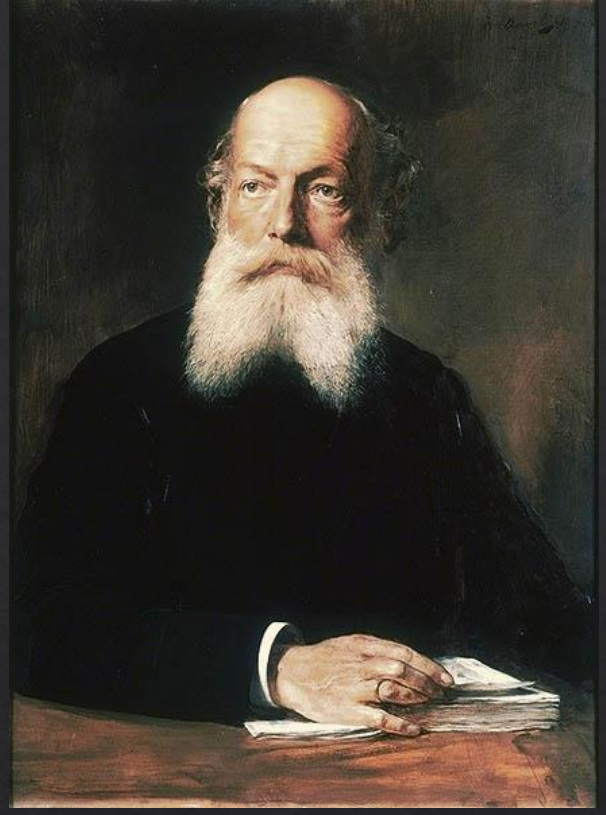
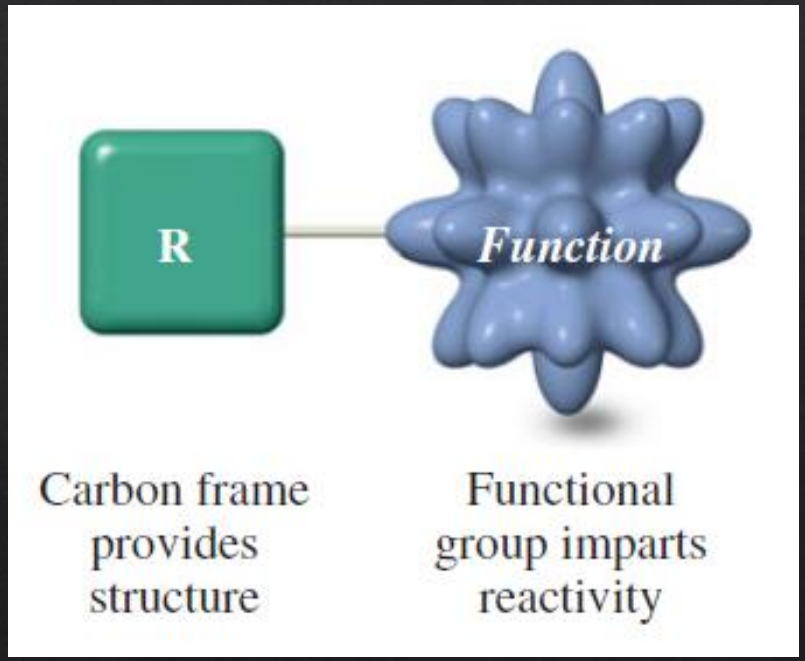


Friedrich August Kekulé

Acid/bases
Nucleophilic/electrophilic
Functional groups

Functional groups



Picture from Vollhardt & Schore

Alkanes, Alkenes and Alkynes

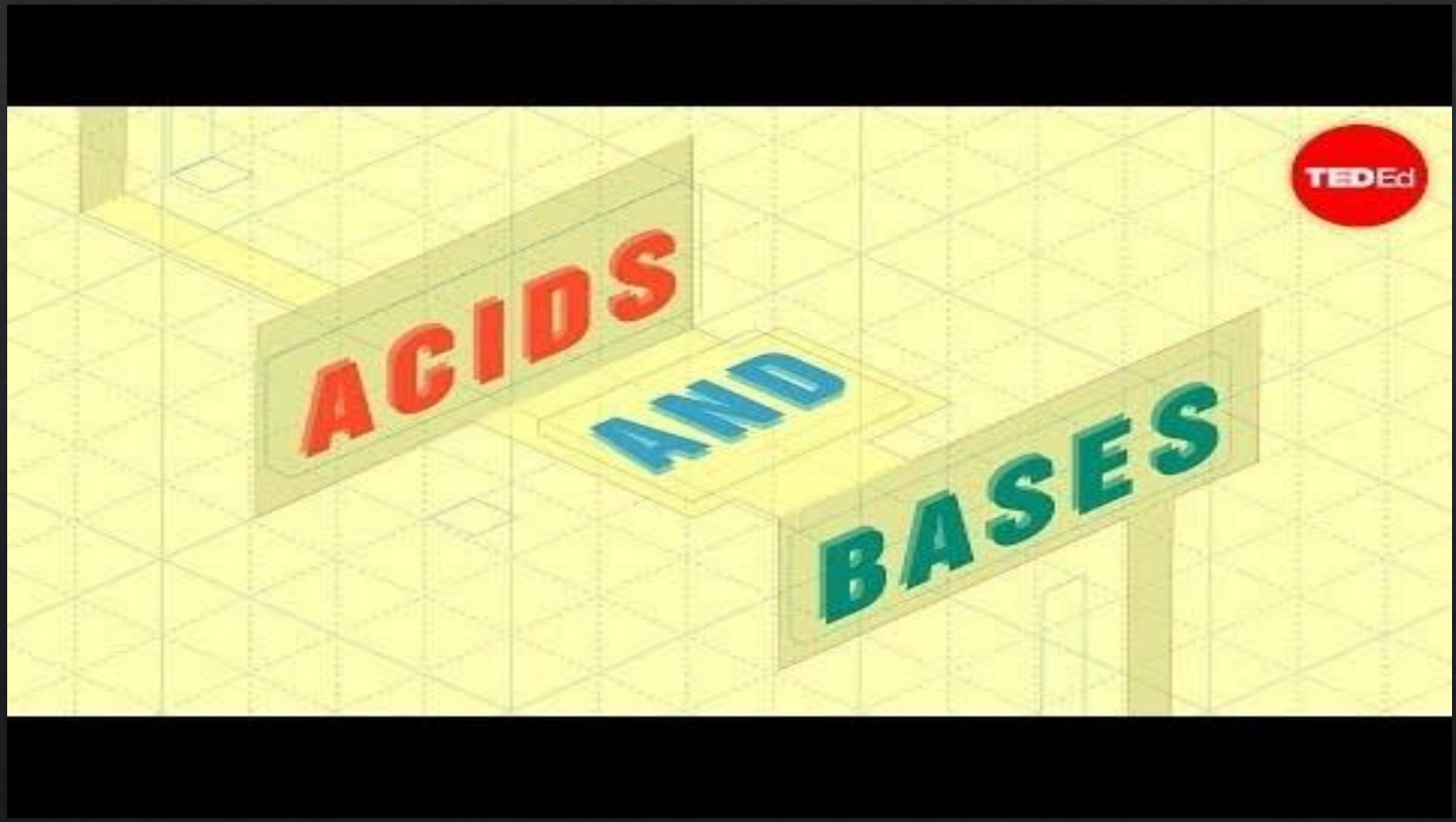
Alkane Name	Alkene name	Alkyne name
Methane	-	-
Ethane	Ethene	Ethyne
Propane	Propene	Propyne
Butane	Butene	Butyne
Pentane	Pentene	Pentyne
Hexane	Hexene	Hexyne
Heptane	Heptene	Heptyne
Octane	Octene	Octyne
Nonane	Nonene	Nonyne
Decane	Decene	Decyne

Picture from modernochem

Functional groups

Name	Formula	Suffix/Prefix
Carboxylic Acids	-COOH	-oic acid
Esters	-COOR	-oate
Halogenoid Acids	-COX	Chloro-/Bromo- etc.
Amides	$-CONH_2$	-ide
Nitriles	-CN	Cyano-
Aldehydes	-CHO	-al
Ketones	-CO-	-one
Alcohols	-OH	-ol
Phenols	-OH	Pheno(l)-
Amines	$-NH_2$	-amine
Ethers	-OR	-ethane

But first…



Electrophiles & Nucleophiles

Acid Base Conjugate Acid Conjugate Base

Brønsted and Lowry:

Acid = proton donor (electrophile)
Base = proton acceptor (nucleophile)

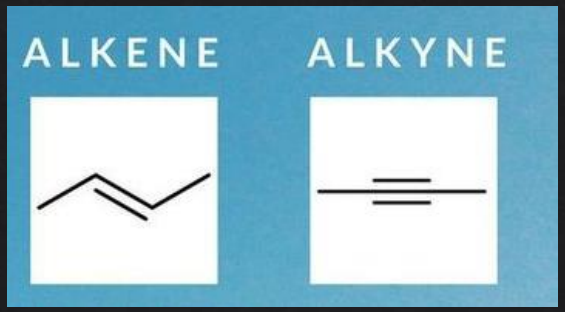
Priority of functional groups

Order of Precedence of Functional Groups

$RCOH$	>	$RCOCR$	>	$RCOR'$	>	RCX	>	$RCNR_2'$	>	RCN	>	RCH	>	RCR'	>	ROH	>	RSH	>	RNH_2
Carboxylic acid		**Anhydride**		**Ester**		**Acyl halide**		**Amide**		**Nitrile**		**Aldehyde**		**Ketone**		**Alcohol**		**Thiol**		**Amine**

Increasing precedence in naming

Picture from Vollhardt & Schore



Picture from modernochem

Alcohols

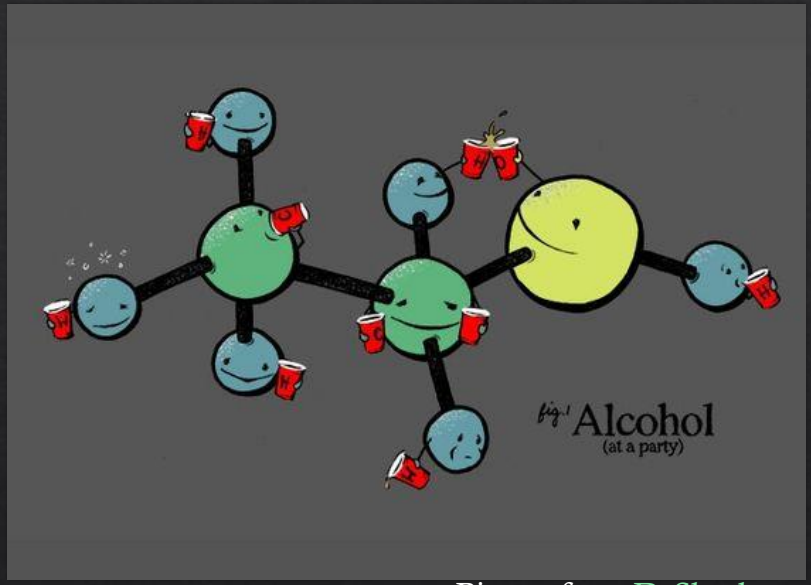
Functional group **–OH** (hydroxy)

IUPAC names: alkane + ending **–ol** (e.g. propanol). Longest carbon chain containing the –OH, not necessarily the longest one.

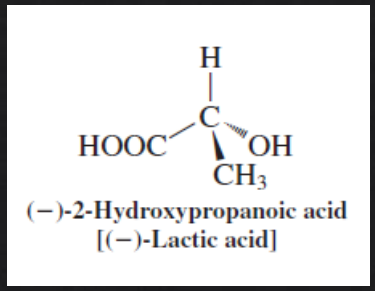
If more –OH present: -diol, -triol, etc.

When a substituent (group with higher priority present): **hydroxy-** (e.g. (-)-2-hydroxypropanoic acid)

Common name: alkyl group + alcohol (e.g. methyl alcohol)



Picture from D. Shoshan



Picture from Vollhardt & Schore

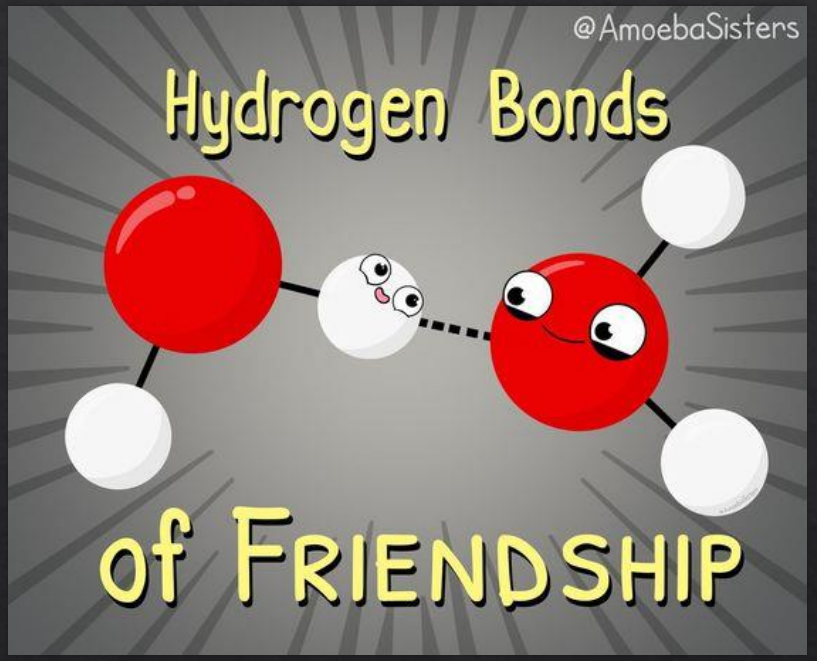
Alcohols properties

O-H bond shorter than C-H bond

Oxygen electronegativity polarizes the O-H bond → formation of **hydrogen bonds** **between** molecules → higher* boiling point

-OH is hydrophilic → increased* solubility in water

The hydrocarbon chain increases the solubility in nonpolar solvents



* Compared to the corresponding hydrocarbon

Ethers

Ethers might be considered alcohols where the H in –OH has been replaced by an alkyl group

The R (alkyl) group can be the same (R-O-R; symmetric ether) or different (R-O-R'; asymmetric ether)

IUPAC names: the shorter hydrocarbon is considered part of the substituent, the longer defines the stem, the two connected by **–oxy-**

$CH_3OCH_2CH_3$ → Meth**oxy**ethane

Water

Alcohol

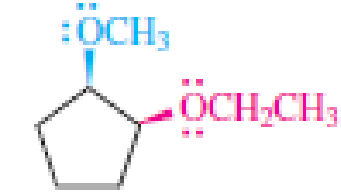
Ether

Common name: two alkyl group + ether (e.g. methyl ethyl ether)

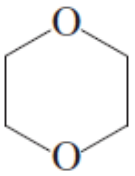
Cyclic ethers

Cyclic ethers can be a cyclic molecule with one or more oxygen atoms and the connected R group are substituents

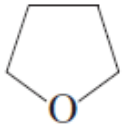
But they can also have the oxygen replacing one or more of the carbon atoms



cis-1-Ethoxy-2-methoxycyclopentane



1,4-Dioxacyclohexane (1,4-Dioxane)



Oxacyclopentane (Tetrahydrofuran, THF)

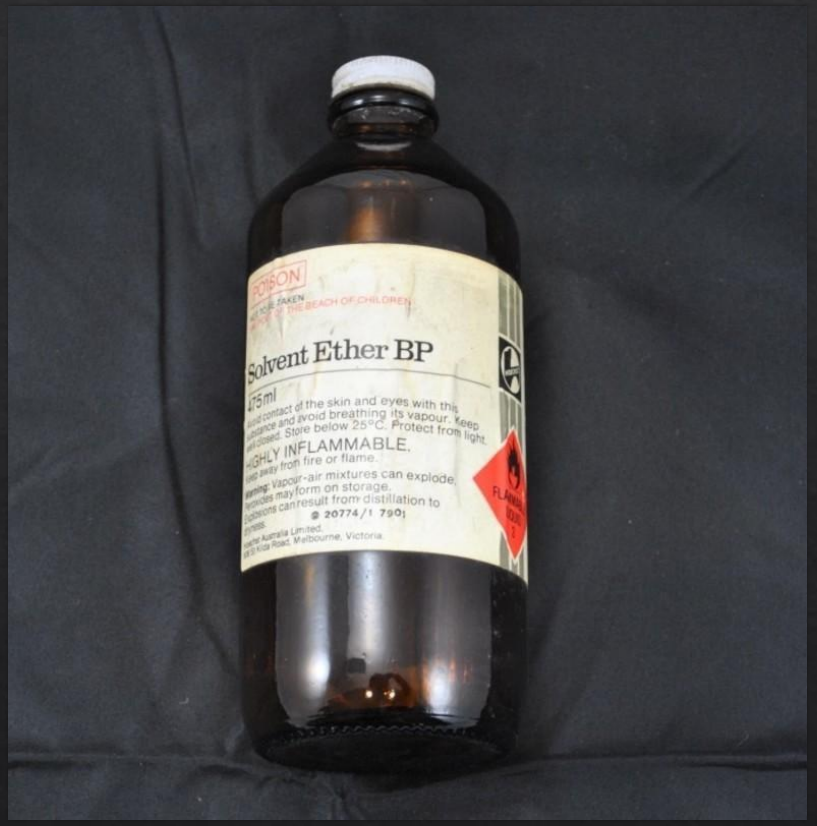
Pictures from Vollhardt & Schore

Ethers properties

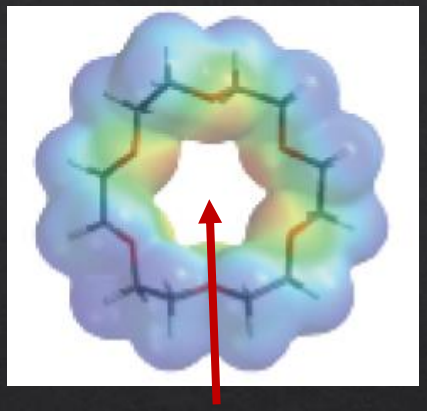
Fairly unreactive → used as solvents

No hydrogen bonding → lower boiling points than isomeric alcohols

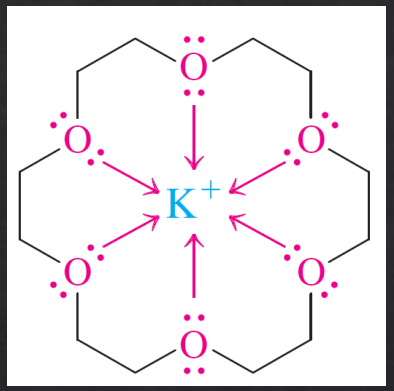
Only the two smallest are soluble in water, with increasing length of the hydrocarbon chain they become less soluble in water



Crown ethers properties



Hole size
perfect for K^+



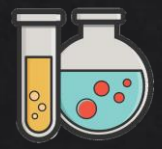
18-Crown-6

Pictures from Vollhardt & Schore

The inside of the crown is Lewis basic

The inside of the crown can bind metal cations and dissolve salts in organic media

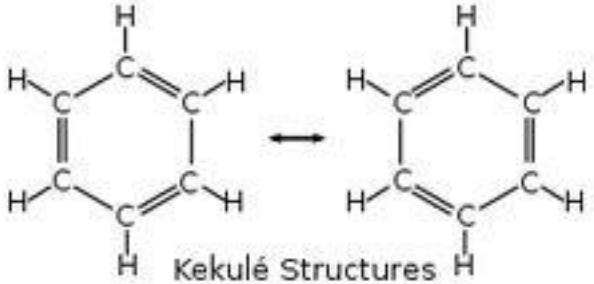
Together with polycyclic ethers (cryptands) they are ion transport agents making ions more soluble in non polar solvents



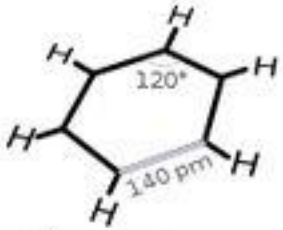
Benzenes

C_6H_6

Benzene
Molecular formula

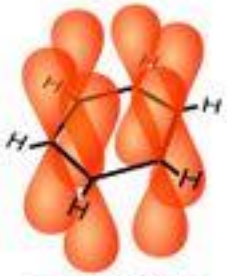


Kekulé Structures
(Isomers)



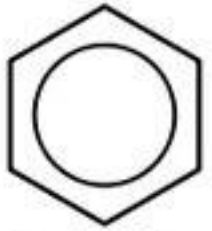
Planar Hexagon
Bond Length 140 pm

Sigma Bonds
sp^2Hybridized orbitals



6 p_z orbitals

delocalized pi
system



Benzene ring
Simplified depiction

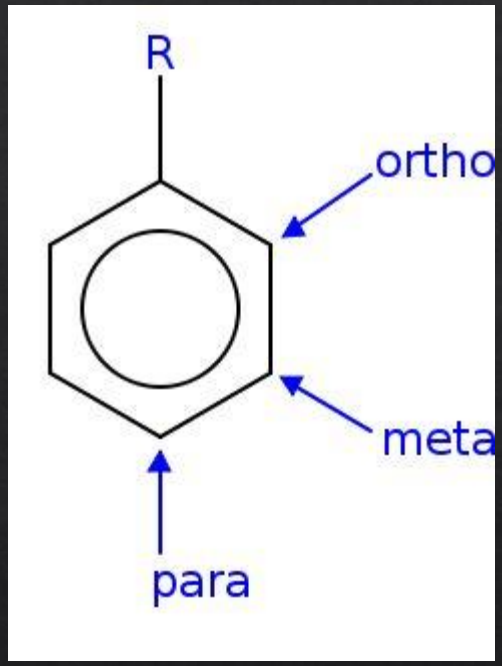
Picture from Vollhardt & Schore

Benzenes

If there's no functional group, monosubstituted benzenes are named substituent prefix + benzene (e.g. fluorobenzene, methylbenzene)

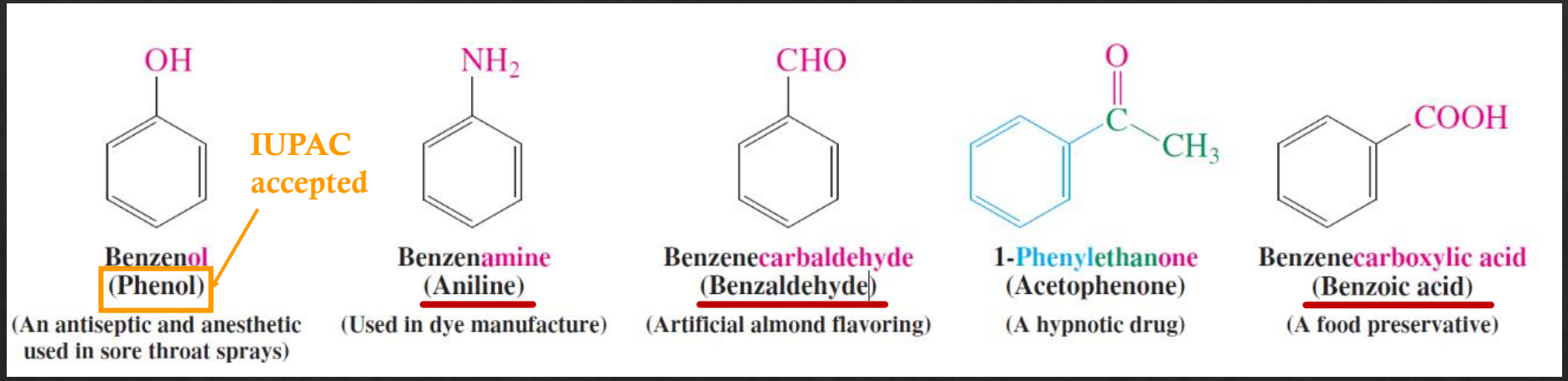
Disubstituted: 1,2-, 1,3-, 1,4- or (o-, m-, p-). Alphabetical order!

Polysubstituted: lowest number, if equal, alphabetical



Picture from Vollhardt & Schore

Benzenes



Picture from Vollhardt & Schore

If there is a functional group, we add the corresponding suffix after benzen.

Common names

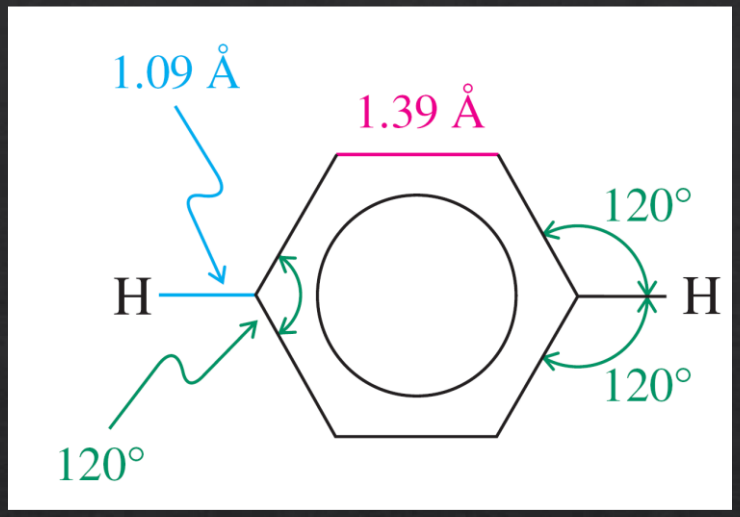
General term for benzene derivatives: Arene.

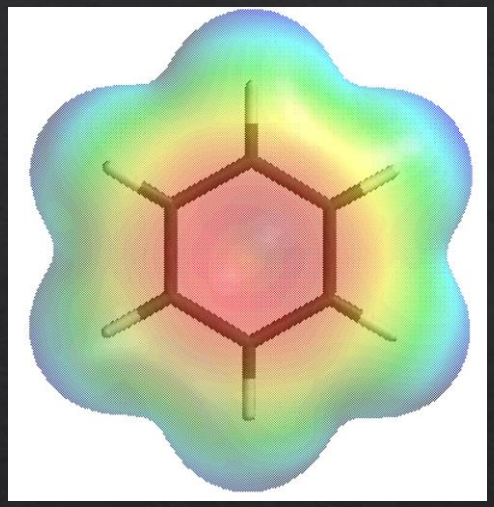
C_6H_5- is phenyl; general aryl.

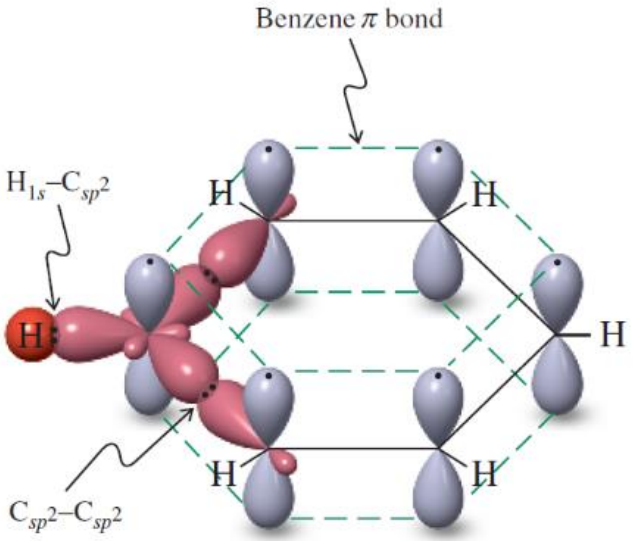
$C_6H_5CH_2$- is phenylmethyl or benzyl.

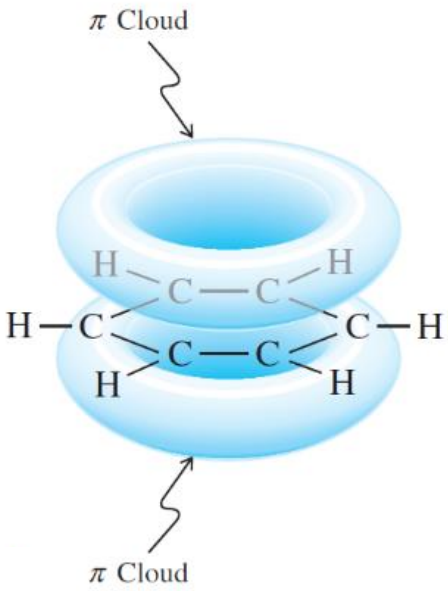
Benzenes properties

Both the π and σ frame symmetrize the structure



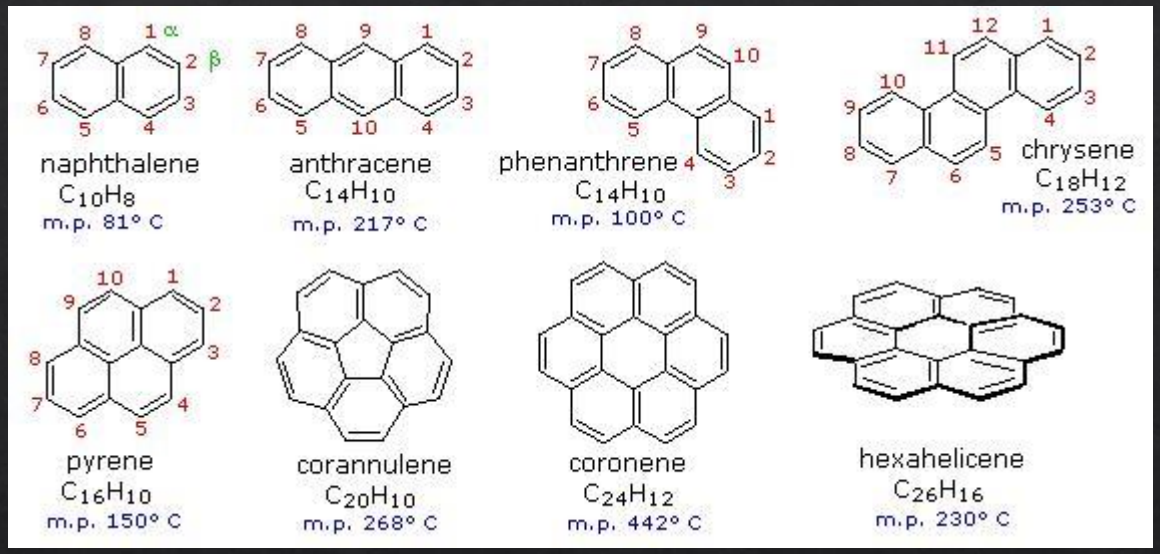






Pictures from Vollhardt & Schore

Benzenes properties



Picture from Vollhardt & Schore

Benzenes

Poly-aromatic hydrocarbons PAH

Naphthalene
Mothballs

Phenanthrene
Steroids

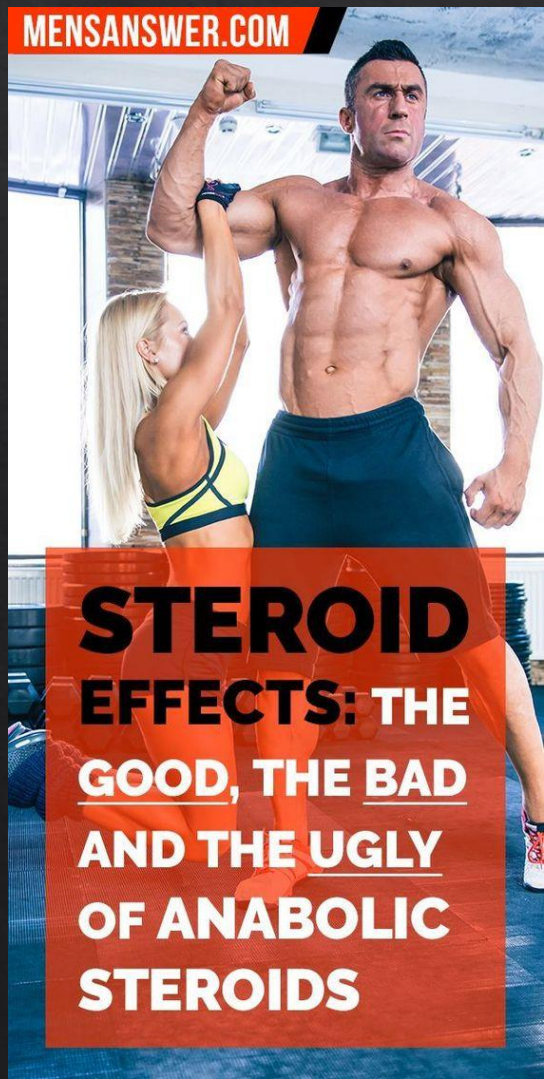
Anthracene
Dyes and perservatives

DDT
dichlorodiphenyl
trichloroethane

Aspirin
2-ethanoyloxybenzenecarboxcyclic acid

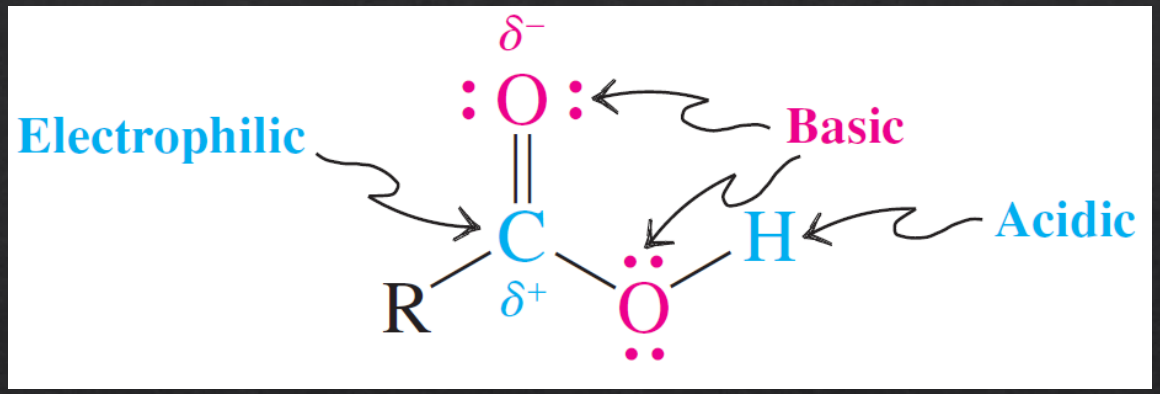
Paracetamol
4-hydroxyphenylethanamide

Picture from Vollhardt & Schore



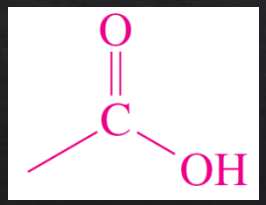

5 minute

Carboxylic acids



Pictures from Vollhardt & Schore

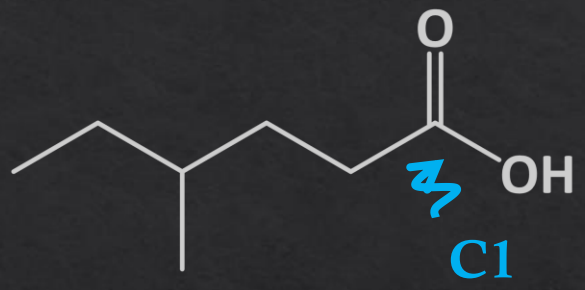
Carboxy group: -COOH, -CO_2H,



Carboxylic acids

Replace –e of alkane name with –oic acid

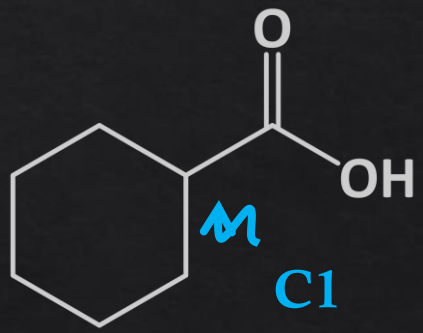
HCOOH Methanoic acid (Formic acid)
CH_3COOH Ethanoic acid (Acetic acid)
CH_3CH_2COOH Propanoic acid



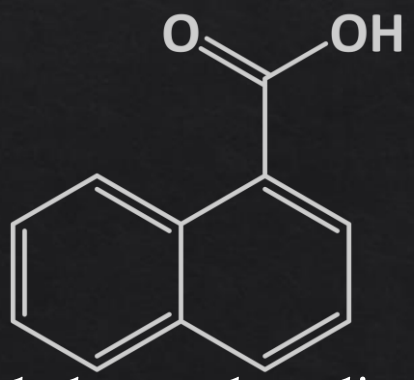
4-Methylhexanoic acid

If two –COOH present: -dioc acid

Cyclic: Cycloalkanecarboxylic acids



Cyclohexanecarboxylic acid



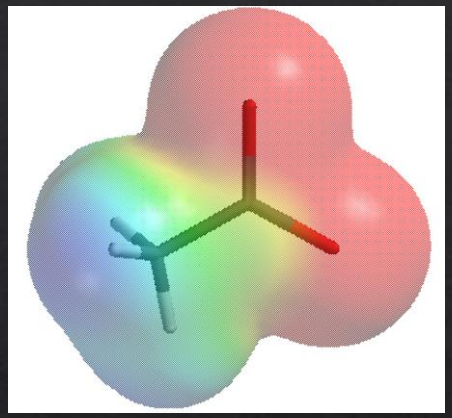
1-Naphthalenecarboxylic acid

Carboxylic acids properties

The carboxy group is relatively acidic.

Strong polarity → hydrogen bond → up to butanoic acid are soluble in water

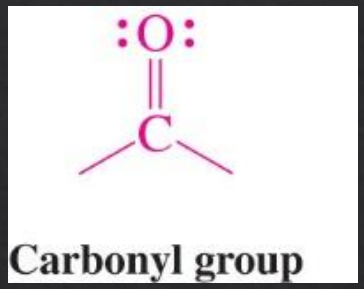
Strong odor



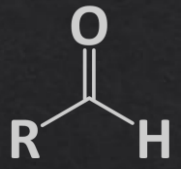
Acetate ion

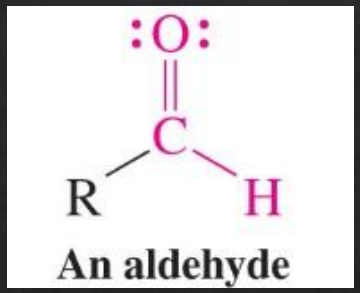
Aldehydes & Ketones

Functional Group: Carbonyl

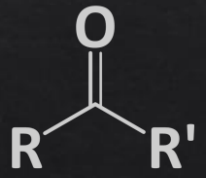


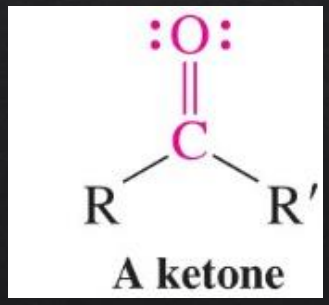
Aldehyde: RCHO,





Ketone: RCOR',

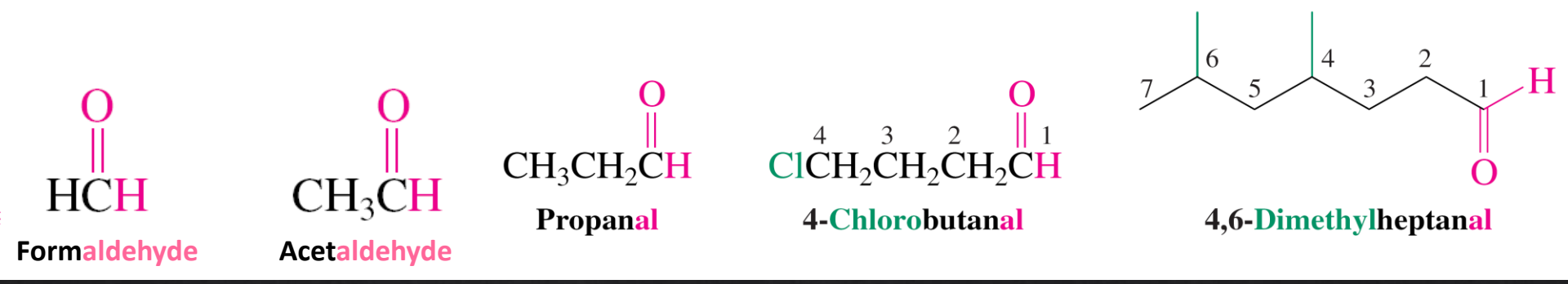




Pictures from Vollhardt & Schore

Aldehydes

Alkane → Alkanal. Longest chain starts at -CH=O, which contains C1 (might not the absolute longest).



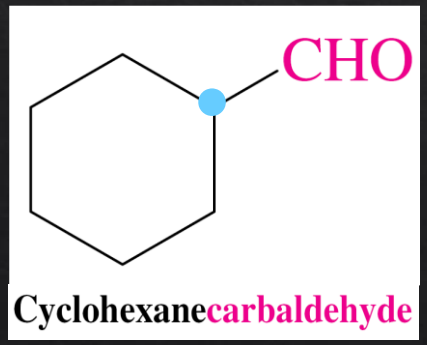
IUPAC-accepted common names

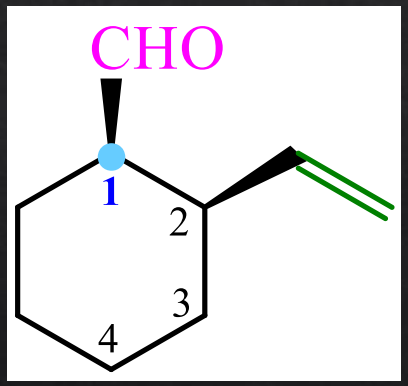
Picture from Vollhardt & Schore

A compound with two carbonyl groups ends in -dial

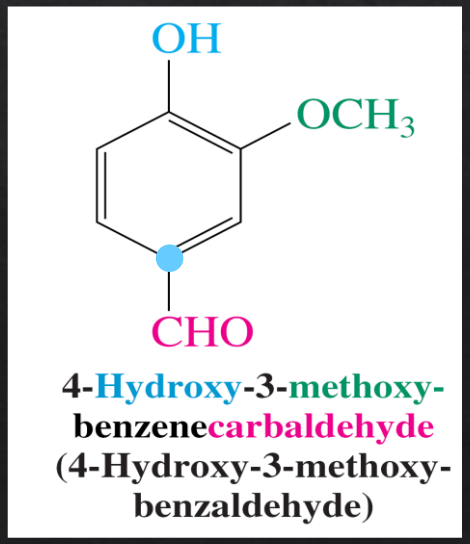
Aldehydes on a ring

-carbaldehyde after cycloalkane name.
The carbon attached to -CH=O is C1.





Cis-2-ethenylcyclo-
hexanecarbaldehyde

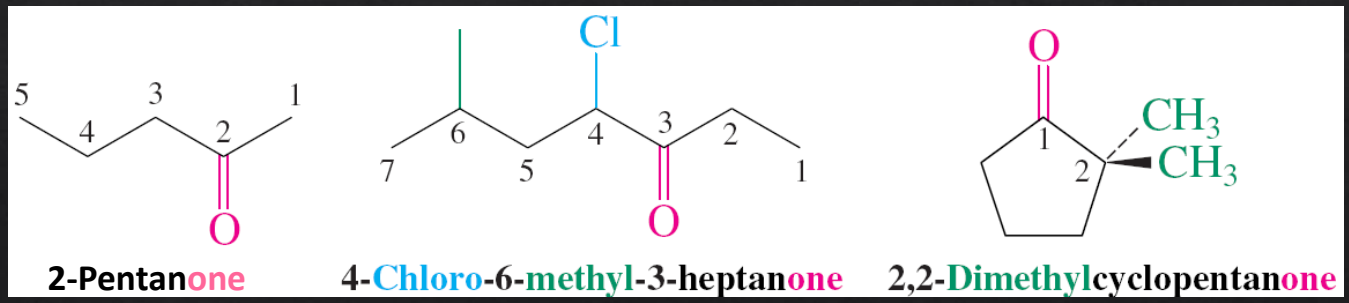


Picture from Vollhardt & Schore

Ketones

Alkane → Alkanone. Longest chain incorporates carbonyl carbon and is numbered from terminus close to C=O.

Cyclic ketones are cycloalkanones



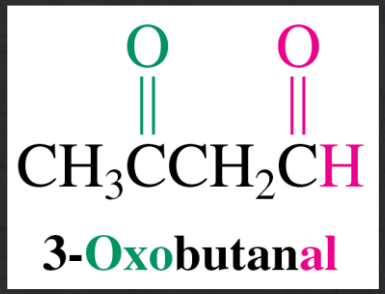
2-Pentanone 4-Chloro-6-methyl-3-heptanone 2,2-Dimethylcyclopentanone

Picture from Vollhardt & Schore

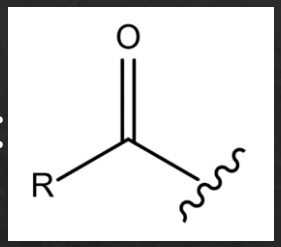
If more C=O present: -dione, -trione, etc.

Aldehydes & Ketones

An aldehyde containing a ketone C=O is called an oxoalkanal.

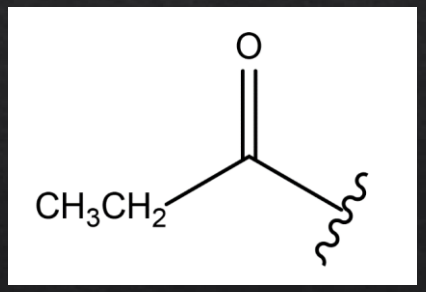


Substituent name:



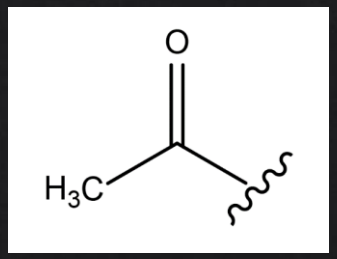
carboxylic acid name +yl

propanoyl



IUPAC accepted common names

formyl

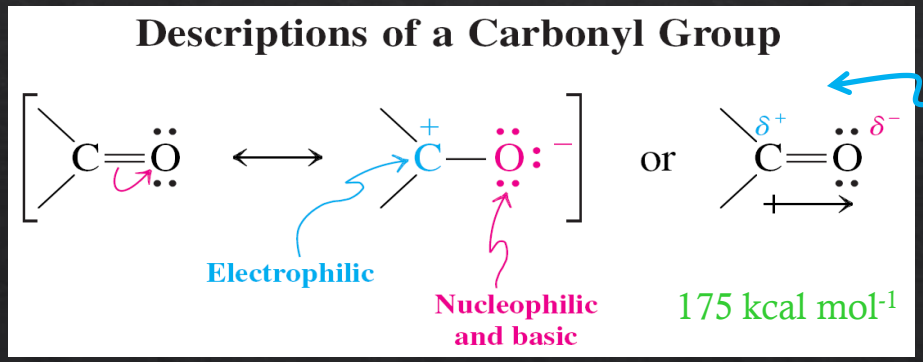


acetyl

Pictures from Vollhardt & Schore

Aldehydes & Ketones properties

The carbonyl group contains a short, strong, and very polar bond.

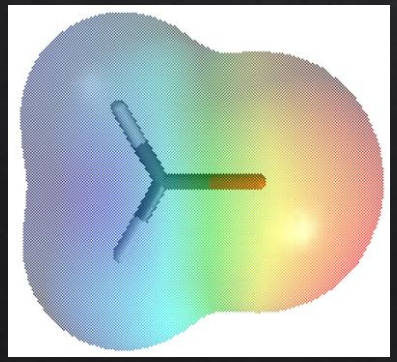


Polarization

C is electrophilic
O nucleophilic and slightly basic

Higher boiling points than corresponding hydrocarbon

Smaller carbonyl derivatives soluble in water, >6C insoluble

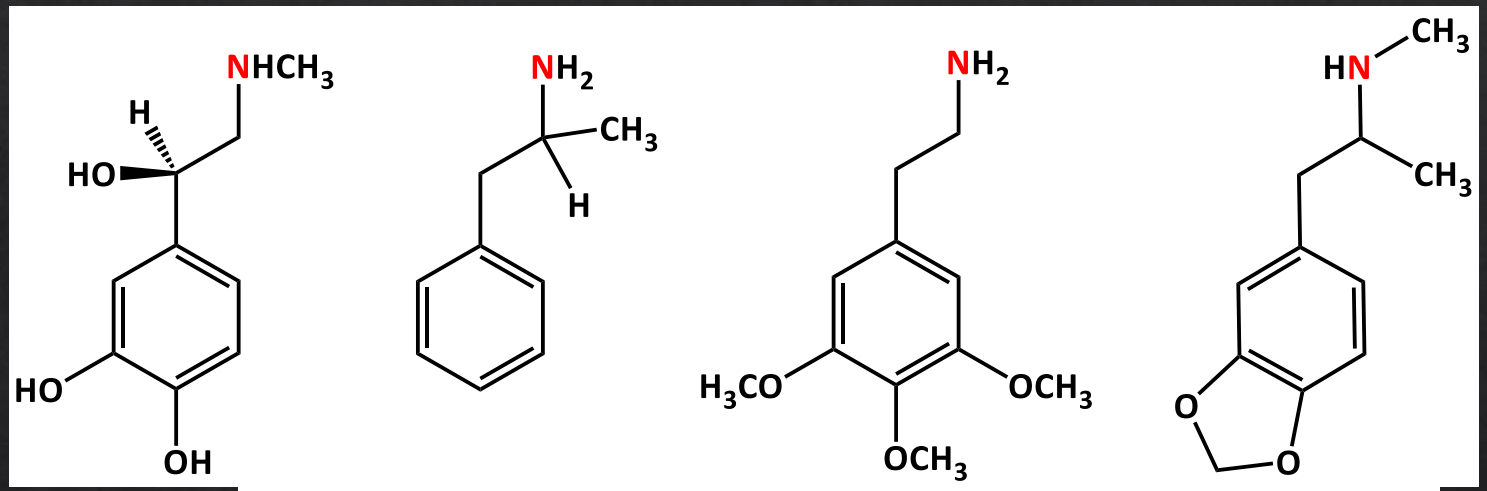


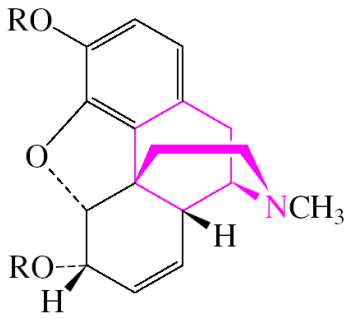
Electrostatic Potential Map

Pictures from Vollhardt & Schore

Amines

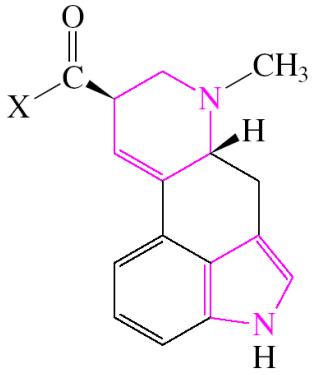
Found in many medicines and alkaloids (natural amines)





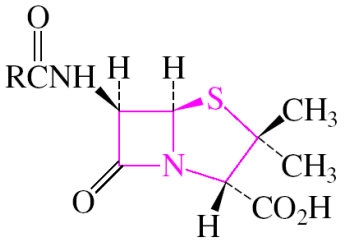
Morphine (R = H)

Heroin (R = $CH_3C(=O)$)



Lysergic acid (X = OH)

Lysergic acid diethylamide, LSD [X = $(CH_3CH_2)_2N$]

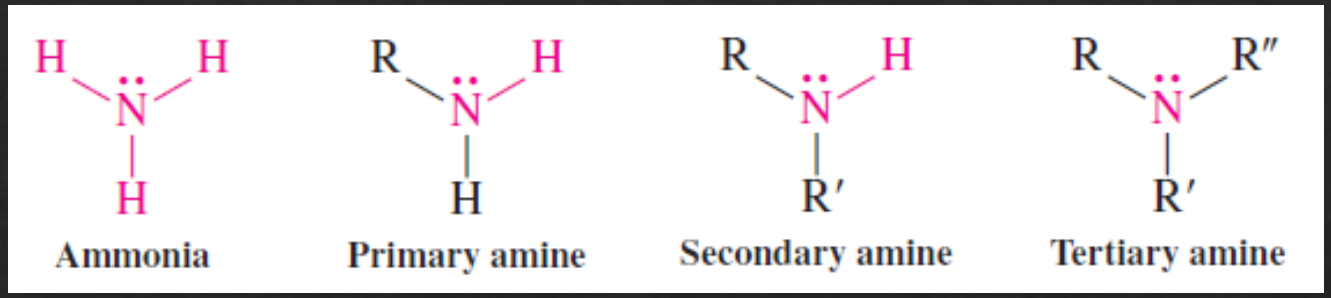


Penicillin

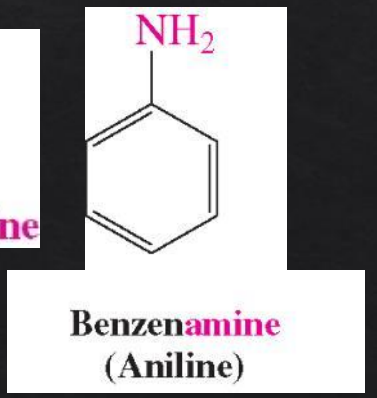
Pictures from Vollhardt & Schore

Amines

Amines are derivatives of ammonia
The number of R substituents determines the amine classification



IUPAC: Primary amines
Alkanamines



Pictures from Vollhardt & Schore

Amines

Amines are derivatives of ammonia
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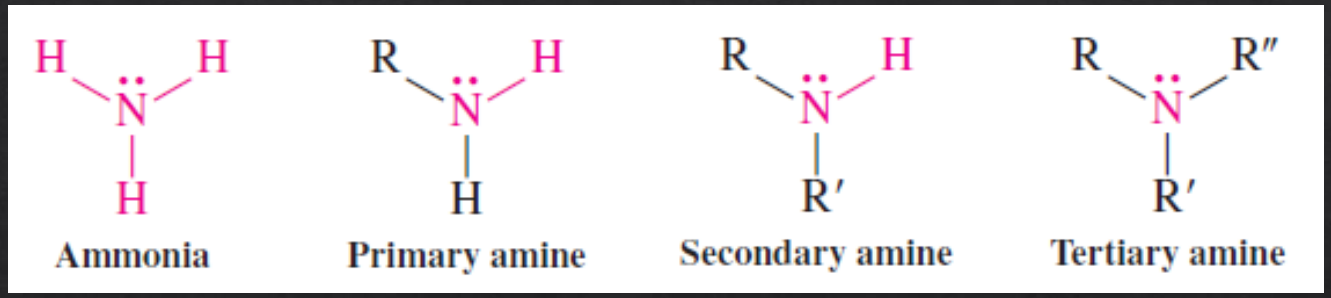


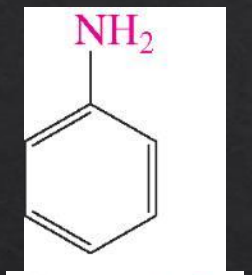
IUPAC: Primary amines
Alkanamines

If two amine functions present: -diamines

Pictures from Vollhardt & Schore

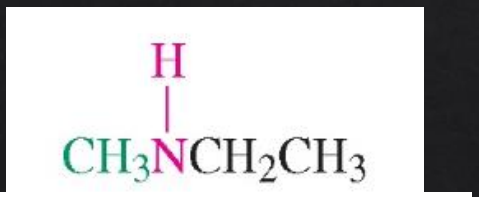
Amines

Aromatic amines are called anilines
But the naming doesn't change, -amine at the end. Or, if more groups present benzendiamines, -triamines, etc.



Benzenamine (Aniline)

Secondary amines
N-alkyl alkan amines



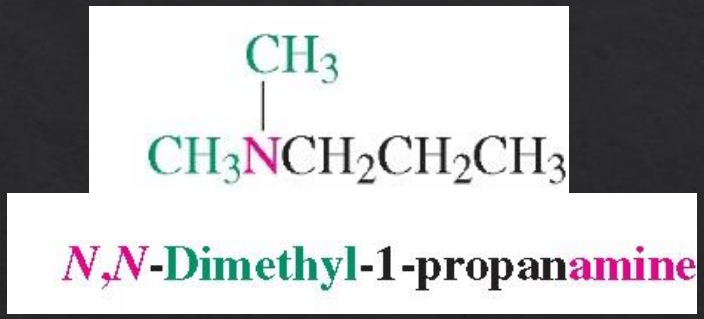
***N*-Methylethanamine**

Pictures from Vollhardt & Schore

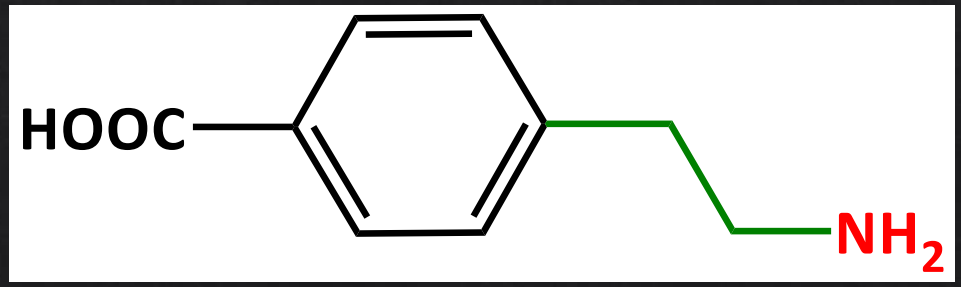
Amines

Tertiary amines

N,N-alkyl alkan amines



Lowest priority group, prefix amino



4-(2-Aminoethyl)benzoic acid

Pictures from Vollhardt & Schore

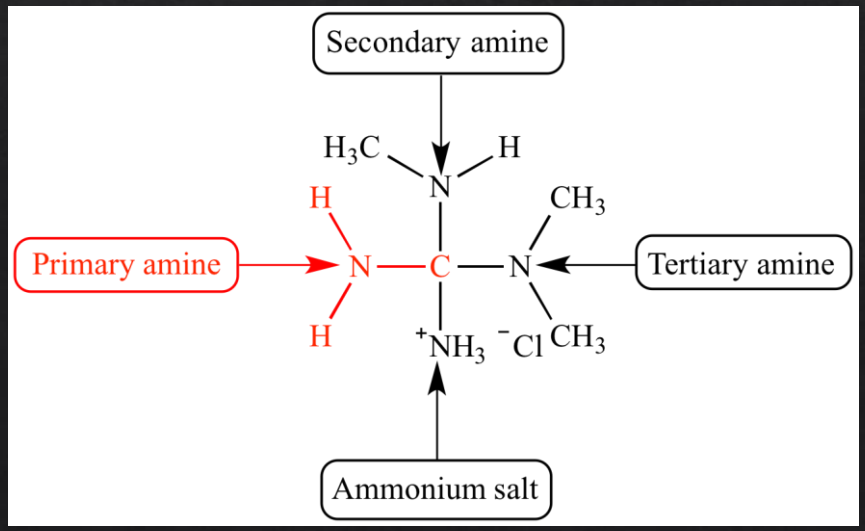
Amines properties

All amines are basic, but primary and secondary amines can also behave like acids

Weak hydrogen bonds → lower boiling points and less soluble in water than alcohols (in between alkanes and alcohols)

Nucleophiles

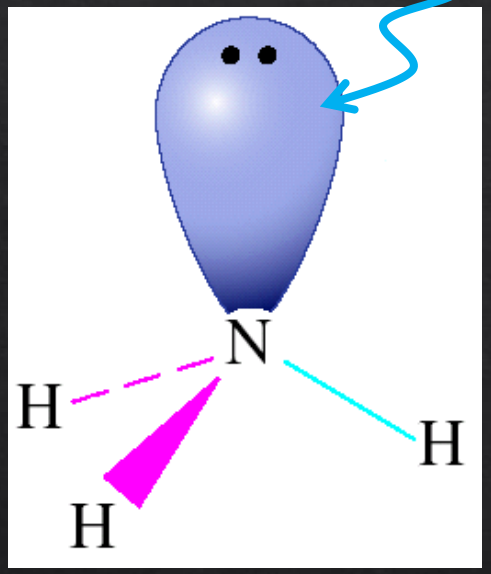
Primary and secondary amines are less acidic and form weaker hydrogen bonds than alcohols, and they are more basic and more nucleophilic



Picture from Vollhardt & Schore

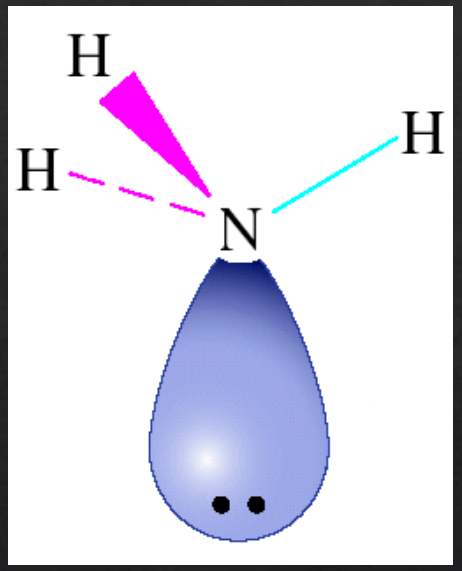
Amines - inversion

Basic



E_a = 5-7 kcal mol^{-1}

Inversion



Although they form enantiomers, it's difficult to maintain an enantiomerically pure form

Pictures from Vollhardt & Schore