Amines

General, Naming

Basicity

Prep / Rxns / Spectroscopy

Intro to DNA

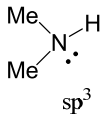
Ref 20: 1 – 6; 25: 4

Prob see Final Practice Questions

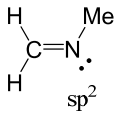
General

Neutral N cmpds have

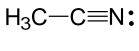
3 covalent bonds + 1 lone pair of e⁻'s ; e.g.,



sp^3



sp^2



sp

1° , 2° , 3° amines, seen before

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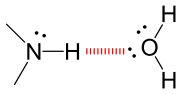
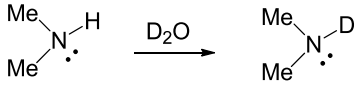
involved in H-Bonding

e.g. 

D_2O exchangeable (nmr)



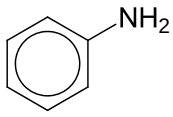
Naming

similar to alcohols; e.g.,

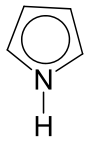
CH_3-CH_2-OH	CH_3-CH_2-NH_2
ethyl alcohol	ethylamine
or	
ethanol	ethanamine
or	
hydroxyethane	aminoethane

more? see Solomons 20:1

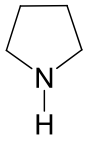
Common Names



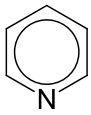
aniline



pyrrole



pyrrolidine

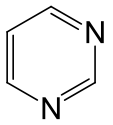


pyridine

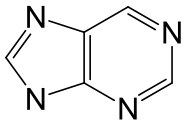
Heterocyclic Amines

- common in nature
- 4 are present in DNA, all derived from

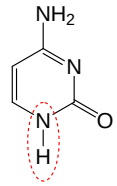
pyrimidine



purine

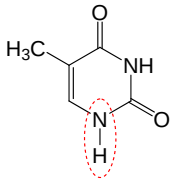


DNA Bases



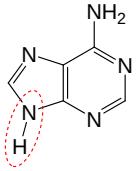
cytosine

C



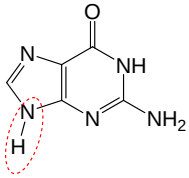
thymine

T



adenine

A



guanine

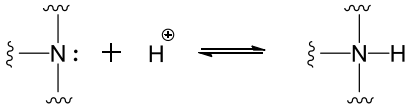
G

linkage where bonding to DNA backbone occurs

Basicity

Lewis: e^- donor

B/L: H^+ acceptor



"strong base"

- attracts H^+'s strongly
- lone pairs highly available
- above equil. to the Right

weak base opposite, of course

Effects on Basicity

basicity ↑ if

- EDG's are present on neighboring C's
- e^- pair is more exposed;
  e.g., sp^3 N is more basic than sp^2 & sp N's;
  b/c sp^3 has 75% p character ....
  (p orbitals are more exposed than s orbitals)

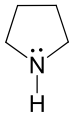
basicity ↓ if

- EWG's are present on neighboring C's
- e^- pair is delocalised
- e^- pair tied up in aromaticity (strong effect)

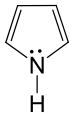
Practice

rank basicity of the following

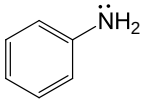
intermediate
(sp^2 hybridized)



strongest
(sp^3 hybridized)



weakest
(aromatic tie-up)



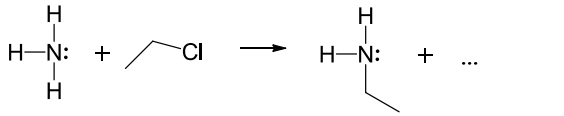
intermediate
(aromatic delocalization)

Prep.

"Seen before":

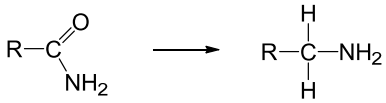
1.) rxn w/ sp^3 electrophiles ("halides");

(S_N rxn, alkylation on N, ...)



(often multi substitution ...)

2.) $LiAlH_4$ reduction of amides (& nitriles)



"New"

3.) reduction of imines/ iminium salts

(reductive amination)

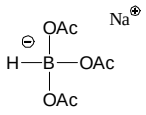
Details of "Reductive Amination"

- imines and iminium salts

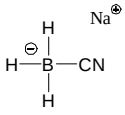
(formed from A/K's on one hand and 1°/2° amines on the other; see A/K section)

can be reduced by mild hydride reducing agents

such as

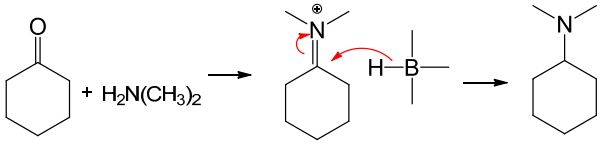


sodium triacetoxyborohydride



sodium cyanoborohydride

to the corresponding amine.



If done as "one-pot" rxn (all reactants present at the same time)

then this reaction is called reductive amination

Rxns

seen before;

most important:

act as nucleophiles in

1.) S_N2 rxns

2.) acyl substitution (→ amides)

3.) A/K carbonyl addition

(→ imines, → enamines)

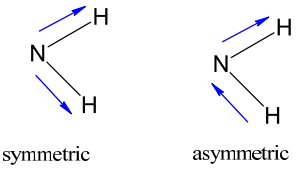
4.) Michael addition (just done)

Spectroscopy

IR N – H ~ 3400 cm^{-1}

may be broad due to H - bonding

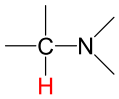
vibrations: double peak if 1° amine



NMR N – H δ = 1 – 5 ppm

variable, broad

D_2O exchangeable



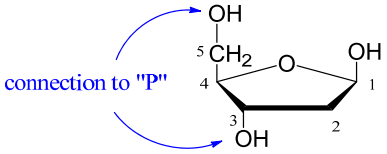
δ ≈ 2.5 ppm

Intro to DNA

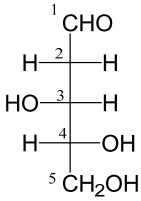
- deoxyribonucleic acid
- holds genetic information ....
- built from:
  - phosphate ester
  - deoxyribose
  - DNA base

Deoxyribose

5 C sugar w/ aldehyde F.G.

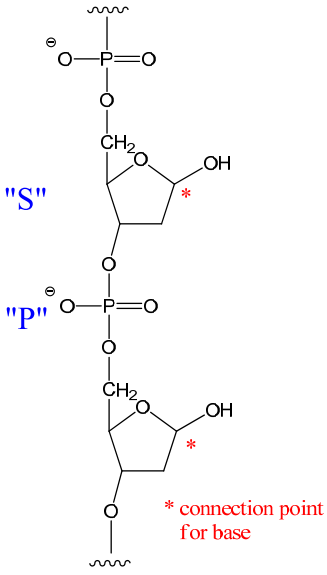


hemiacetal form



open form

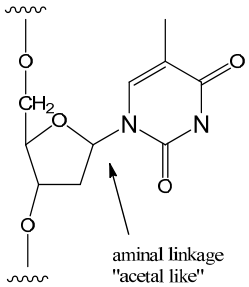
DNA Structure, General



DNA Backbone

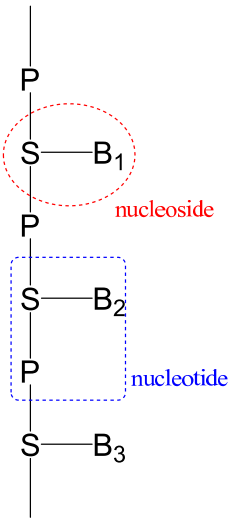
"B"

(here:thymine, T)



Base Linkage

DNA Structure ...



B_1, B_2, B_3, B_4 can be A, G, C or T

- long chain molecule
- sequence in basis varies
- form double helix

  carries genetic information