Organic chemistry background III

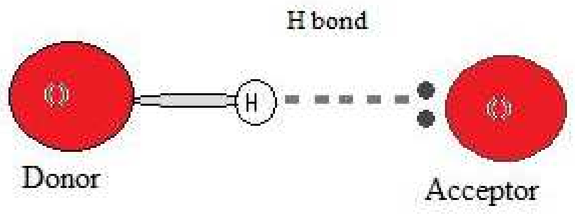
Hydrogen donors and acceptors

- **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**

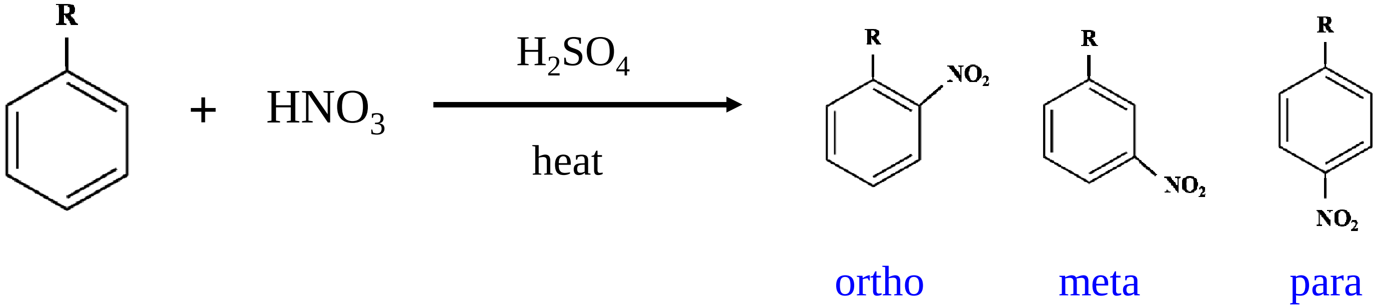
  An electronegative ion or molecule which possesses a lone electron pair in order to form a hydrogen bond



Electron donating and withdrawing groups

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

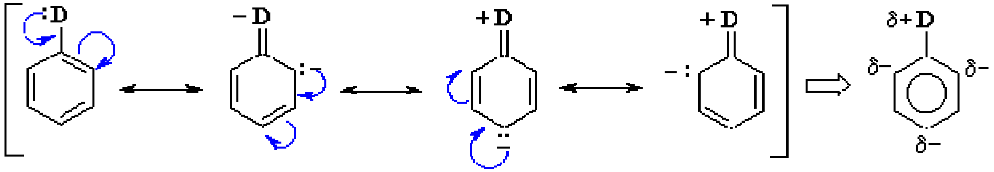
ex) Nitration of a substituted benzene



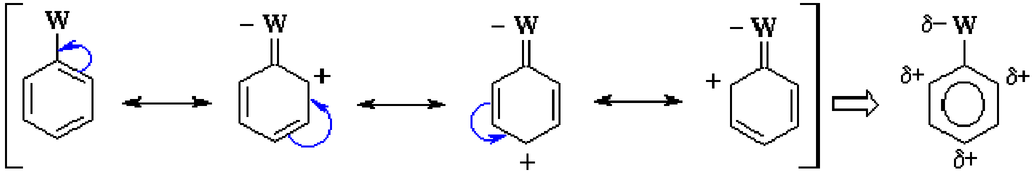
R	Reaction rate relative to benzene	Product ratio			Comments
		ortho	**meta**	**para**	
CH_3	25	63%	3%	34%	**Activated** (ortho/para directed)
CF_3	2.5×10^{-5}	6%	91%	3%	**Deactivated** (meta directed)

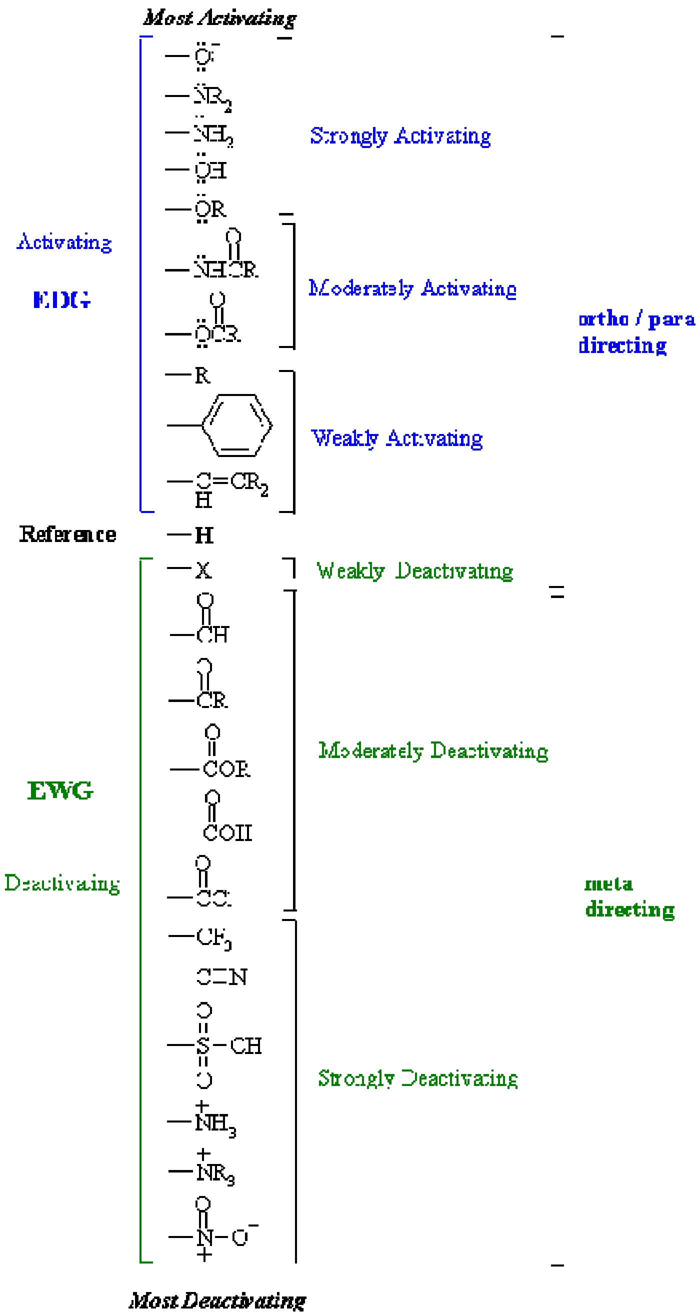
Electron donating and withdrawing groups

- **Electron donating groups**
  - 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



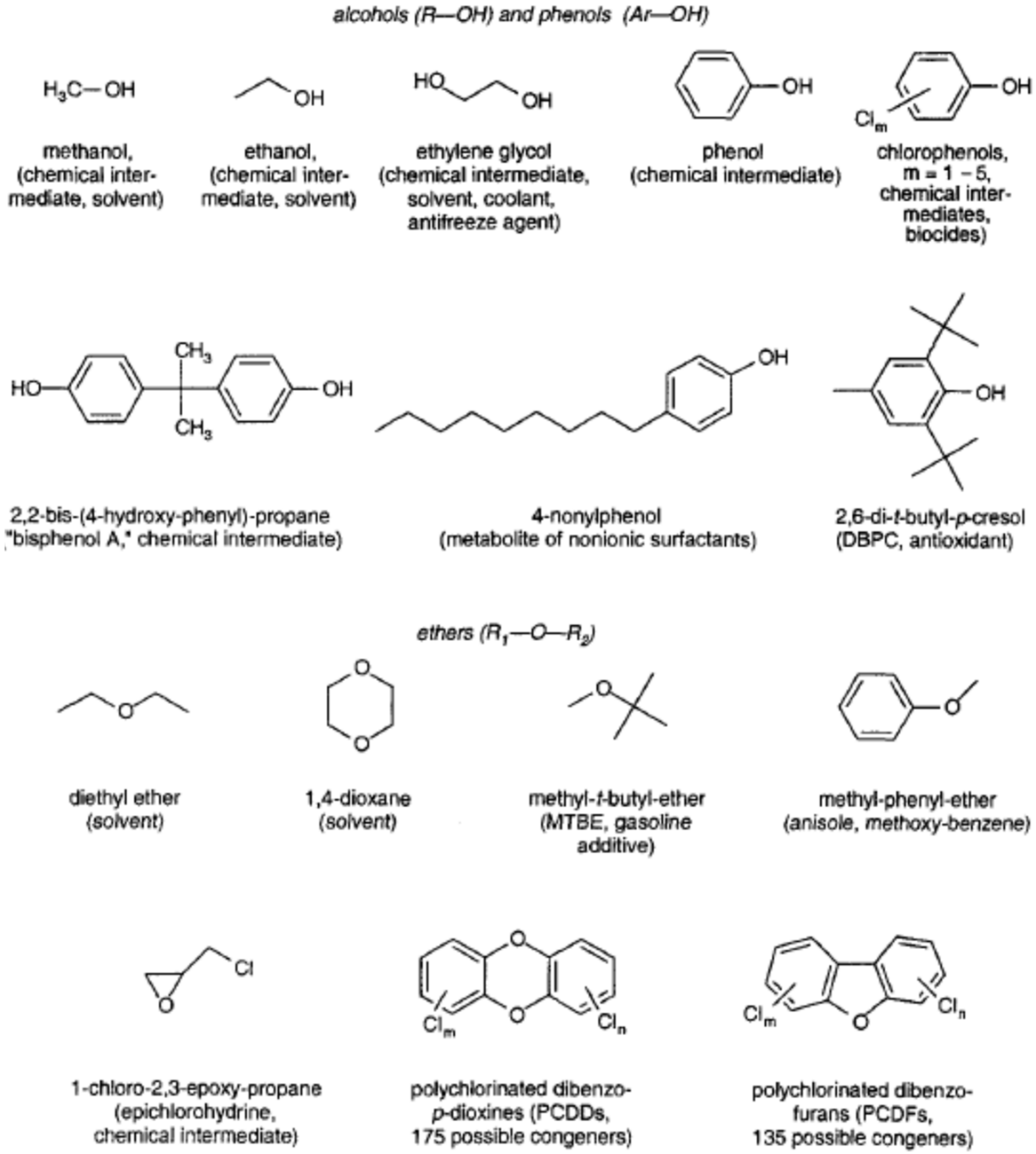
- **Electron withdrawing groups**
  - Decrease the electron density of the aromatic ring
  - Make the molecule less nucleophilic (deactivated)
  - The molecule tends to react with electrophiles at meta-sites




Most Activating
—O⁻
—NR₂
—NH₂
—OH
—OR
Strongly Activating
—NHCR
—OCR
Moderately Activating
—R
—C=CR₂
H
Weakly Activating
Activating
EDG
ortho / para
directing
Reference
—H
—X
Weakly Deactivating
—CH
—CR
—COR
COH
—CCl
Moderately Deactivating
—CF₃
C≡N
—S–CH
—NH₃
—NR₃
—N–O⁻
Strongly Deactivating
EWG
Deactivating
meta
directing
Most Deactivating

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

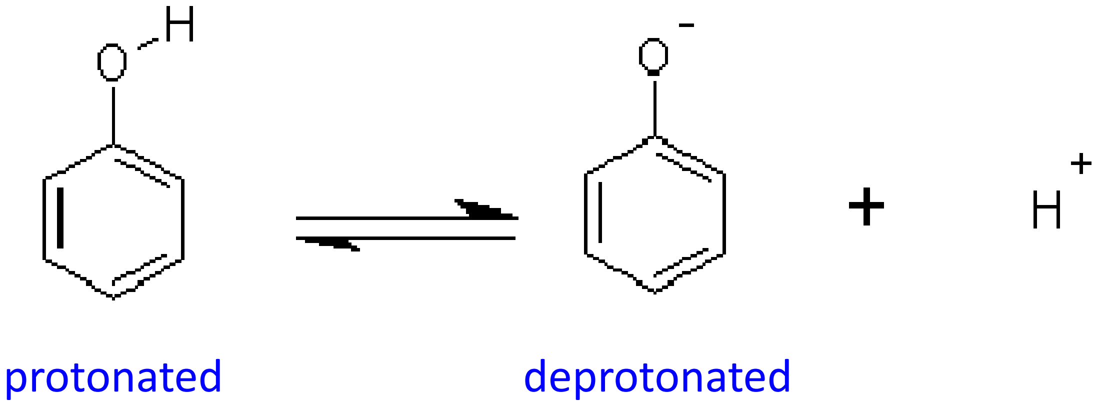


Oxygen-containing functional groups

- **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

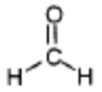
Dissociation of phenols

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%)

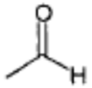


Oxygen-containing functional groups

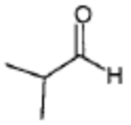
- **Aldehyde and keto groups**
  - C=O bonds
  - Aldehyde: C-CHO; keto: R_1-CO-R_2
  - H-acceptors
  - Quite reactive



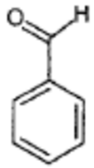
formaldehyde
(disinfectant,
chemical intermediate)



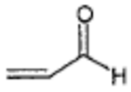
acetaldehyde
(chemical intermediate,
solvent)



isobutylaldehyde
(chemical intermediate,
solvent, desinfection
byproduct in drinking water)

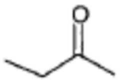


benzaldehyde
(chemical intermediate,
solvent)

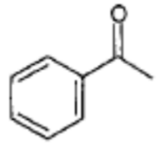


acrolein
(chemical intermediate
for polymer production)

acetone
(chemical intermediate,
solvent)



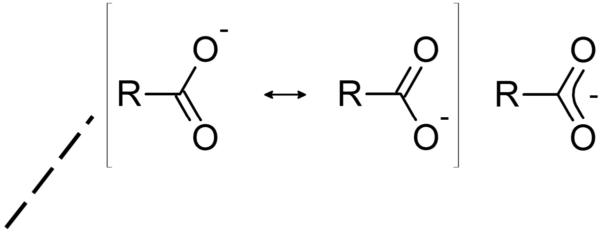
2-butanone
(solvent)

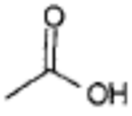


methyl phenylketone
(acetophenone; chemical
intermediate, solvent)

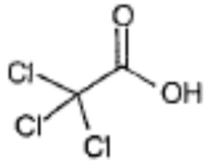
Oxygen-containing functional groups

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

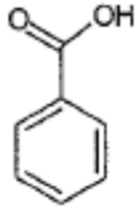




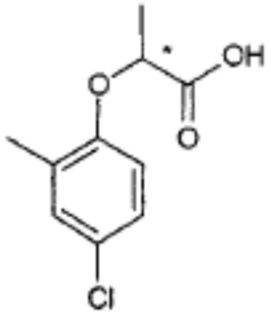
acetic acid



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



benzoic acid (food preservative, additive, chemical intermediate)

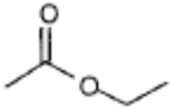


(R,S)-2-(4-chloro-2-methyl phenyl) - propionic acid ((R,S)-mecoprop; herbicide)

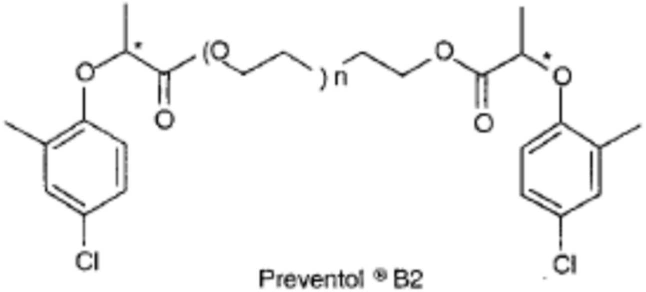
Oxygen-containing functional groups

- **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

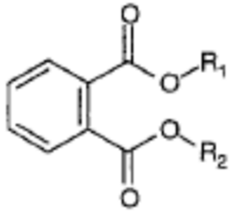


ethylacetate
(acetic acid ethyl
ester; solvent)



Preventol ® B2

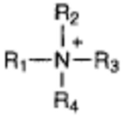
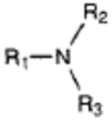
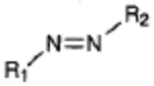
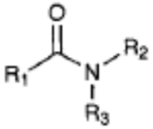
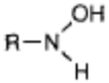
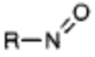
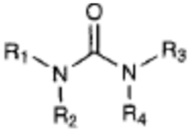
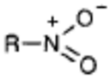
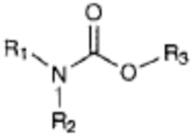
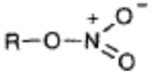
(roof protection agent)



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

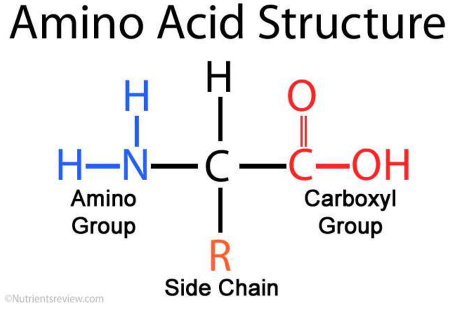
Nitrogen-containing functional groups

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

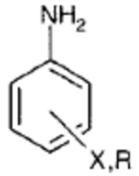
Group	Name (oxidation state of nitrogen)	Group	Name (oxidation state of nitrogen)
	ammonium (-III)	$R_1-NH-NH-R_2$	hydrazo (-II)
	amino[a] (-III) (amine)		azo (-I)
	carboxylic acid amide[a] (-III)		hydroxyl-amine (-I)
$R-C\equiv N$	cyano, nitrilo (-III)		nitroso (+I)
	urea (-III)		nitro (+III)
	carbamate (-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 $R_3 \neq H$.

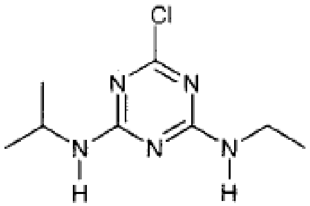
Nitrogen-containing functional groups



- **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



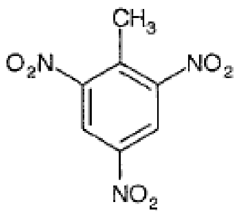
aniline and substituted anilines (chemical intermediates)



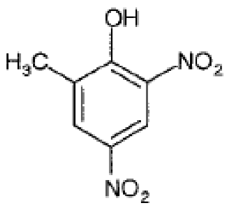
atrazine (a triazine herbicide)

Nitrogen-containing functional groups

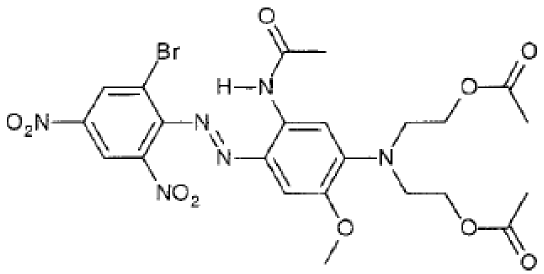
- **Nitro groups**
  - Widely used in the chemical industry
    - Explosives (ex: TNT), agrochemicals (ex: DNOC), dyes (ex: Dispersive Blue 79)
  - Strong electron-withdrawing characteristics
    - Significantly affect the electron distribution in a molecule
    - Significantly affect the chemical properties 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)



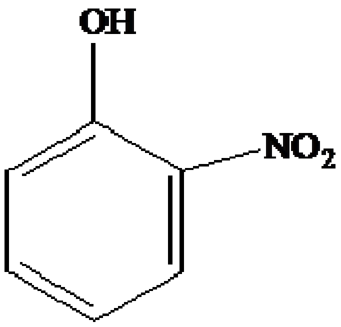
2,4-dinitro-*o*-cresol
(DNOC, herbicide)



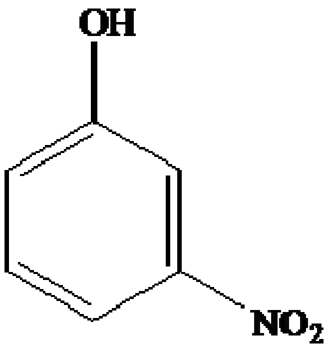
Dispersive Blue 79
(textile dye)

Dissociation of nitrophenols

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

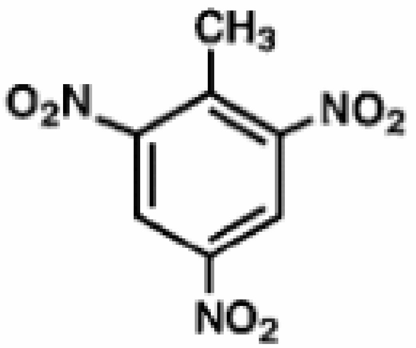


ortho-Nitrophenol or
2-Nitrophenol

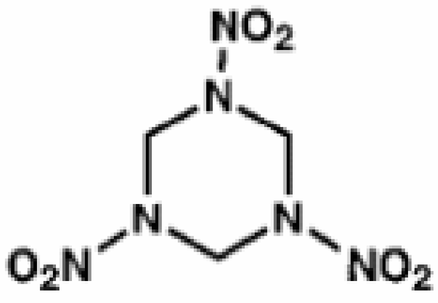


meta-Nitrophenol or
3-Nitrophenol

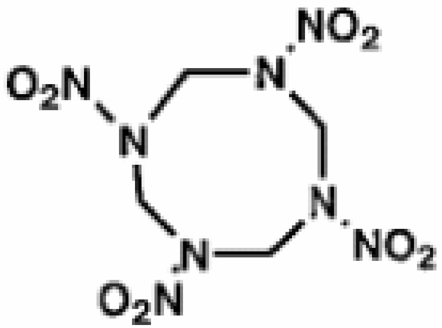
Examples of explosives containing nitro groups



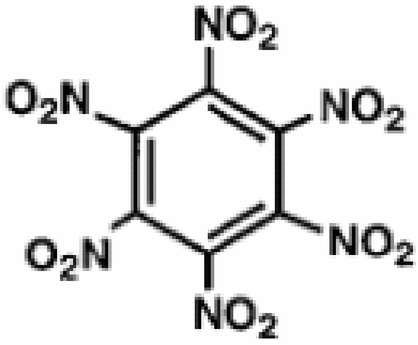
TNT



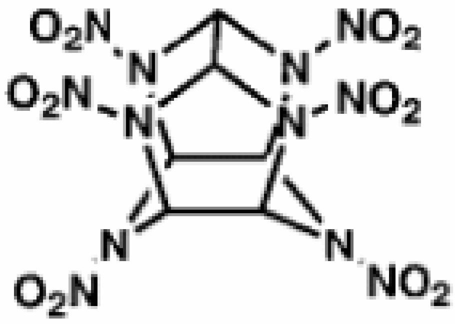
RDX



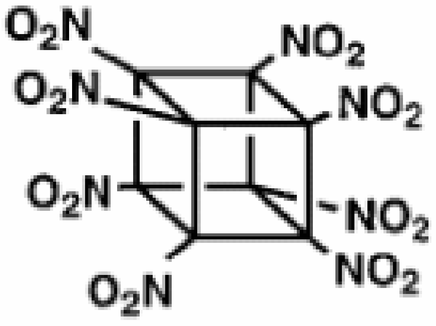
HMX



HNB



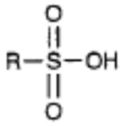
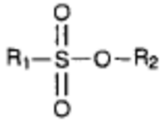
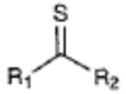
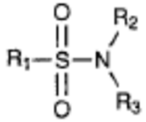
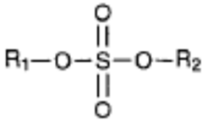
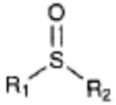
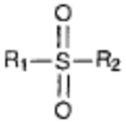
CL-20



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)
$R-SH$	thiol, mercaptan (-II)	 $R-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-OH$	sulfonic acid (+IV)
R_1-S-R_2	thioether, sulfide (-II)	 $R_1-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-O-R_2$	sulfonic acid ester (+IV)
	thiocarbonyl (-II)		sulfonic acid amide, sulfonamide (+IV)
$R_1-S-S-R_2$	disulfide (-I)	 $R_1-O-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-O-R_2$	sulfuric acid ester, sulfate (+VI)
	sulfoxide (0)		
 $R_1-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-R_2$	sulfone (+II)		