OC2

Synthesis
–
Introduction to Amines

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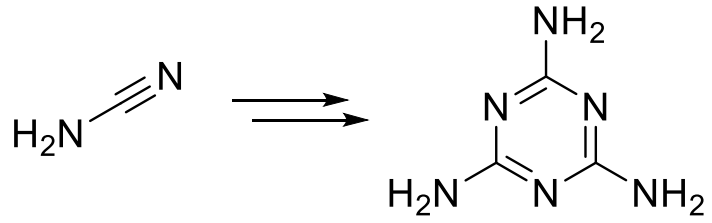
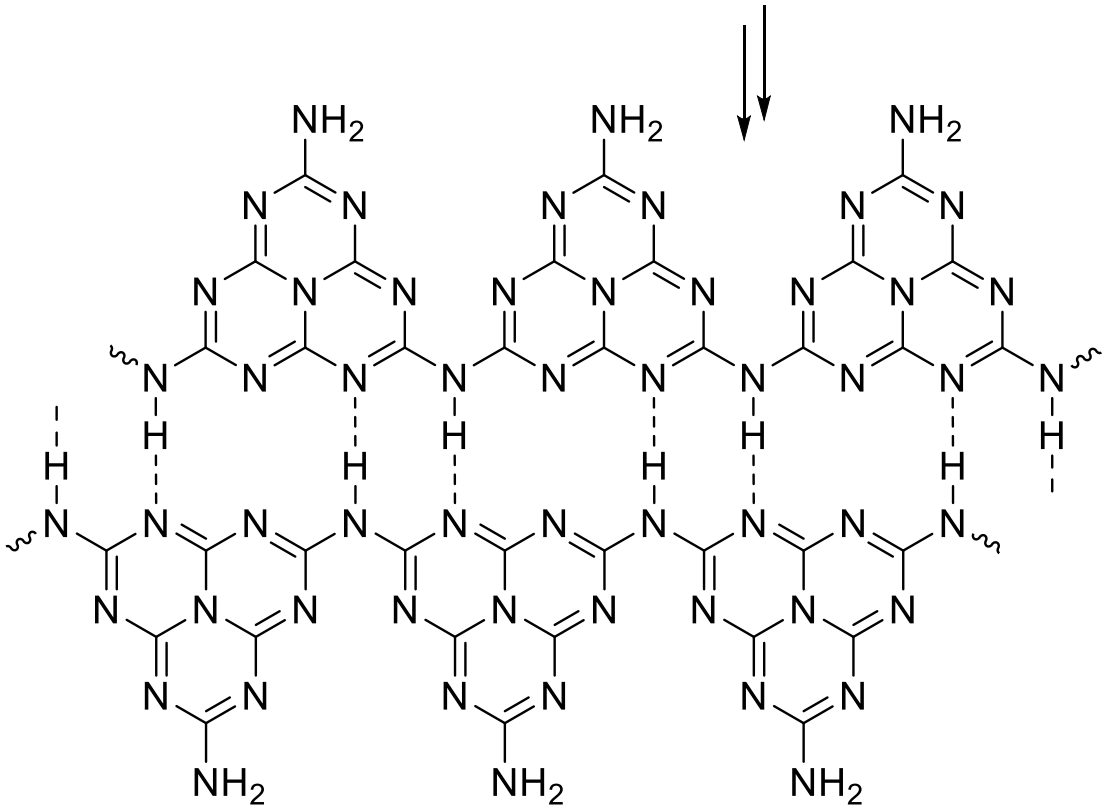
Amines

Hist. “alkaloids” – naturally occurring compounds with at least one N-atom

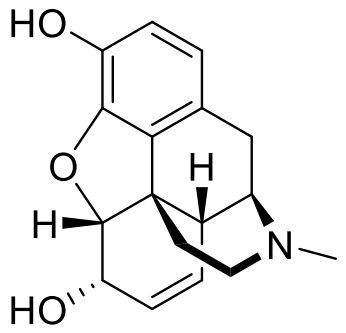


cyanamide

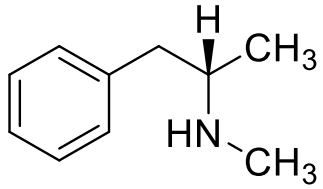
melamine



Liebig's "Melon" (1834)

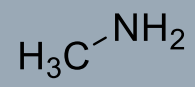


morphine
(isolated from opium poppy, 1804)



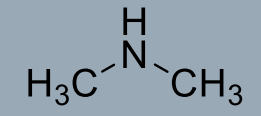
(S)-2-methylamino-1-phenylpropan
(Methaphetamine, "Pervitin" in WW2)

primary

1° 

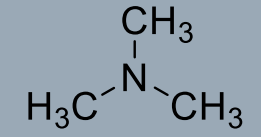
methylamine

secondary

2° 

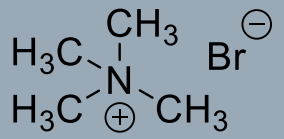
dimethylamine

tertiary

3° 

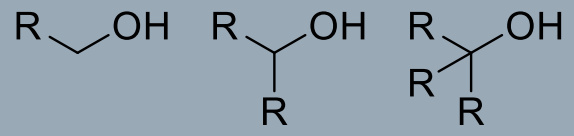
trimethylamine

quaternary

4° 

tetramethyl
ammonium
bromide

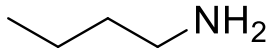
Compare: alcohols



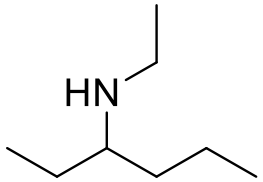
1° **2°** **3°**

Nomenclature of Amines

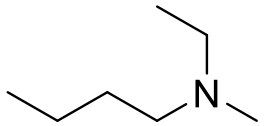
- alkyl group with the suffix “–amine”
- numbering usually before the “–amin” suffix (sometimes before the alkyl)
- nitrogen-bonded alkyl groups are denoted with an italic “*N*”



butan-1-amine

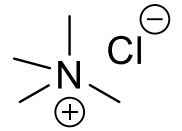


N-ethylhexan-3-amine

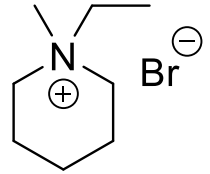


N-ethyl-*N*-methylbutan-1-amine

- quaternary amines are named as salts of the corresponding amine

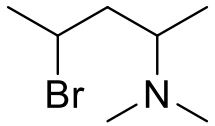


tetramethyl ammonium chloride



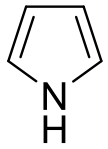
1-ethyl-1-methyl piperidinium chloride

- chose the lowest possible numbering (in relation to the N-atom)

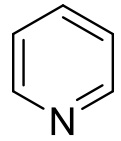


4-bromo-*N*,*N*-dimethylpentan-2-amine

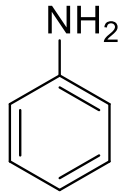
- in aromatic systems



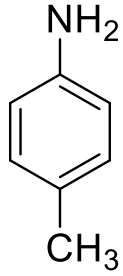
pyrrole



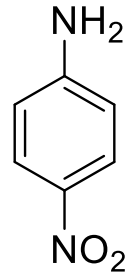
pyridine



aniline



p-methylaniline (IUPAC)

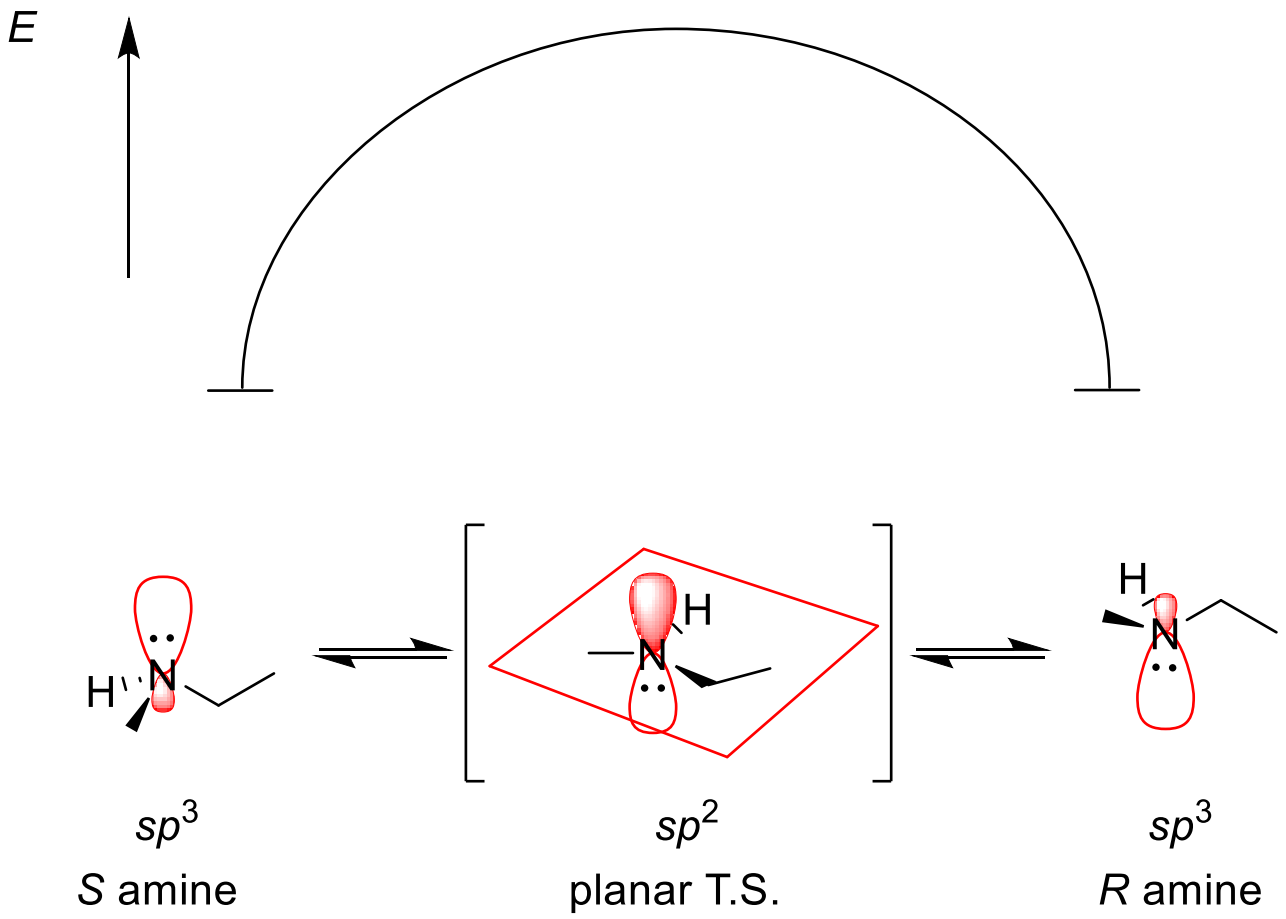


p-nitroaniline (IUPAC)

Geometry and Orbitals of Amines

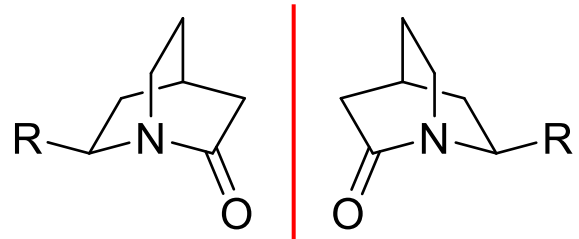
Consider the free electron pair as a “fourth group” → tetrahedral arrangement around N-atom (chiral?)

In practice, rapid interconversion between amine enantiomers (low energy barrier):

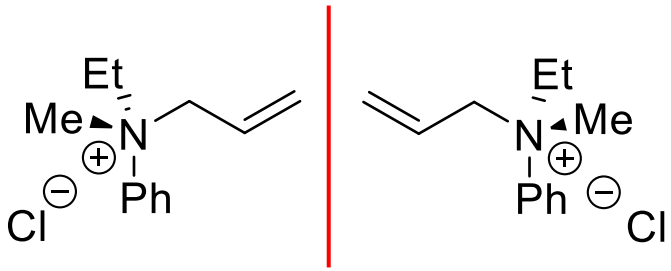


Exceptions:

- locked cyclic systems

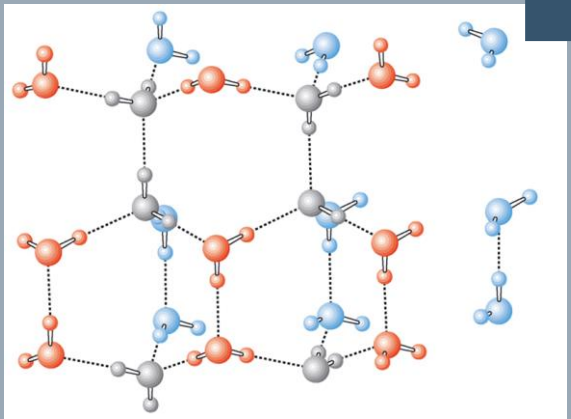


- quaternary salts



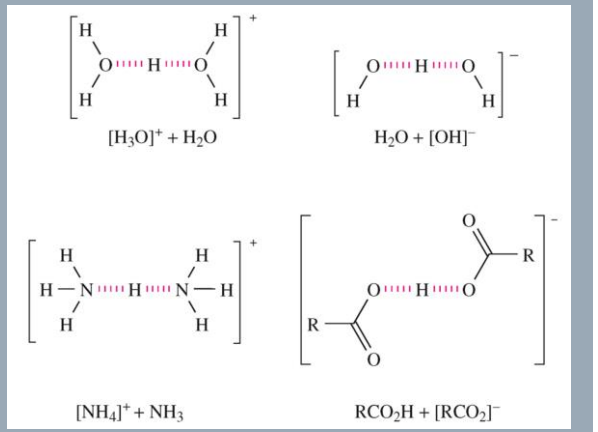
Physical Properties of Amines

Hydrogen bonding



frozen water is a 3-dimensional network of H_2O-molecules

Seen in polar, protic compounds:



	H_3C-CH_3	H_3C-NH_2	CH_3-OH
bp / °C	-88.6	-6.3	65.0
van der Waals	**(+)**	**+**	**+**
dipole-dipole	**-**	**+**	**+**
H-bonding	**-**	**+**	**+**

What’s next?

Properties of Amines

Academic Insights #4

The last evening before the deadline