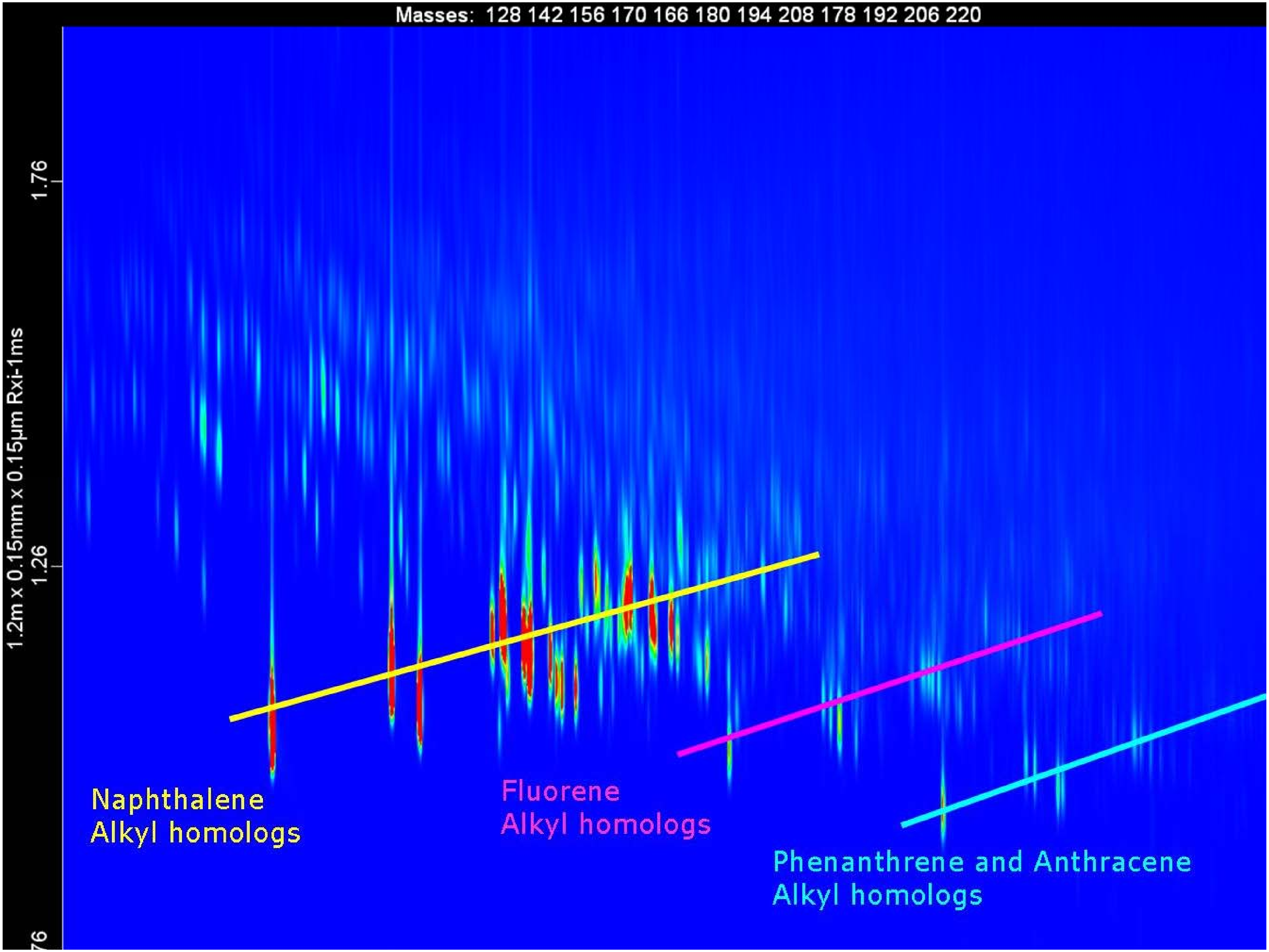









Masses: TIC
GCxGC Contour Plot o
Oil from Riser Pipe in
Gulf Oil Spill
1.2m x 0.15mm x 0.15µm Rxi-1ms
3.54
2.54
1.54

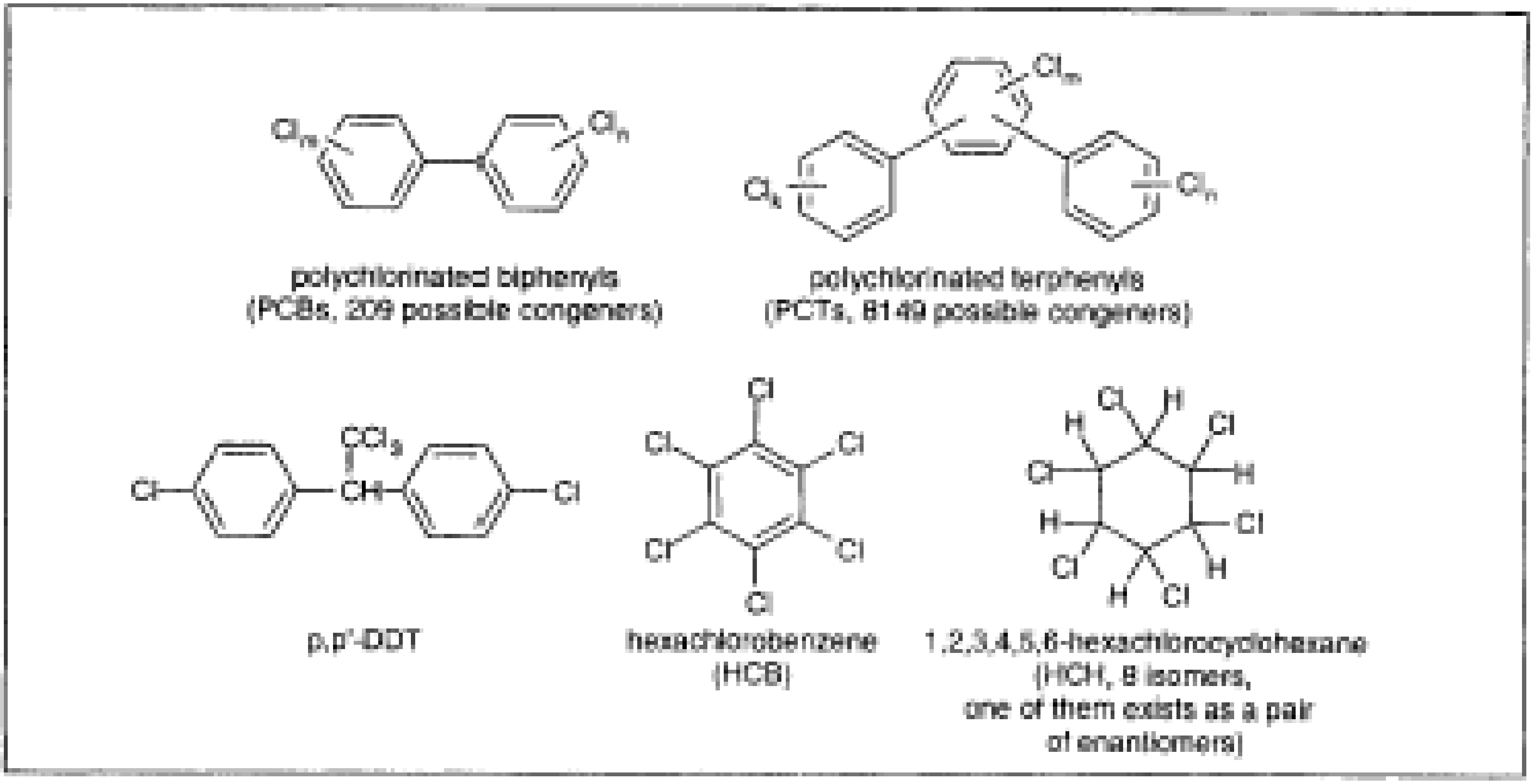

Masses: 128 142 156 170 166 180 194 208 178 192 206 220
1.76
1.26
.76
1.2m x 0.15mm x 0.15µm Rxi-1ms
Naphthalene
Alkyl homologs
Fluorene
Alkyl homologs
Phenanthrene and Anthracene
Alkyl homologs

Structure and nomenclature: Halogens

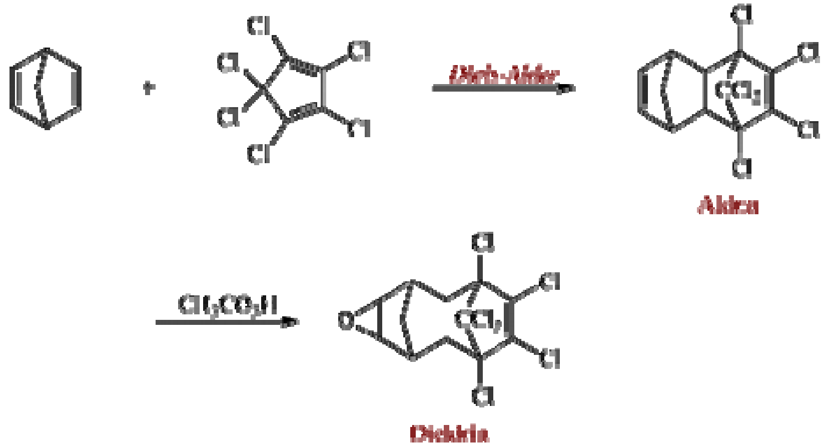
Table 2.4 Examples of Important Industrially Produced C_1- and C_2-Halocarbons

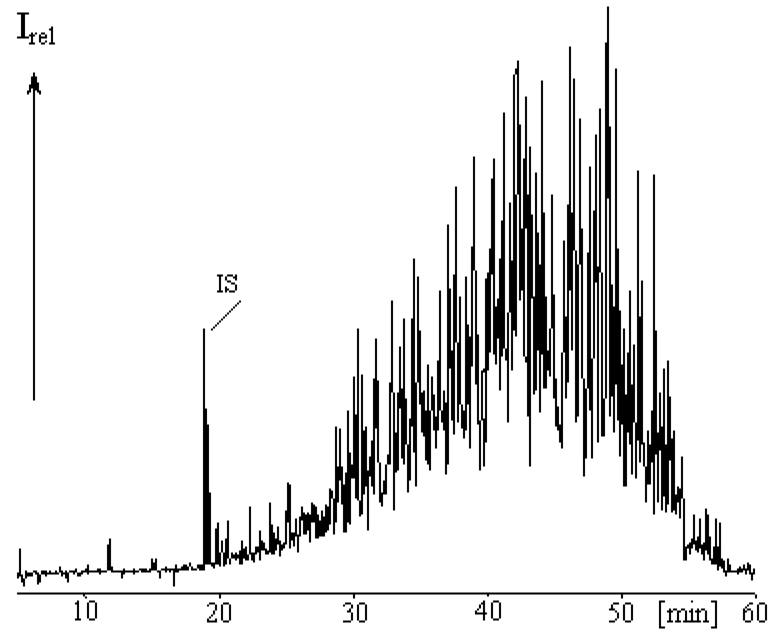
Compound Name(s)	Formula	Major Use
Dichlorodifluoromethane (CFC-12)	CCl_2F_2	Aerosol propellants, refrigerants (domestic, automobile air conditioning), flowing agents for plastic foams, etc.
Trichlorofluoromethane (CFC-11)	CCl_3F	
Chlorodifluoromethane (HCFC-22)	$CHClF_2$	
1,1,1,2-Tetrafluoroethane (HCFC-134a)	CF_3-CHF	
1,1-Dichloro-1-fluoroethane (HCFC-141b)	CCl_2F-CH_3	
Dichloromethane (Methylene chloride)	CH_2Cl_2	solvent
Trichloroethene (Trichloroethylene, TRI)	$CHCl{=}CCl_2$	solvent
Tetrachloroethene (Tetrachloroethylene, Perchloroethylene, PER)	$CCl_2{=}CCl_2$	solvent
1,1,1-Trichloroethane	CCl_3-CH_3	solvent

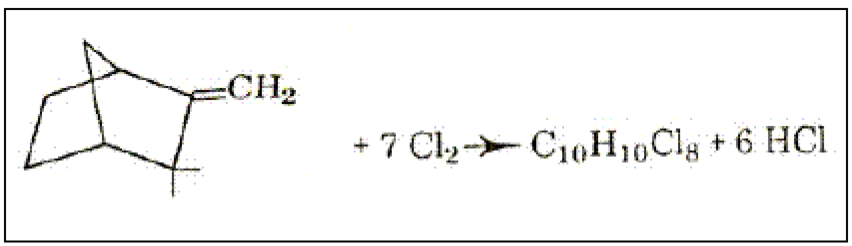
Structure and nomenclature: Halogens

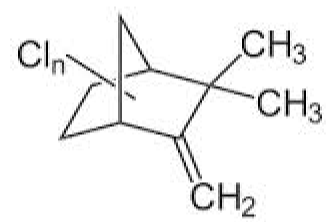


Chlorinated cyclodienes!

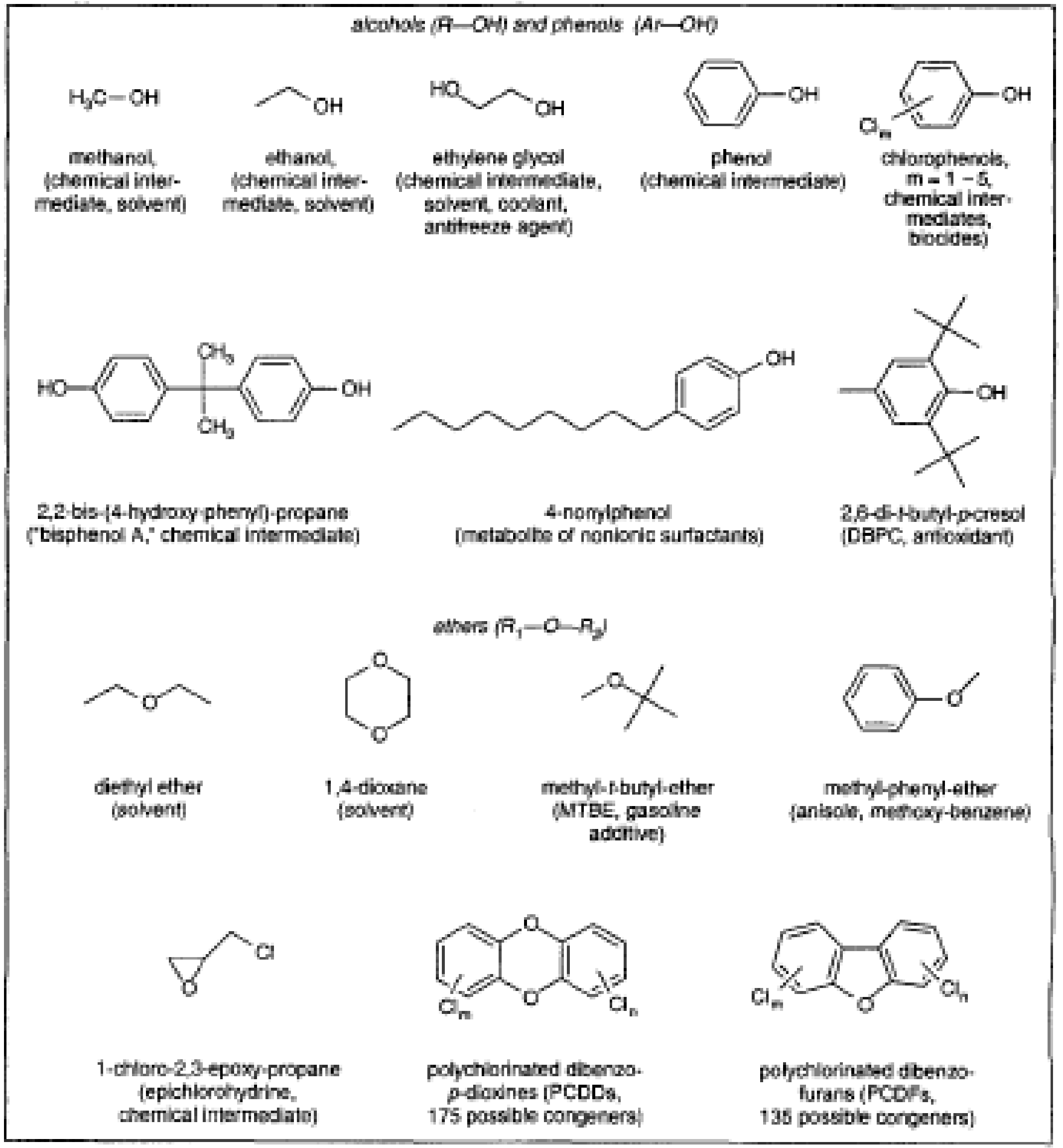




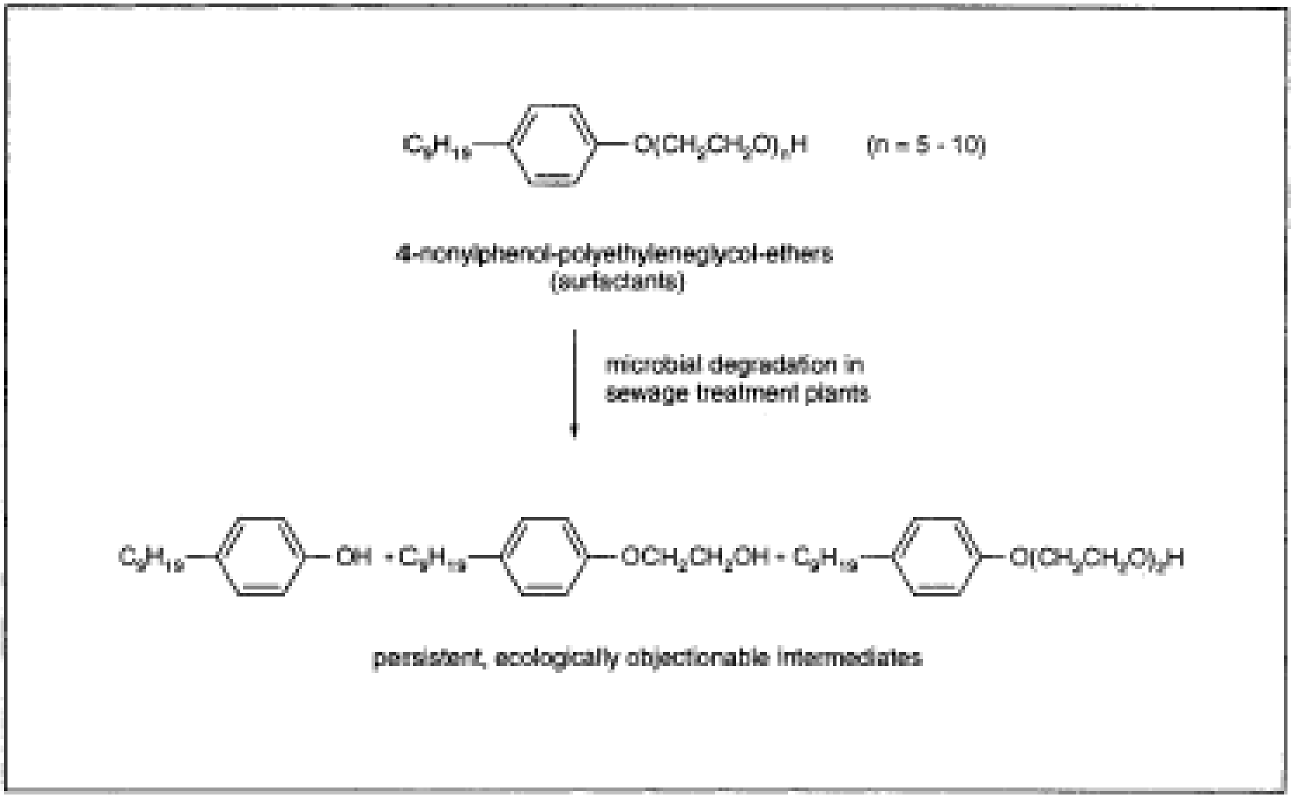




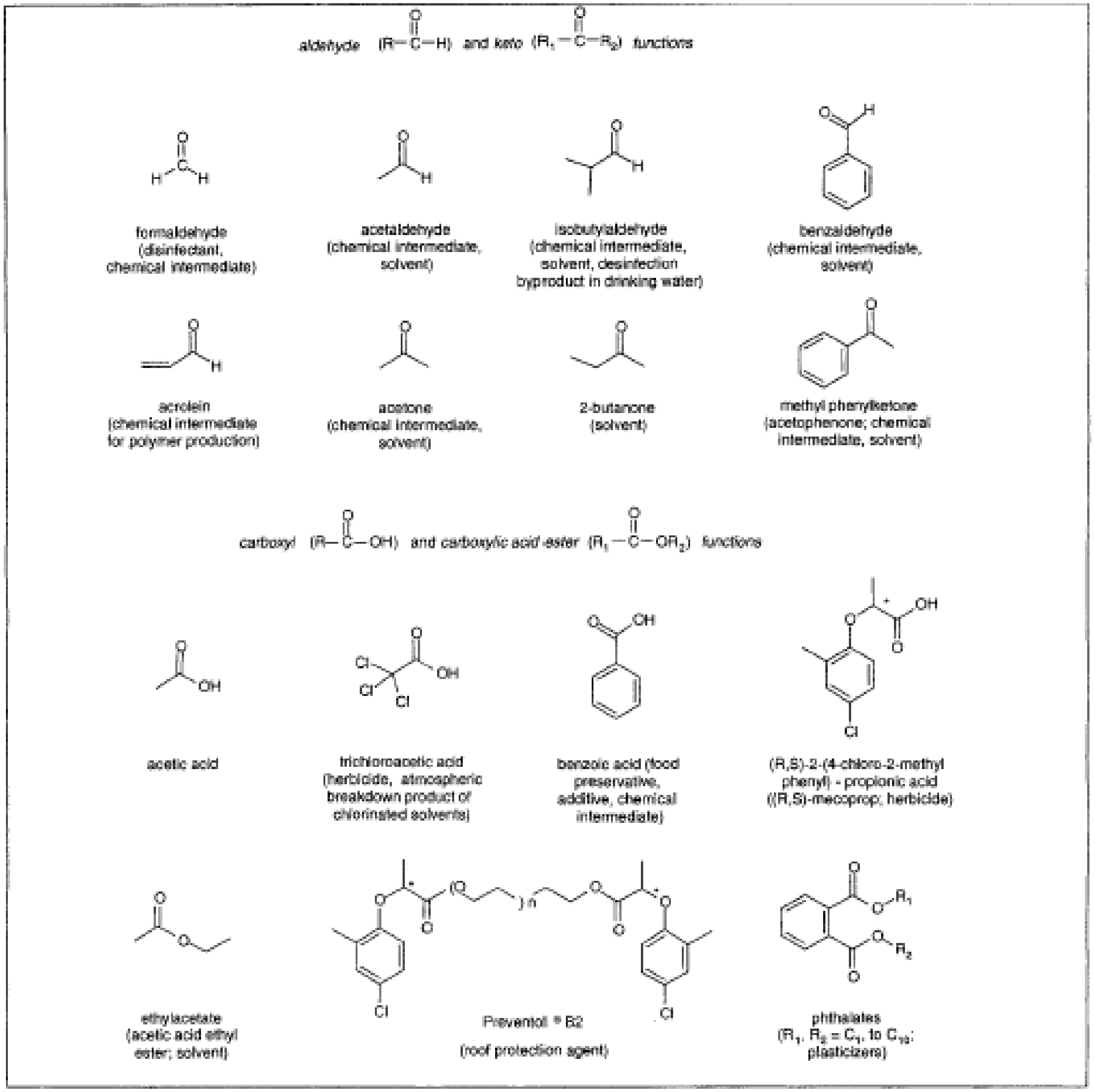
Structure and nomenclature: Oxygenated



Structure and nomenclature: WOW!

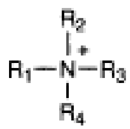
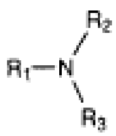
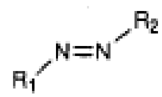
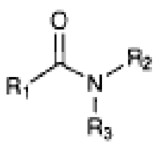
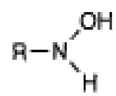
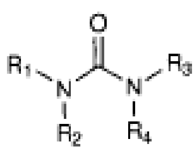
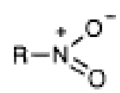
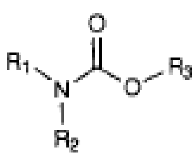
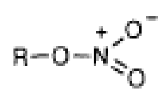


Structure and nomenclature: Oxygenated



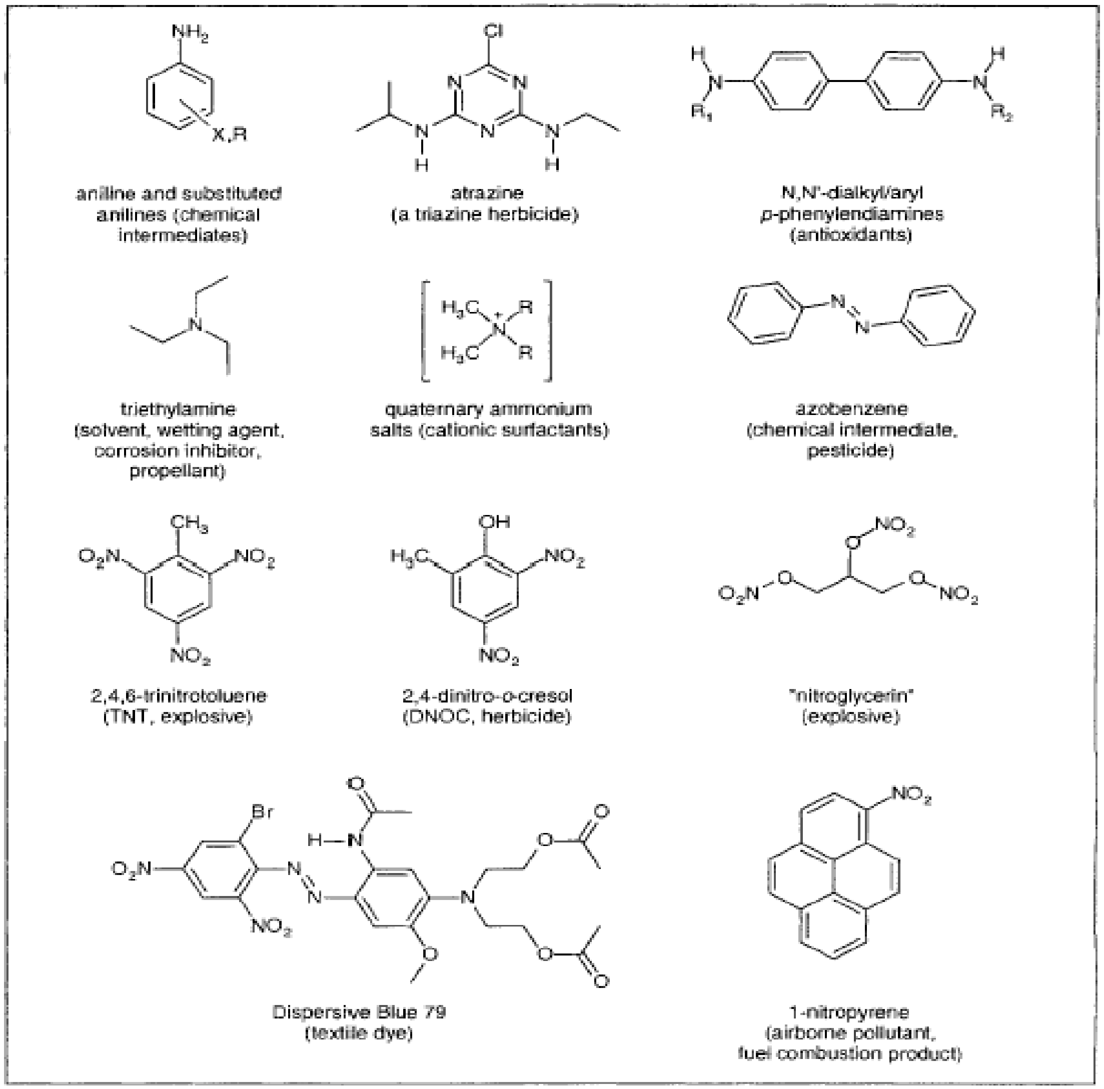
Structure and nomenclature: Nitrogen

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)		hydrazo (-II)
	amino[a] (-III) (amine)		azo (-I)
	carboxylic acid amide[a] (-III)		hydroxyl-amine (-I)
	cyano, nitrilo (-III)		nitroso (+I)
	urea (-III)		nitro (+III)
	carbamate (-III)		nitrato (+V) (nitrate)

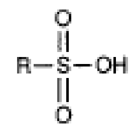
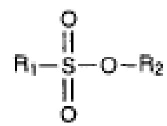
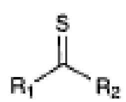
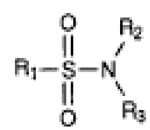
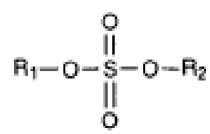
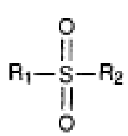
[a]Primary if $R_2 = R_3 = H$; secondary if $R_2 = H$ and $R_3 \neq H$; tertiary if $R_2 \neq H$ and $R_3 \neq H$.

Structure and nomenclature: Nitrogen

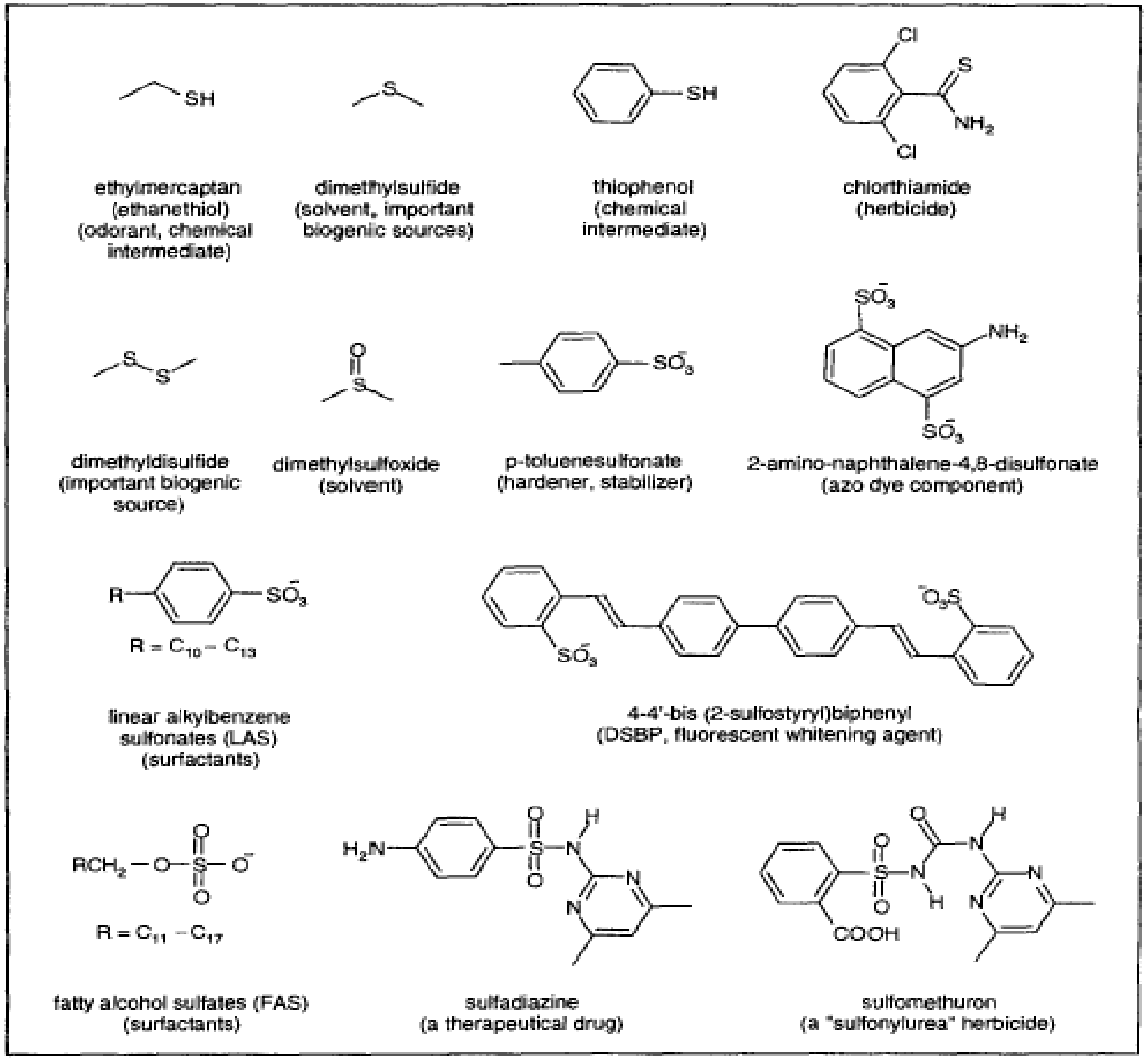


Structure and nomenclature: Sulfur

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)
$R-SH$	thiol, mercaptan (-II)		sulfonic acid (+IV)
R_1-S-R_2	thioether, sulfide (-II)		sulfonic acid ester (+IV)
	thiocarbonyl (-II)		sulfonic acid amide, sulfonamide (+IV)
$R_1-S-S-R_2$	disulfide (-I)		sulfuric acid ester, sulfate (+VI)
	sulfoxide (0)		
	sulfone (+II)		

Structure and nomenclature: Sulfur



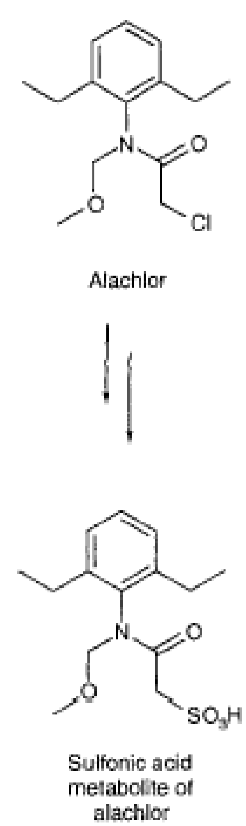
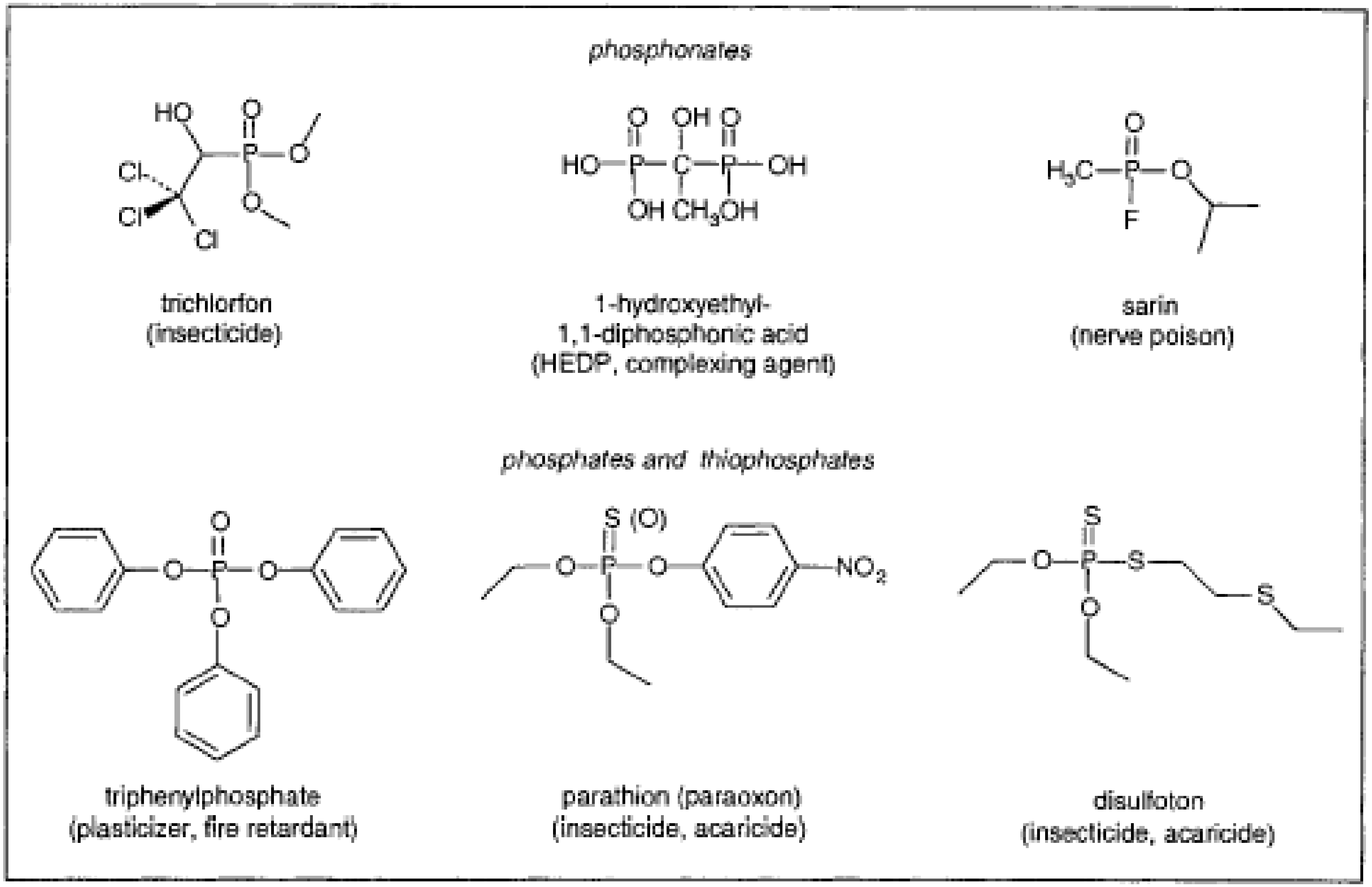
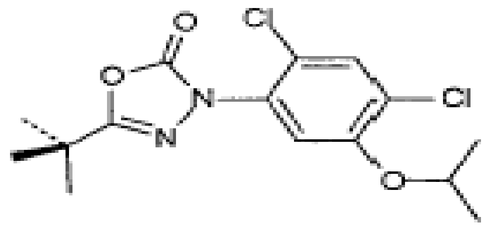


Figure 2.21 Gluthathione S-transferase *enzyme-mediated* reaction ultimately yielding a sulfonated metabolite (from Field and Thurman, 1996).

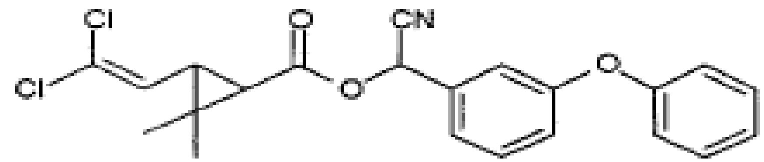
Structure and nomenclature: Phosphorous



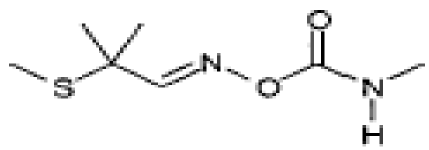
Structure and nomenclature: ALL



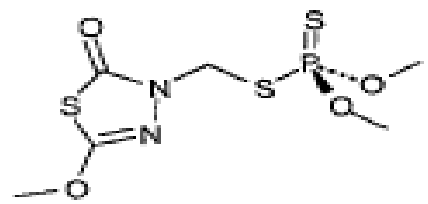
oxadiazon
(herbicide)



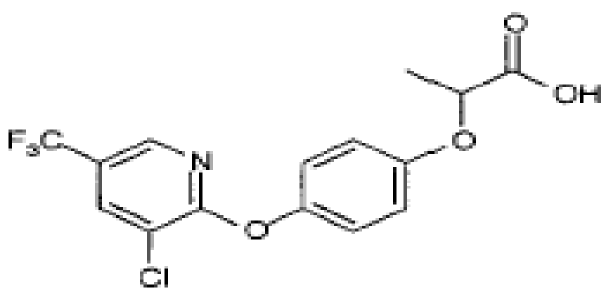
cypermethrin
(a pyrethroid insecticide;
mixtures of diastereomers)



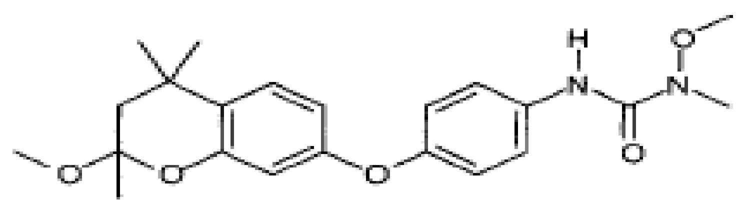
aldicarb
(insecticide, acaricide, nematicide)



methidathion
(insecticide, acaricide)

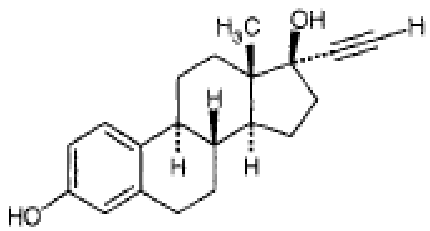


haloxyfop
(herbicide)

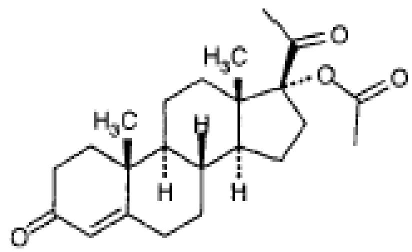


metobenzuron
(herbicide)

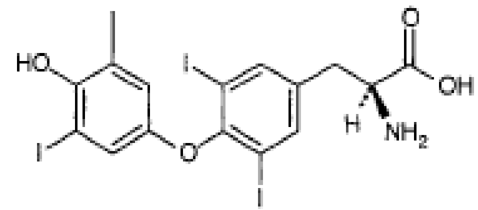
Structure and nomenclature: ALL



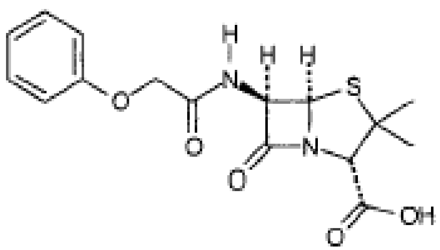
17-ethynyl estradiol
(hormone, birth control pill)



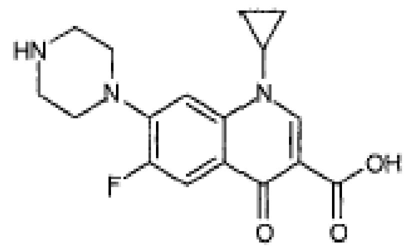
17α-acetoxy-progesterone
(hormone)



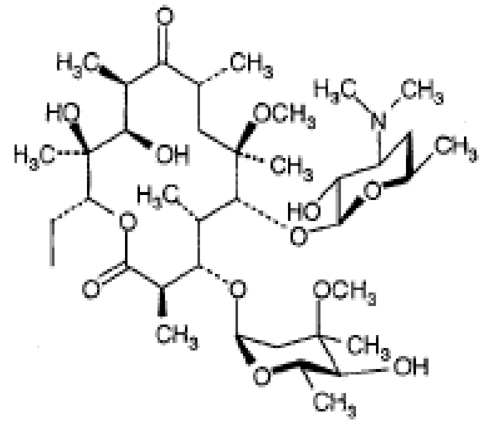
levothyroxine
(hormone)



penicillin V
(β-lactam antibiotic)



ciprofloxacin
(fluoroquinolone antibiotic)



clarithromycin
(macrolide antibiotic)

Organic Molecules are Boring

Titanium Dioxin will kill you?

Any true to the story?