10.11: SPECTROSCOPY OF AMINES

OBJECTIVES

After completing this section, you should be able to

1. identify the region of the infrared spectrum that shows absorptions resulting from the $N-H$ bonds of primary and secondary amines.
2. describe a characteristic change that occurs in the infrared spectrum of an amine when a small amount of mineral acid is added to the sample.
3. use ^1H NMR spectra in determining the structure of an unknown amine.
4. use the "nitrogen rule" of mass spectrometry to determine whether a compound has an odd or even number of nitrogen atoms in its structure.
5. predict the prominent peaks in the mass spectrum of a given amine.
6. use the mass spectrum of an unknown amine in determining its structure.

KEY TERMS

Make certain that you can define, and use in context, the key term below.
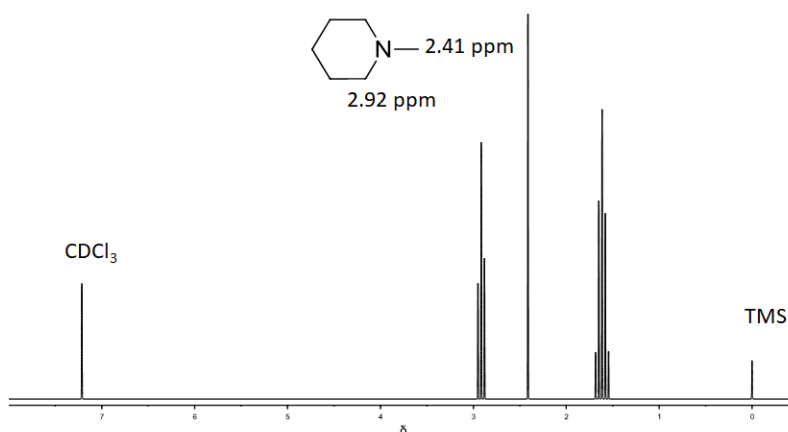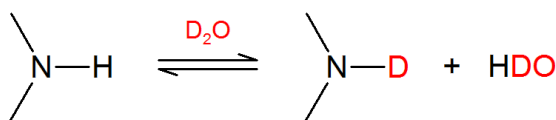
- nitrogen rule

STUDY NOTES

You should note the spectroscopic similarities between amines and alcohols: both have infrared absorptions in the 3300–3360 cm^{-1} region, and in both cases, the proton that is attached to the heteroatom gives rise to an often indistinct signal in the ^1H NMR spectrum.
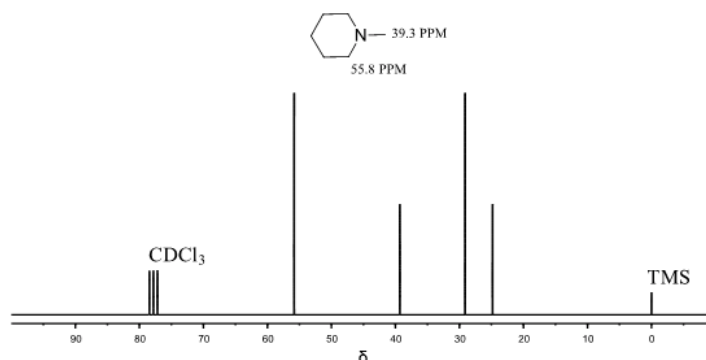
^1H NMR OF AMINES

The hydrogens attached to an amine show up ~ 0.5-5.0 ppm. The location is dependent on the amount of hydrogen bonding and the sample's concentration. The hydrogens on carbons directly bonded to an amine typically appear ~2.3-3.0 ppm. These hydrogens are deshielded by the electron-withdrawing effects of nitrogen and appear downfield in an NMR spectra compared to alkane hydrogens.

Addition of D_2O will normally cause all hydrogens on non-carbon atoms to exchange with deuterium, thus making these resonances "disappear." Addition of a few drops of D_2O causing a signal to vanish can help confirm the presence of -NH.
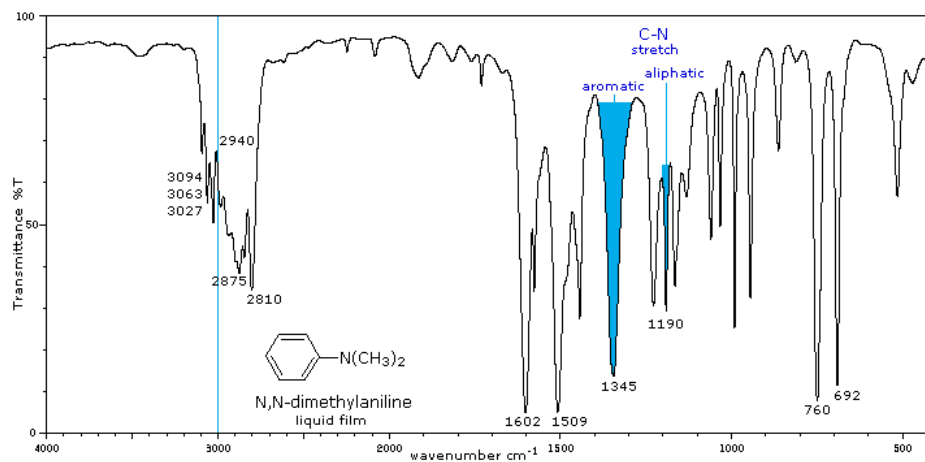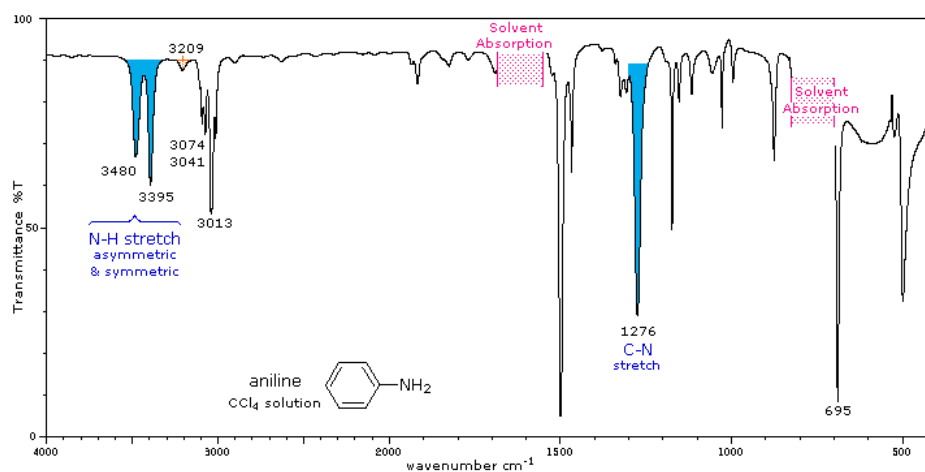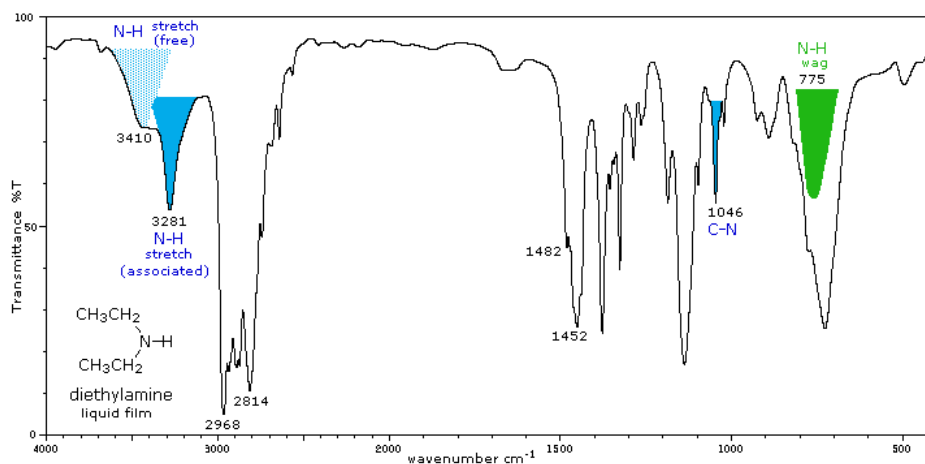
^{13}C NMR OF AMINES

Carbons directly attached to the nitrogen appear in 10-65 ppm region of a ^{13}C NMR spectra. They are shifted slightly downfield compared to alkane carbons due to the electron-withdrawing effect of nitrogen again causing deshielding.

IR OF AMINES

The infrared spectra of several amines are shown beneath the following table. Some of the characteristic absorptions for C-H stretching and aromatic ring substitution are also marked, but not colored.

Amine Class	Stretching Vibrations	Bending Vibrations
Primary (1°)	The N-H stretching absorption is less sensitive to hydrogen bonding than are O-H absorptions. In the gas phase and in dilute CCl_4 solution free N-H absorption is observed in the 3400 to 3500 cm^{-1} region. Primary aliphatic amines display two well-defined peaks due to asymmetric (higher frequency) and symmetric N-H stretching, separated by 80 to 100 cm^{-1}. In aromatic amines these absorptions are usually 40 to 70 cm^{-1} higher in frequency. A smaller absorption near 3200 cm^{-1} (shaded orange in the spectra) is considered to be the result of interaction between an overtone of the 1600 cm^{-1} band with the symmetric N-H stretching band. C-N stretching absorptions are found at 1200 to 1350 cm^{-1} for aromatic amines, and at 1000 to 1250 cm^{-1} for aliphatic amines.	Strong in-plane NH_2 scissoring absorptions at 1550 to 1650 cm^{-1}, and out-of-plane wagging at 650 to 900 cm^{-1} (usually broad) are characteristic of 1°-amines.
Secondary (2°)	Secondary amines exhibit only one absorption near 3420 cm^{-1}. Hydrogen bonding in concentrated liquids shifts these absorptions to lower frequencies by about 100 cm^{-1}. Again, this absorption appears at slightly higher frequency when the nitrogen atom is bonded to an aromatic ring. The C-N absorptions are found in the same range, 1200 to 1350 cm^{-1} (aromatic) and 1000 to 1250 cm^{-1} (aliphatic) as for 1°-amines.	A weak N-H bending absorption is sometimes visible at 1500 to 1600 cm^{-1}. A broad wagging absorption at 650 to 900 cm^{-1} may be discerned in liquid film samples.
Tertiary (3°)	No N-H absorptions. The C-N absorptions are found in the same range, 1200 to 1350 cm^{-1} (aromatic) and 1000 to 1250 cm^{-1} (aliphatic) as for 1°-amines.	Aside from the C-N stretch noted on the left, these compounds have spectra characteristic of their alkyl and aryl substituents.

Diethylamine IR spectrum (liquid film): N-H stretch (free), N-H stretch (associated) 3410, 3281, N-H wag 775, C-N 1046, 2968, 2814, 1482, 1452. Structure: CH₃CH₂–N–H, CH₃CH₂

Aniline IR spectrum (CCl₄ solution): N-H stretch asymmetric & symmetric 3480, 3395, 3209, 3074, 3041, 3013, C-N stretch 1276, 695, Solvent Absorption regions.

N,N-dimethylaniline IR spectrum (liquid film): 3094, 3063, 3027, 2940, 2875, 2810, C-N stretch aromatic 1345, aliphatic, 1190, 1602, 1509, 760, 692.
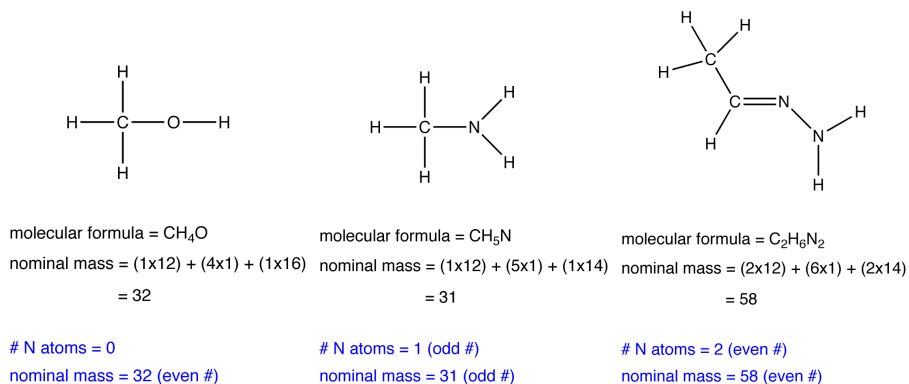
UV/VIS SPECTRA OF AMINES

Alky Amines absorb in the region around 200 nm which make them of little value. In arylamines, the lone pair electron on the nitrogen interacts with pi electron system of the aromatic ring shifting the ring 's absorption to longer wavelengths. An example is benzene's lambda max of 256 nm while aniline's lambda max of 280 nm.
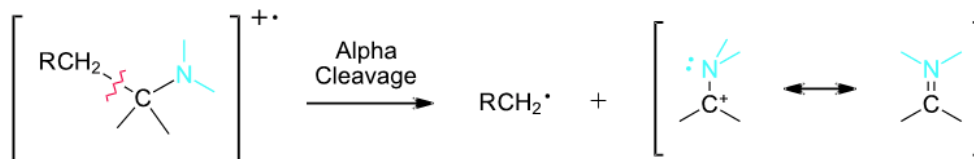
MASS SPECTRA OF AMINES

Nitrogen Rule

The nitrogen rule states that a molecule that has no or even number of nitrogen atoms has an even nominal mass, whereas a molecule that has an odd number of nitrogen atoms has an odd nominal mass.

Example

molecular formula = CH_4O

nominal mass = (1x12) + (4x1) + (1x16)

= 32

N atoms = 0

nominal mass = 32 (even #)

molecular formula = CH_5N

nominal mass = (1x12) + (5x1) + (1x14)

= 31

N atoms = 1 (odd #)

nominal mass = 31 (odd #)

molecular formula = $C_2H_6N_2$

nominal mass = (2x12) + (6x1) + (2x14)

= 58

N atoms = 2 (even #)
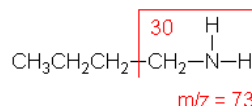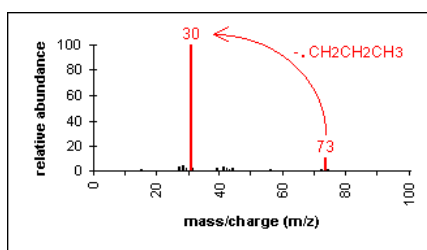
nominal mass = 58 (even #)

Fragmentation Patterns

The molecular ion peak is an odd number any time there is an odd number of nitrogen atoms in a molecule.. The mass spectra of amines is dominated by alpha-cleavage which produces an alkyl radical on a resonance stabilized nitrogen containing cation. Secondary and tertiary amines have the possibility of multiple alpha-cleavages.
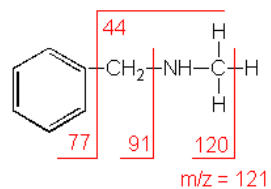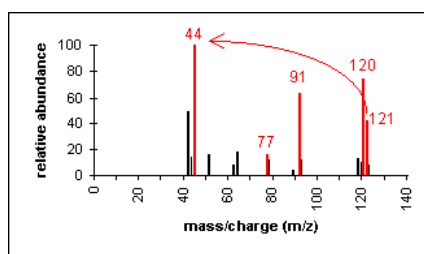

N-Butylamine ($C_4H_{11}N$) with MW = 73.13

Another example is a secondary amine shown below. Again, the molecular ion peak is an odd number. The base peak (m/z = 44) is from the C-C cleavage adjacent to the C-N bond. Other important peaks come from the cleavage of the N-H bond (m/z = 120) and cleavage at the benzylic position (m/z = 91).

N-Methylbenzylamine ($C_8H_{11}N$) with MW = 121.18

$m/z = 121$

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