Chapter 22

Amines

22.1

Amine Nomenclature

Classification of Amines

Alkylamine

N attached to alkyl group

Arylamine

N attached to aryl group

Primary, secondary, or tertiary

determined by number of carbon atoms directly attached to nitrogen

Nomenclature of Primary Alkylamines (RNH$_2$)

Two IUPAC styles

1) analogous to alcohols: replace -*e* ending by -*anamine*

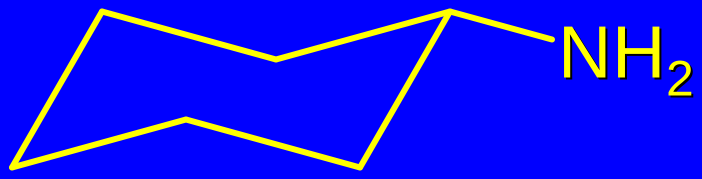
2) name alkyl group and attach -*amine* as a suffix

Examples: some primary alkylamines

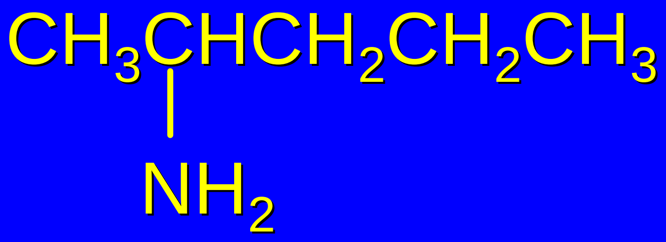
(RNH_2: one carbon directly attached to N)

$CH_3CH_2NH_2$

ethylamine or ethanamine



cyclohexylamine or
cyclohexanamine



$$\underset{\displaystyle NH_2}{CH_3\overset{}{C}H}CH_2CH_2CH_3$$

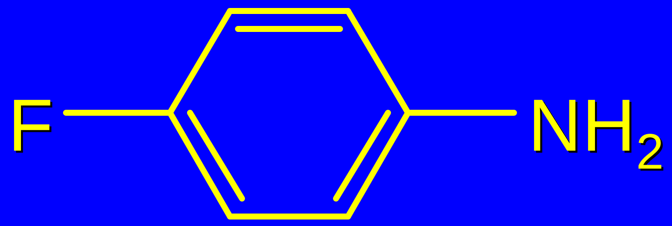
1-methylbutylamine or
2-pentanamine

Nomenclature of Primary Arylamines ($ArNH_2$)

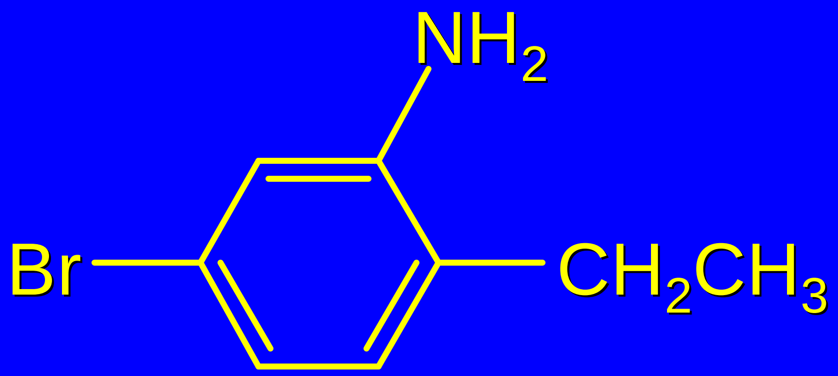
Name as derivatives of aniline.

Examples: some primary arylamines

($ArNH_2$: one carbon directly attached to N)



p-fluoroaniline



5-bromo-2-ethylaniline

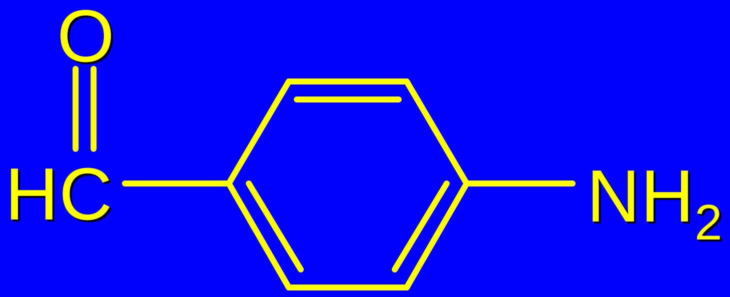
Amino groups as substituents

amino groups rank below OH groups and higher oxidation states of carbon

in such cases name the amino group as a substituent

$HOCH_2CH_2NH_2$

2-aminoethanol



p-aminobenzaldehyde

Secondary and Tertiary Amines

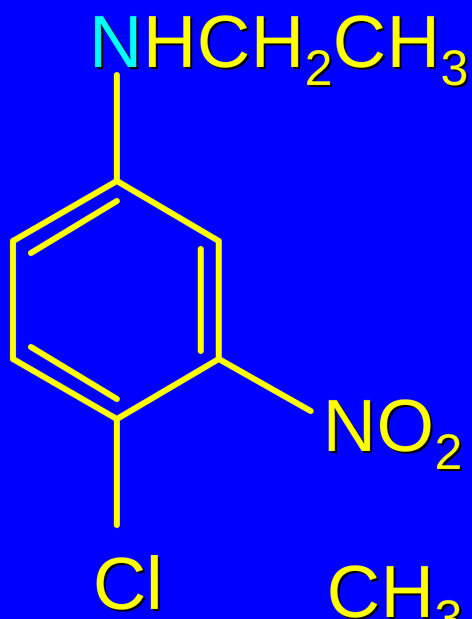
Name as *N*-substituted derivatives of parent primary amine.

(N is a locant-it is not alphabetized, but is treated the same way as a numerical locant)

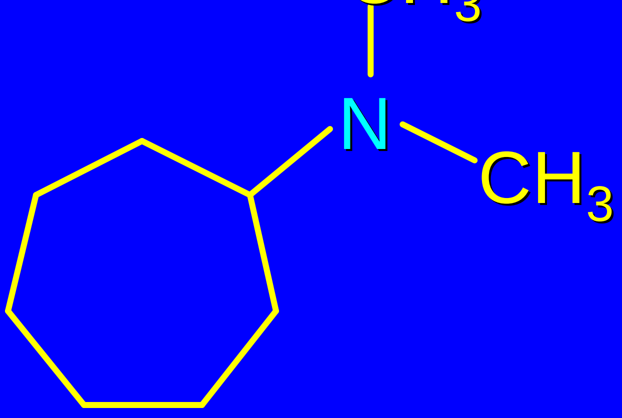
Parent amine is one with longest carbon chain.

Examples

$CH_3NHCH_2CH_3$ *N*-methylethylamine



4-chloro-*N*-ethyl-3-nitroaniline



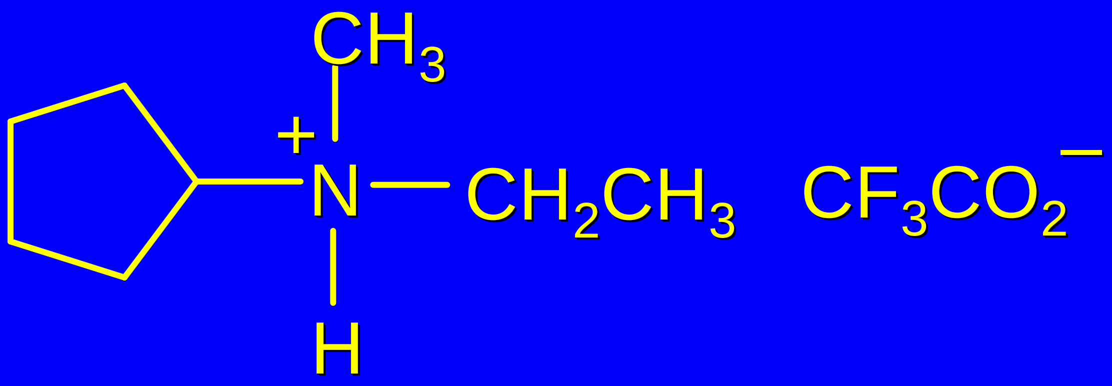
N,*N*-dimethylcycloheptylamine

Ammonium Salts

A nitrogen with four substituents is positively charged and is named as a derivative of *ammonium* ion (NH_4^+).

$CH_3\overset{+}{N}H_3\quad Cl^-$

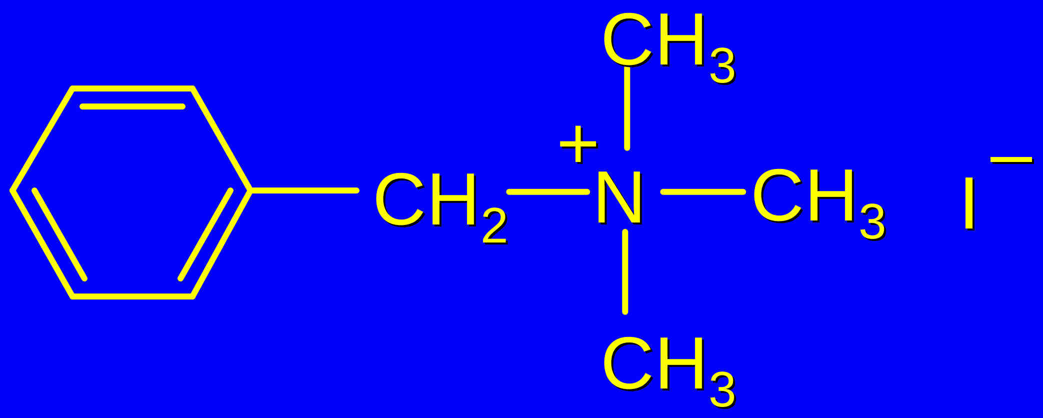
methylammonium chloride



N-ethyl-*N*-methylcyclopentylammonium trifluoroacetate

Ammonium Salts

When all four atoms attached to N are carbon, the ion is called a *quaternary ammonium* ion and salts that contain it are called *quaternary ammonium* salts.

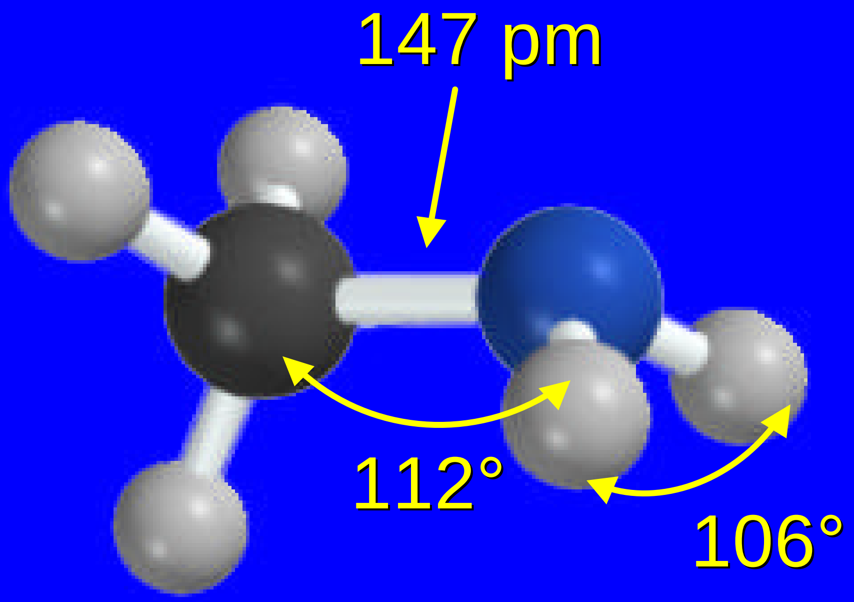


benzyltrimethylammonium iodide

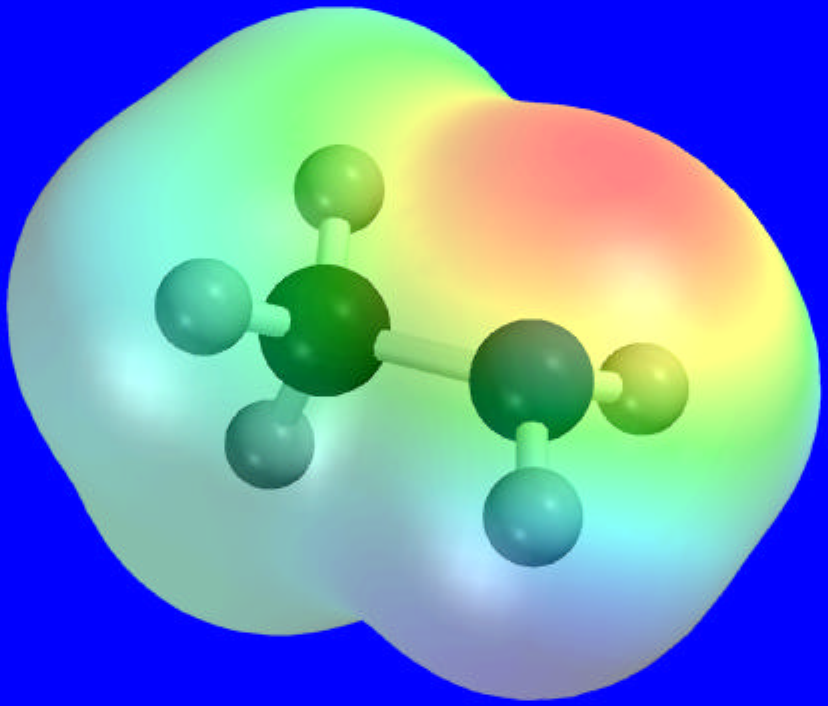
22.2

Structure and Bonding

Alkylamines



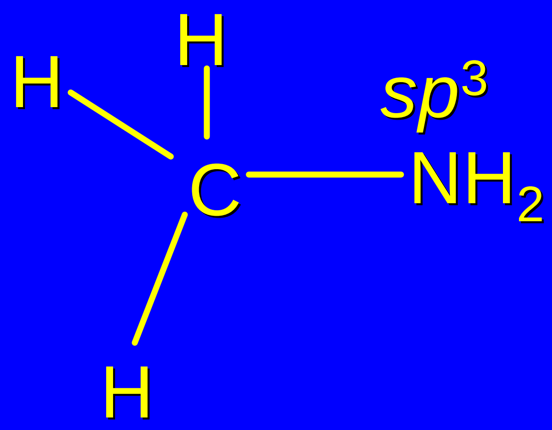
Alkylamines

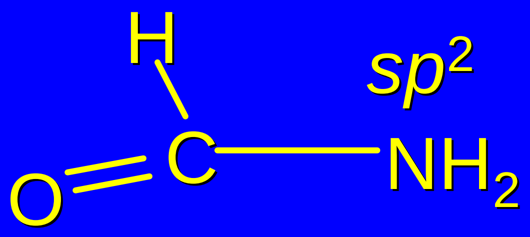


Most prominent feature is high electrostatic potential at nitrogen. Reactivity of nitrogen lone pair dominates properties of amines.

Geometry at N

Compare geometry at N of methylamine, aniline, and formamide.





Pyramidal geometry at *sp*^{3}-hybridized N in methylamine.

Planar geometry at *sp*^{2}-hybridized N in formamide.

Geometry at N

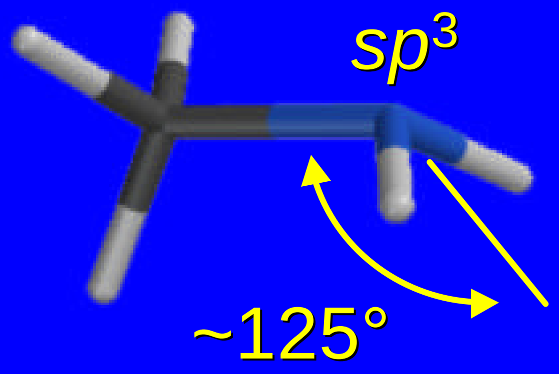
Compare geometry at N of methylamine, aniline, and formamide.

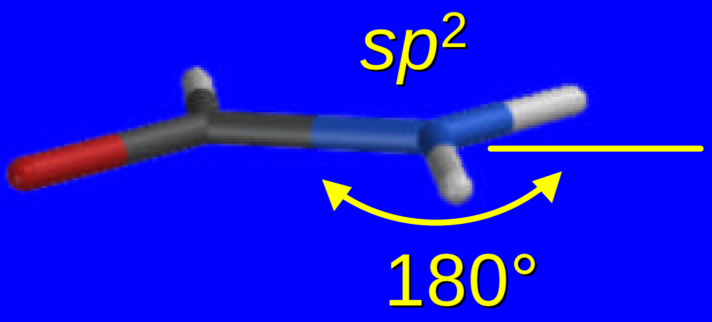
Pyramidal geometry at sp^3-hybridized N in methylamine.

Planar geometry at sp^2-hybridized N in formamide.

Geometry at N

Angle that the C—N bond makes with bisector of H—N—H angle is a measure of geometry at N.

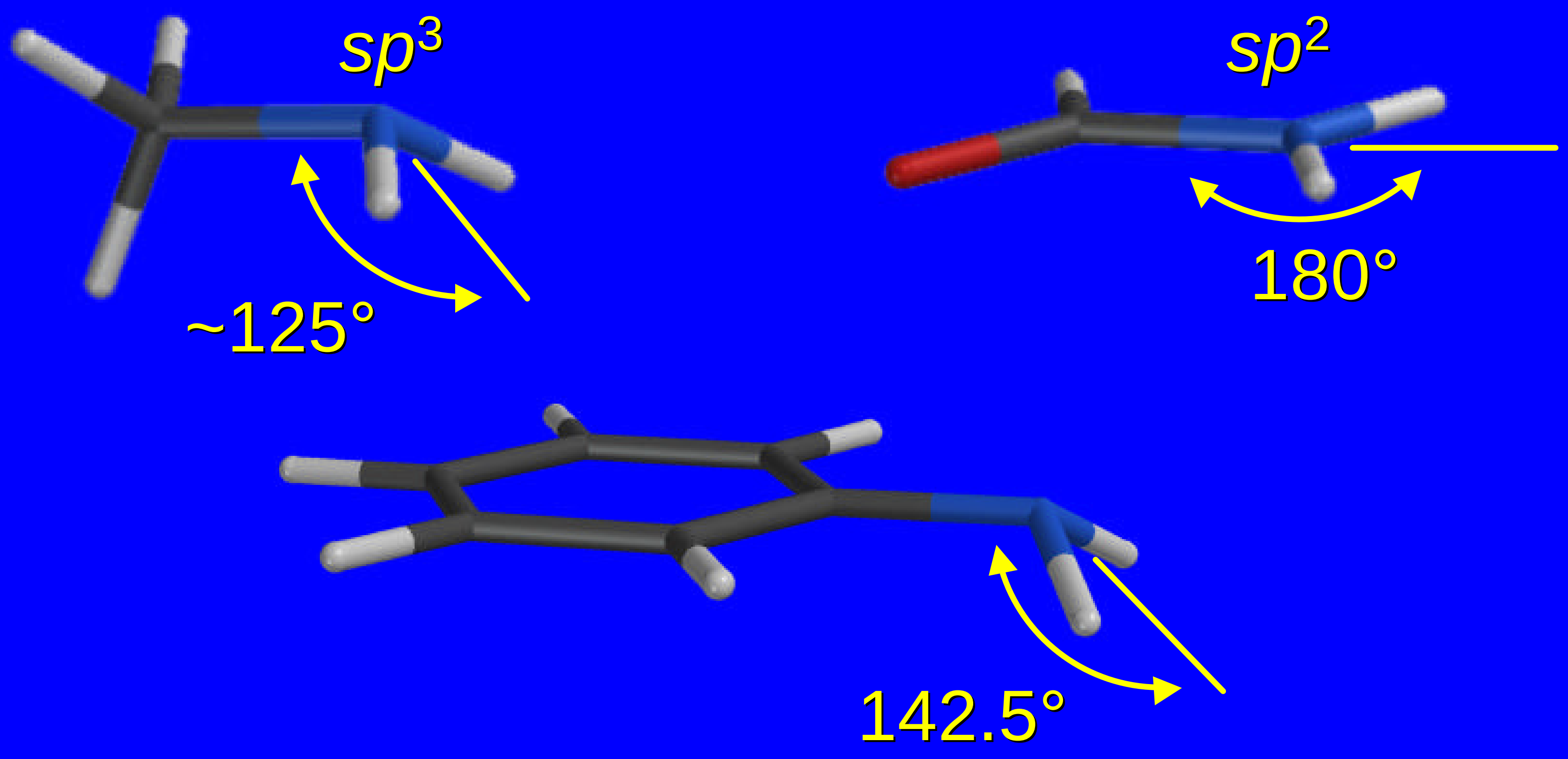




Note: this is not the same as the H—N—H bond angle

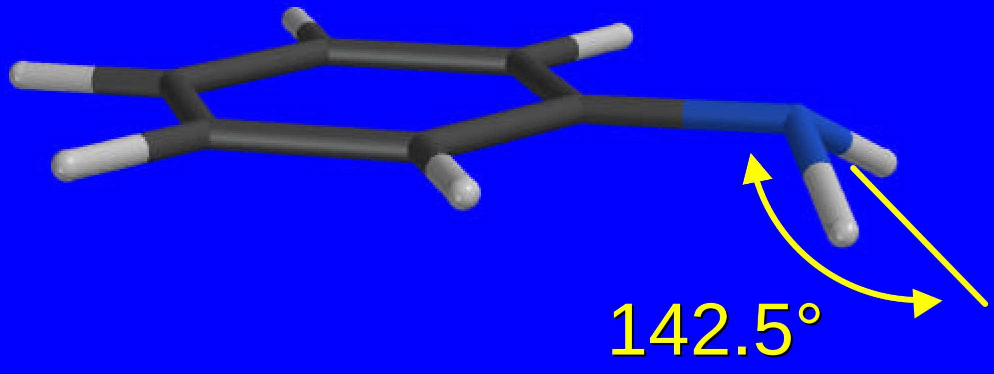
Geometry at N

Angle that the C—N bond makes with bisector of H—N—H angle is a measure of geometry at N.



Geometry at N

Geometry at N in aniline is pyramidal; closer to methylamine than to formamide.



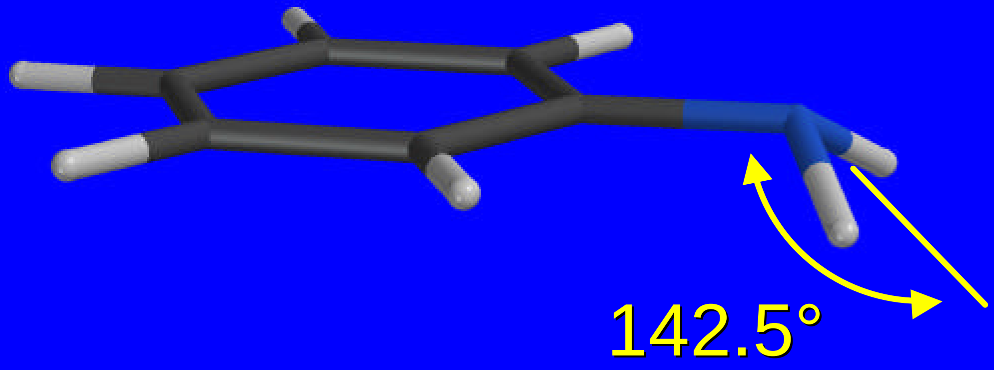
Geometry at N

Hybridization of N in aniline lies between *sp*^{3} and *sp*^{2}.

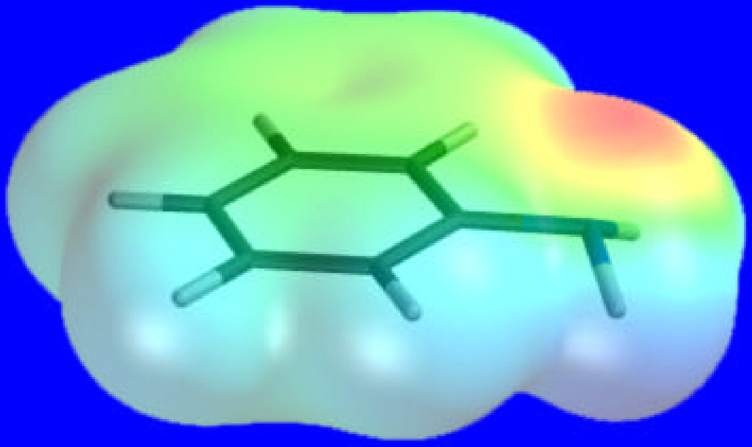
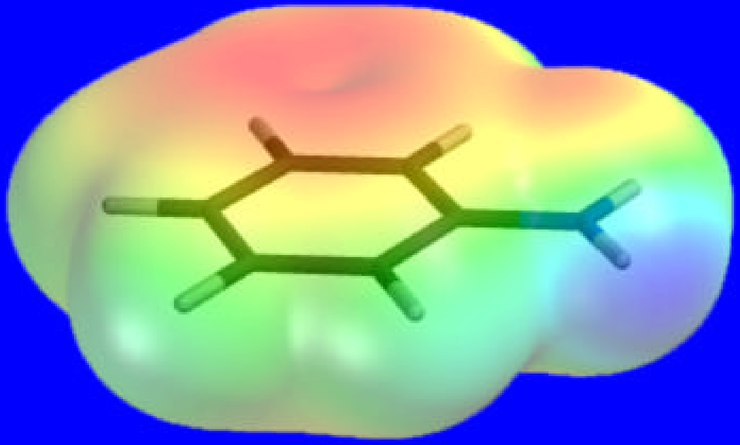
Lone pair of N can be delocalized into ring best if N is *sp*^{2} and lone pair is in a *p* orbital.

Lone pair bound most strongly by N if pair is in an *sp*^{3} orbital of N, rather than *p*.

Actual hybridization is a compromise that maximizes binding of lone pair.



Electrostatic Potential Maps of Aniline

Nonplanar geometry at N. Region of highest negative potential is at N.

Planar geometry at N. High negative potential shared by N and ring.

Figure 22.3 (page 862)

22.3

Physical Properties

Physical Properties

Amines are more polar and have higher boiling points than alkanes; but are less polar and have lower boiling points than alcohols.

	$CH_3CH_2CH_3$	$CH_3CH_2NH_2$	CH_3CH_2OH
dipole moment (μ):	0 D	1.2 D	1.7 D
boiling point:	-42°C	17°C	78°C

Physical Properties

	$CH_3CH_2CH_2NH_2$	$CH_3CH_2NHCH_3$	$(CH_3)_3N$
boiling point:	50°C	34°C	3°C

Boiling points of isomeric amines decrease in going from primary to secondary to tertiary amines.

Primary amines have two hydrogens on N capable of being involved in intermolecular hydrogen bonding. Secondary amines have one. Tertiary amines cannot be involved in intermolecular hydrogen bonds.