Objectives

After completing this section, you should be able to

1. identify the region of the infrared spectrum that shows absorptions resulting from the \(\text{N}^{-}\text{H}\) 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 \(^1\text{H}\) 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 \(^1\text{H}\) NMR spectrum.

NMR

The hydrogens attached to an amine show up \(\sim 0.5-5.0\) 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 \(\sim 2.3-3.0\) ppm. Addition of D\(_2\)O will normally cause all hydrogens on non-carbon atoms to exchange with deuteriums, thus making these resonances "disappear." Addition of a few drops of D\(_2\)O causing a signal to vanish can help confirm the presence of \(-\text{NH}\).

\[\begin{align*}
\text{N}^{-}\text{H} & \xrightarrow{\text{D}_2\text{O}} \text{N}^{-}\text{D} + \text{HDO} \\
\end{align*}\]
The infrared spectrum of aniline is shown beneath the following table. Some of the characteristic absorptions for C-H stretching and aromatic ring substitution are also marked, but not colored.

<table>
<thead>
<tr>
<th>Amine Class</th>
<th>Stretching Vibrations</th>
<th>Bending Vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary (1°)</td>
<td>The N-H stretching absorption is less sensitive to hydrogen bonding than are O-H absorptions. In the gas phase and in dilute CCl₄ 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.</td>
<td>Strong in-plane NH₂ scissoring absorptions at 1550 to 1650 cm⁻¹, out-of-plane wagging at 650 to 900 cm⁻¹ (usually broad) are characteristic of 1°-amines.</td>
</tr>
<tr>
<td>Secondary (2°)</td>
<td>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.</td>
<td>A weak N-H bending absorption 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.</td>
</tr>
<tr>
<td>Tertiary (3°)</td>
<td>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.</td>
<td>Aside from the C-N stretch noted on the left, these compounds have spectra characteristic of their alkyl and aryl substituents.</td>
</tr>
</tbody>
</table>
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.

eg. 1:
molecular formula = CH$_4$O
nominal mass = (1x12) + (4x1) + (1x16)
  = 32

# N atoms = 0
nominal mass = 32 (even #)

eg. 2:

molecular formula = CH$_3$N
nominal mass = (1x12) + (5x1) + (1x14)
  = 31

# N atoms = 1 (odd #)
nominal mass = 31 (odd #)

eg. 3:

molecular formula = C$_2$H$_6$N$_2$
nominal mass = (2x12) + (6x1) + (2x14)
  = 58

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