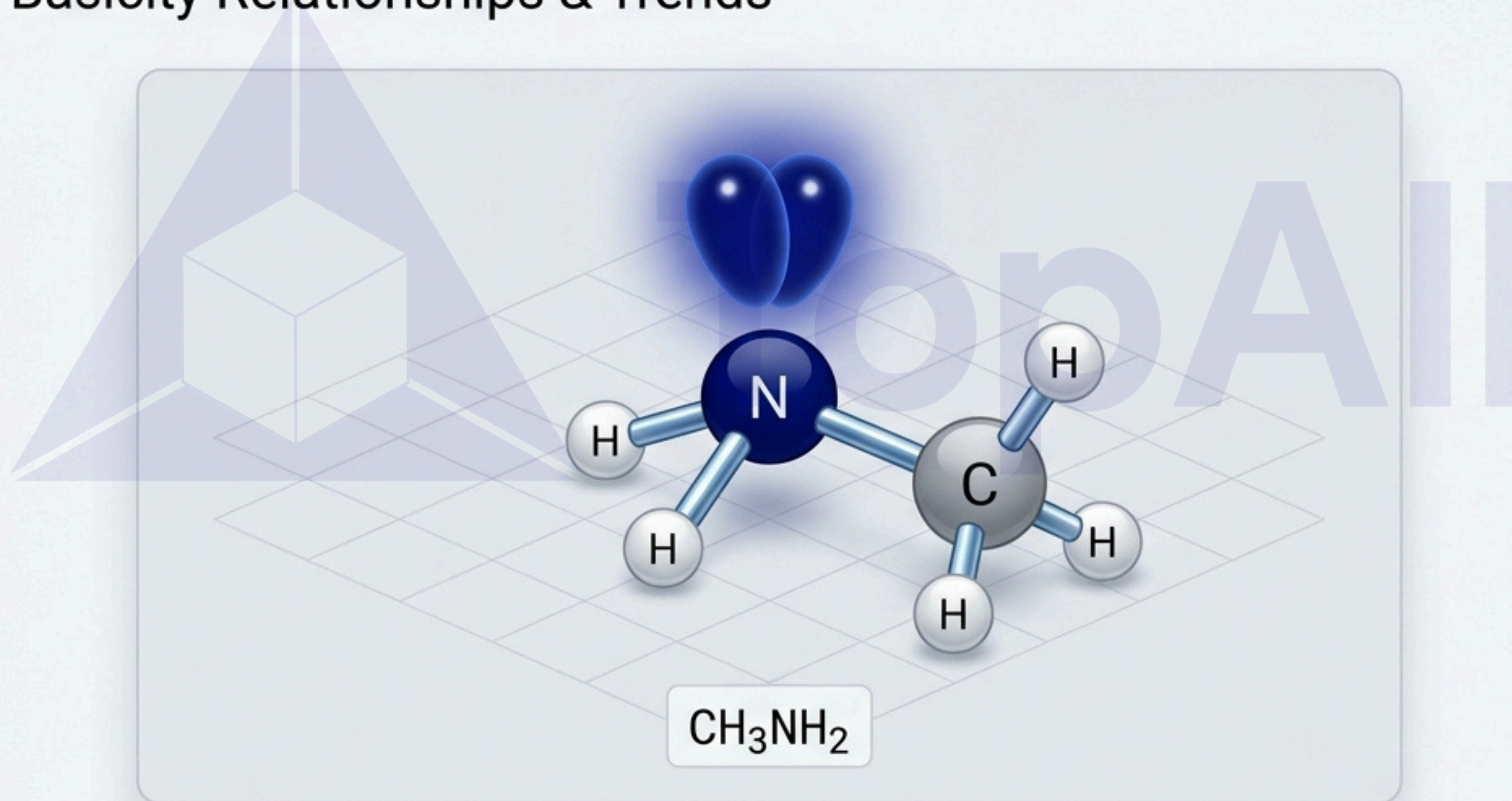
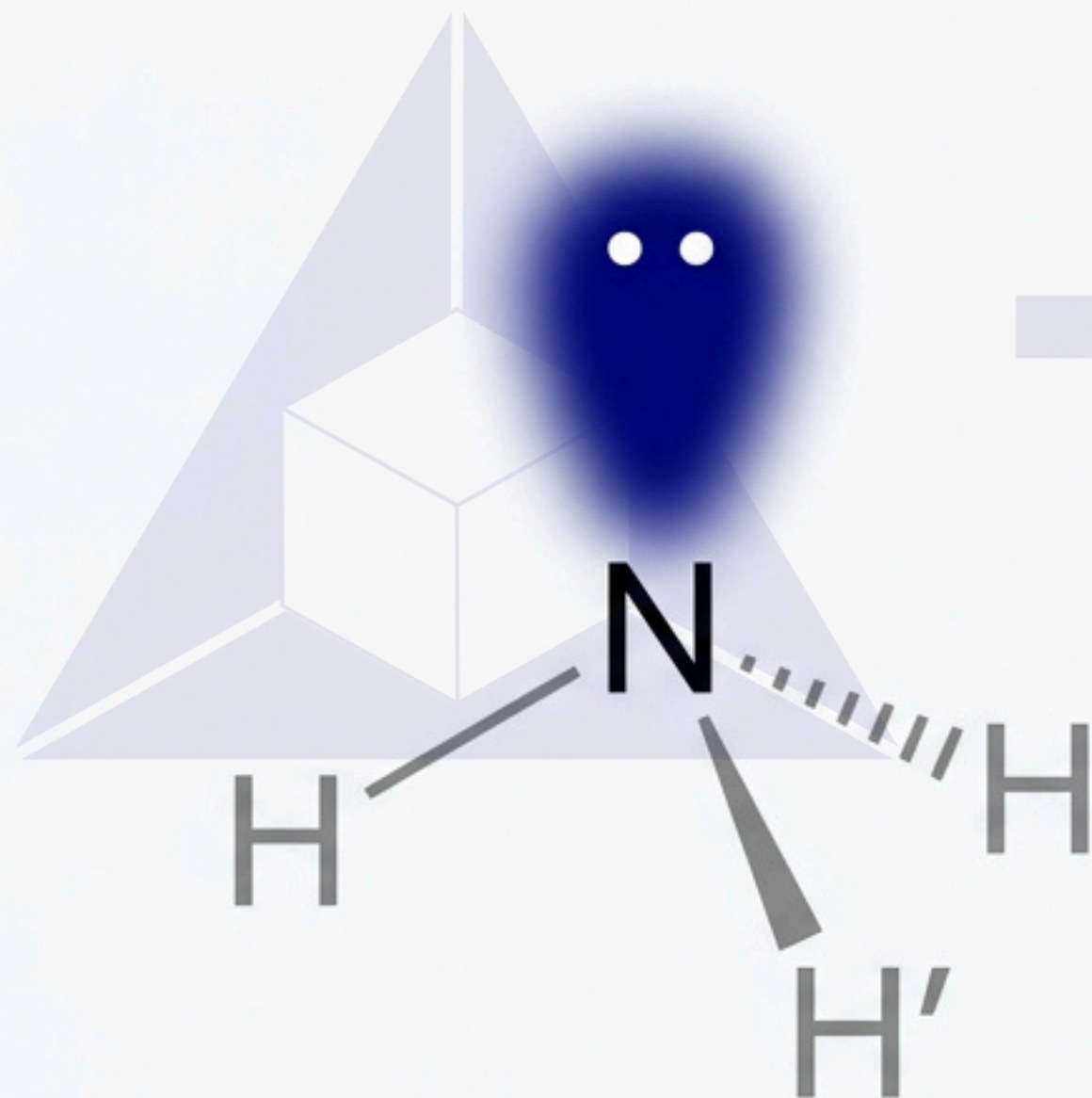


9.6.1 Basic Character of Amines

Structure-Basicity Relationships & Trends



The Lewis Base Behavior of Amines



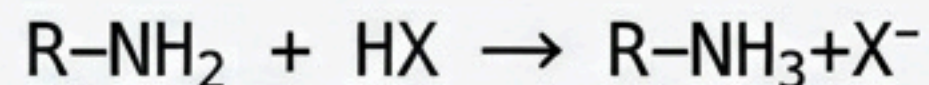
Lewis Base

Amines are basic because the nitrogen atom contains an unshared pair of electrons, making it a proton acceptor (Lewis base).

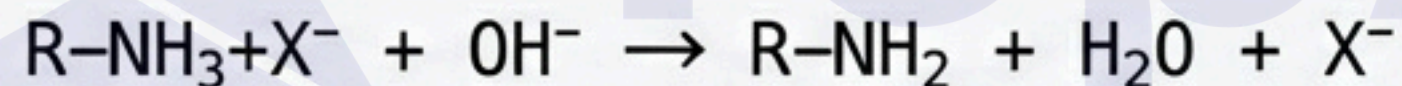
sp³ Hybridized

The trivalent nitrogen is sp³ hybridized with pyramidal geometry. The lone pair sits in the fourth orbital, ready for protonation.

Amine Salt Formation & Regeneration



Amine + Acid → Ammonium Salt



Step Card 2 (Base Regeneration)

Treatment with strong base regenerates parent amine.



This reaction separates amines from non-basic, water-insoluble organic compounds. Amine salts are water-soluble; parent amines are not.

Quantitative Basicity

Measuring Basic Strength

$$K_b = \frac{[R-NH_3^+][OH^-]}{[R-NH_2]}$$

$$pK_b = -\log(K_b)$$

Larger K_b
Smaller pK_b

K_b

pK_b

Smaller K_b
Larger pK_b

Stronger Base

Weaker Base

Aliphatic Amines
 $pK_b = 3.00 - 4.22$

Ammonia
 $pK_b = 4.75$

Aniline
 $pK_b = 9.38$



You've Learned the Theory. Let's Test Them Now.

$$E=mc^2$$



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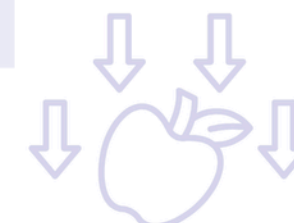
Practice Now



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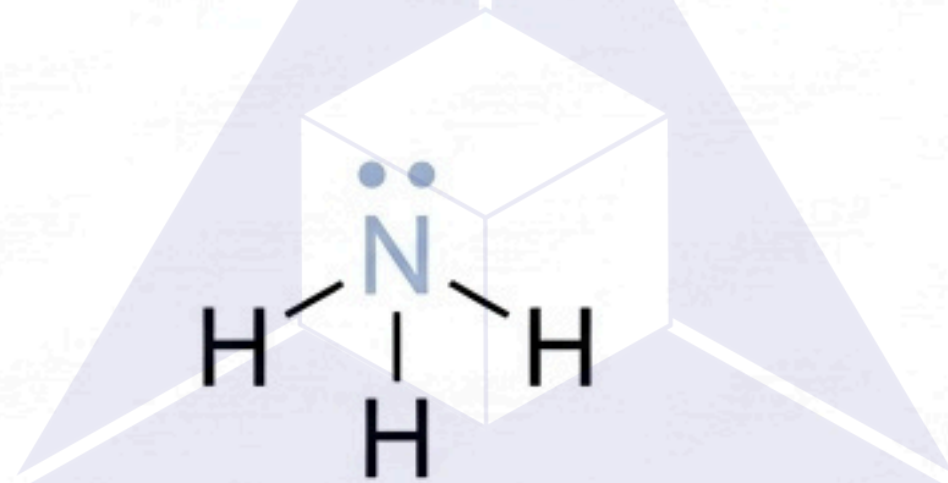
Key Highlights

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- » Track Your Performance Smarter

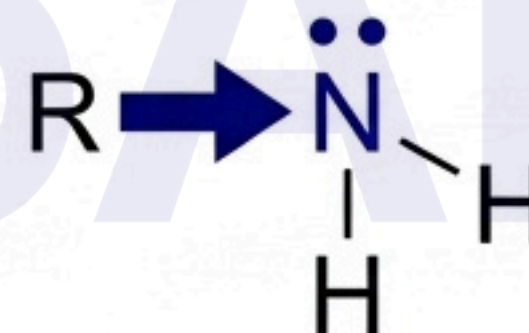


Why Aliphatic Amines are Stronger Bases

Ammonia - The Baseline

 NH_3 $\text{pK}_b = 4.75$ 

Alkylamines - The Stronger Base

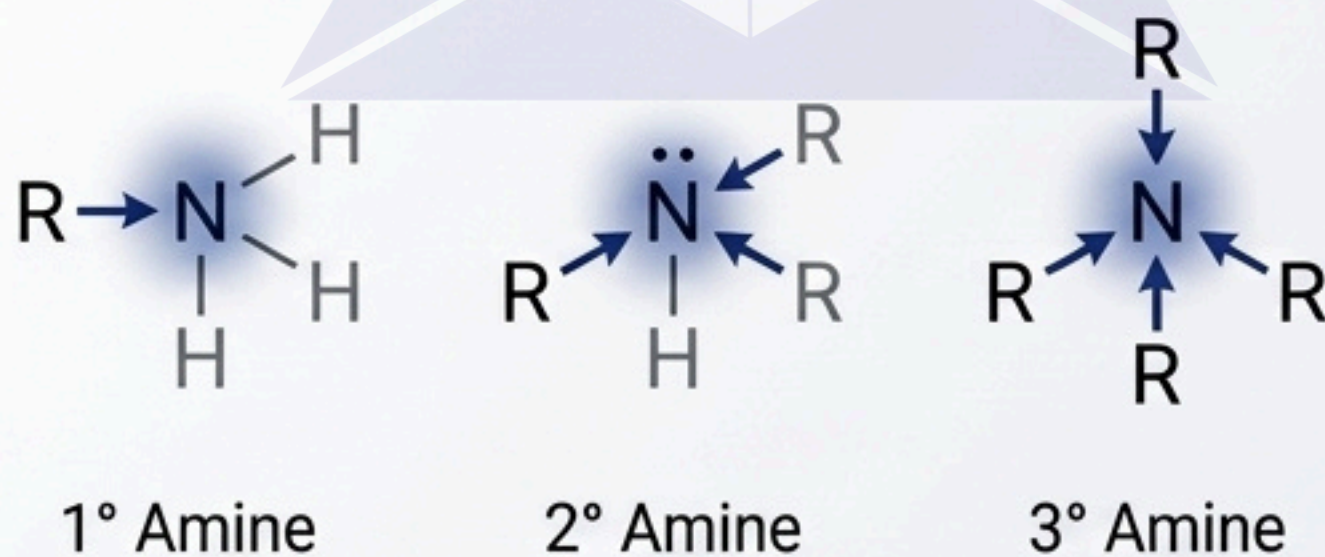
 $\text{R} \rightarrow \text{NH}_2$ $\text{pK}_b < 4.22$ 

The +I (Inductive) effect of alkyl groups pushes electron density onto the nitrogen. This makes the unshared pair more available for protonation and stabilizes the resulting substituted ammonium cation.

Conflicting Trends in Basicity

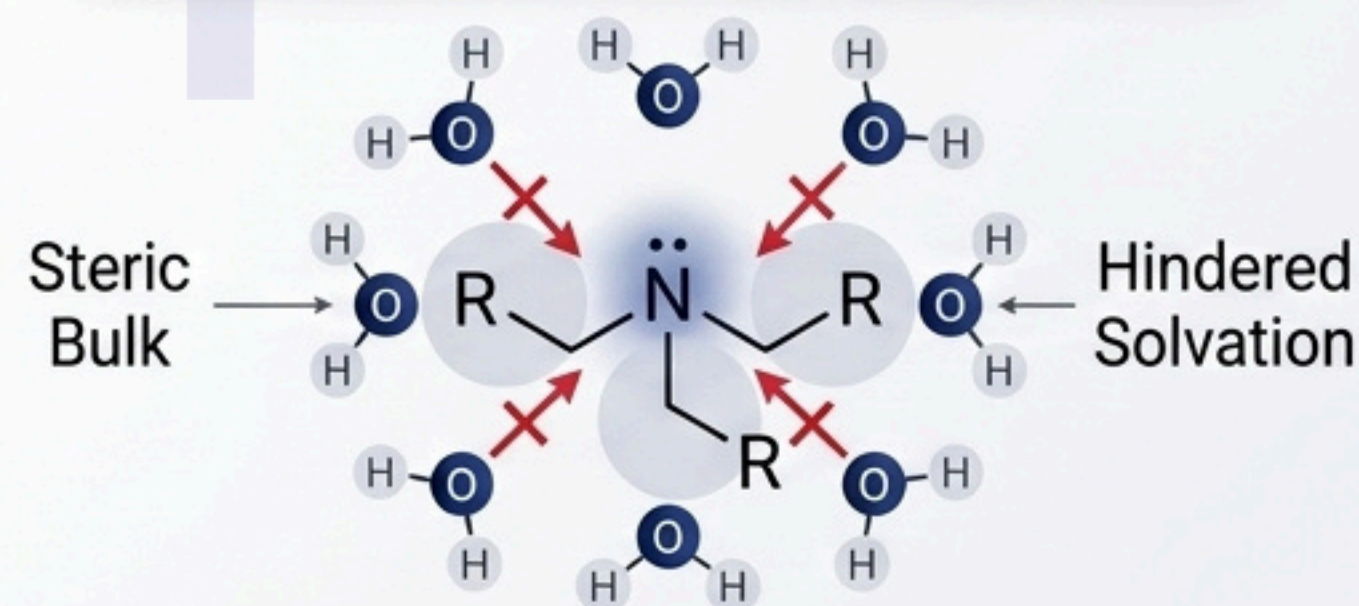
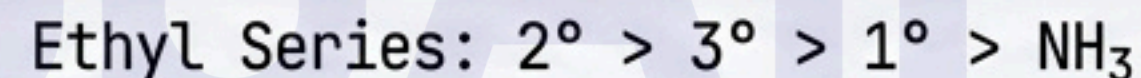
Gas Phase

Inductive effect (+I) dominates exclusively.
More alkyl groups = stronger base.



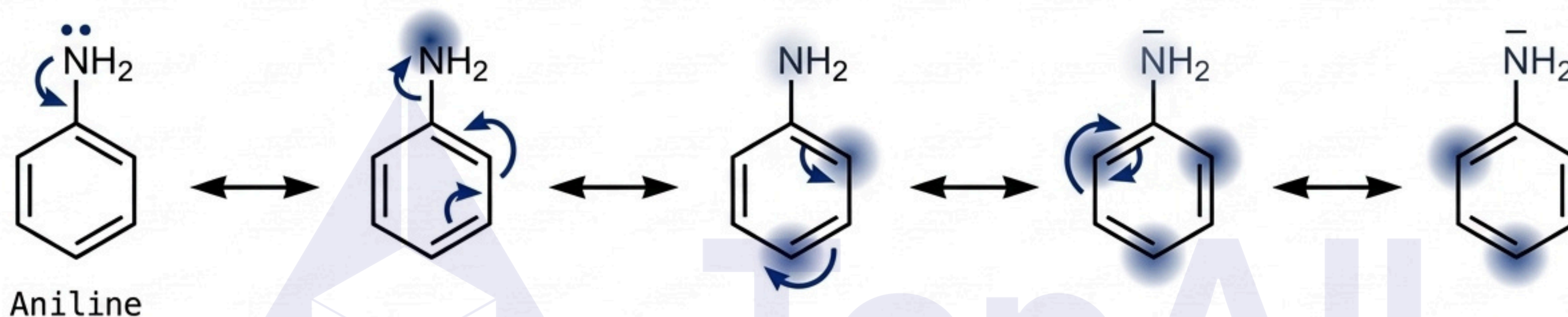
Aqueous Phase

A subtle interplay of **+I effect**, **Solvation** (H-bonding stabilization favors 1°), and **Steric Hindrance**.



Resonance Effect

Why Aniline is a Weaker Base



Aniline $pK_b = 9.38$ (Weaker than NH_3)

Delocalization

The $-NH_2$ lone pair is in conjugation with the benzene ring. This delocalization makes the electrons less available for protonation.

Stability

Aniline has 5 resonance structures, making it far more stable than the protonated anilinium ion, which only has 2 Kekulé structures. The molecule resists forming the less stable cation.

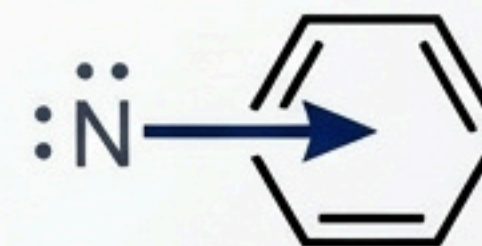
The 4 Structural Factors of Basicity

+I Effect



Alkyl groups push electron density onto N, increasing basicity.

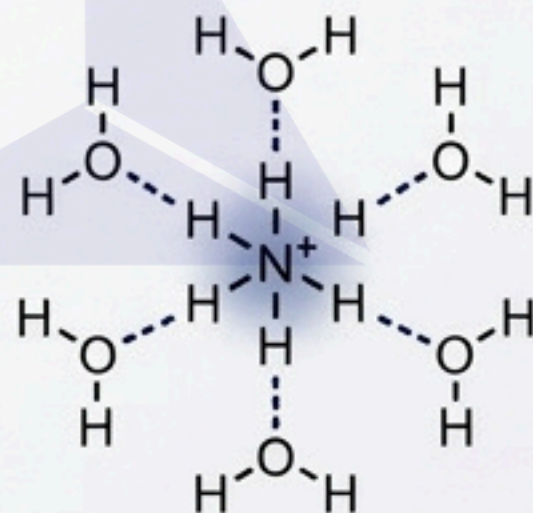
-R Effect



Delocalization of the lone pair into an aryl ring decreases basicity.

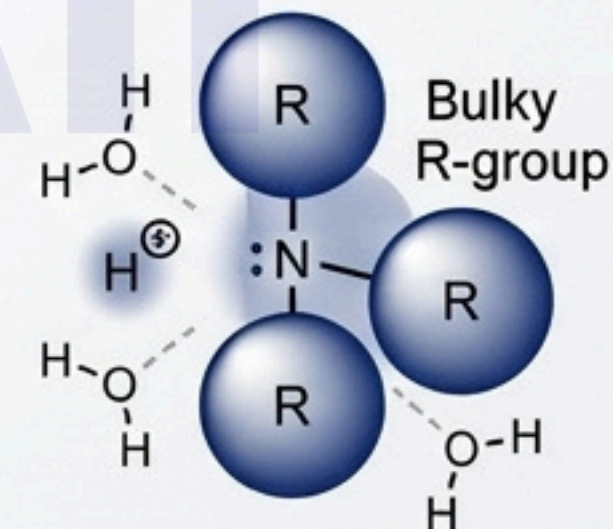
H-Bonding

H-bonding stabilizes the ammonium cation in water. Highly favors less substituted amines ($1^\circ > 2^\circ > 3^\circ$).



Crowding

Bulky alkyl groups block both proton approach and solvation, decreasing basicity in 3° amines.



Recap Panel

Basicity is the ultimate tug-of-war between making the lone pair available (+I) and stabilizing the resulting cation (Solvation vs. Sterics).



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