

16.3: Properties of Amines

Learning Objectives

- Explain why the boiling points of primary and secondary amines are higher than those of alkanes or ethers of similar molar mass but are lower than those of alcohols.
- Compare the boiling points of tertiary amines with alcohols, alkanes, and ethers of similar molar mass.
- Compare the solubilities in water of amines of five or fewer carbon atoms with the solubilities of comparable alkanes and alcohols in water.

Primary and secondary amines have hydrogen atoms bonded to a nitrogen atom and are therefore capable of hydrogen bonding (part (a) of Figure 16.3.1), although not as strongly as alcohol molecules (which have hydrogen atoms bonded to an oxygen atom, which is more electronegative than nitrogen). These amines boil at higher temperatures than alkanes but at lower temperatures than alcohols of comparable molar mass. For example, compare the boiling point of methylamine (CH_3NH_2 ; -6°C) with those of ethane (CH_3CH_3 ; -89°C) and methanol (CH_3OH ; 65°C). Tertiary amines have no hydrogen atom bonded to the nitrogen atom and so cannot participate in intermolecular hydrogen bonding. They have boiling points comparable to those of ethers (Table 16.3.1).

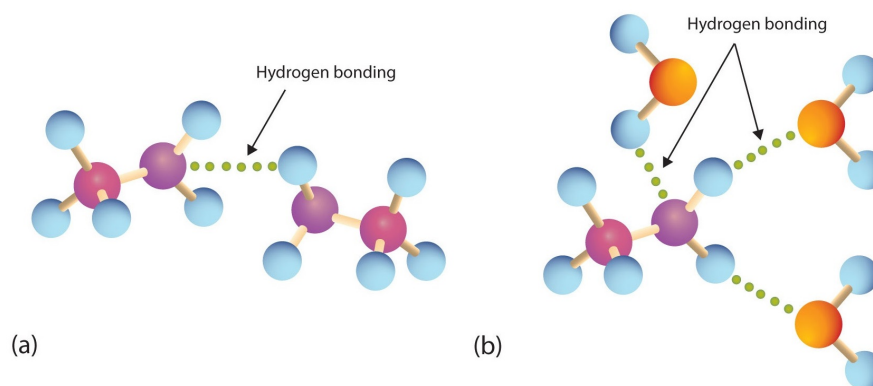


Figure 16.3.1: Hydrogen Bonding. (a) Amine molecules are associated through hydrogen bonding. (b) An amine molecule can form a hydrogen bond with water molecules.

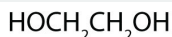
Table 16.3.1: Physical Properties of Some Amines and Comparable Oxygen-Containing Compounds

Name	Condensed Structural Formula	Class	Molar Mass	Boiling Point ($^\circ\text{C}$)	Solubility at 25°C (g/100 g Water)
butylamine	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	1°	73	78	miscible
diethylamine	$(\text{CH}_3\text{CH}_2)_2\text{NH}$	2°	73	55	miscible
butyl alcohol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	—	74	118	8
dipropylamine	$(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}$	2°	101	111	4
triethylamine	$(\text{CH}_3\text{CH}_2)_3\text{N}$	3°	101	90	14
dipropyl ether	$(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{O}$	—	102	91	0.25

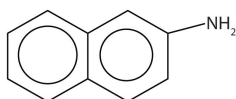
All three classes of amines can engage in hydrogen bonding with water (Figure 16.3.1b). Amines of low molar mass are quite soluble in water; the borderline of solubility in water is at five or six carbon atoms.

📌 To Your Health: Amines in Death and Life

Amines have “interesting” odors. The simple ones smell very much like ammonia. Higher aliphatic amines smell like decaying fish. Or perhaps we should put it the other way around: Decaying fish give off odorous amines. The stench of rotting fish is due in part to two diamines: putrescine and cadaverine. They arise from the decarboxylation of ornithine and lysine, respectively, amino acids that are found in animal cells.



Aromatic amines generally are quite toxic. They are readily absorbed through the skin, and workers must exercise caution when handling these compounds. Several aromatic amines, including β -naphthylamine, are potent carcinogens.



Key Takeaways

- Primary and secondary amines have higher boiling points than those of alkanes or ethers of similar molar mass because they can engage in intermolecular hydrogen bonding. Their boiling points are lower than those of alcohols because alcohol molecules have hydrogen atoms bonded to an oxygen atom, which is more electronegative.
- The boiling points of tertiary amines, which cannot engage in hydrogen bonding because they have no hydrogen atom on the nitrogen atom, are comparable to those of alkanes and ethers of similar molar mass.
- Because all three classes of amines can engage in hydrogen bonding with water, amines of low molar mass are quite soluble in water.

Concept Review Exercises

- Which compound has the higher boiling point, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$? Explain.
- Which compound is more soluble in water, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$? Explain.

Answers

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ because the nitrogen-to-hydrogen (N–H) bonds can engage in hydrogen bonding; $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ cannot engage in hydrogen bonding
- $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$ because amines can engage in hydrogen bonding with water; alkanes cannot engage in hydrogen bonding

Exercises

- Which compound of each pair has the higher boiling point? Explain.
 - butylamine or pentane
 - CH_3NH_2 or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
- Which compound of each pair has the higher boiling point? Explain.
 - butylamine or butyl alcohol
 - trimethylamine or propylamine
- Which compound is more soluble in water— $\text{CH}_3\text{CH}_2\text{CH}_3$ or $\text{CH}_3\text{CH}_2\text{NH}_2$? Explain.
- Which compound is more soluble in water— $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$? Explain.

Answers

- butylamine because the N–H bonds can engage in hydrogen bonding; pentane cannot engage in hydrogen bonding
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ because it has a greater molar mass than CH_3NH_2
- $\text{CH}_3\text{CH}_2\text{NH}_2$ because amines can engage in hydrogen bonding with water; alkanes cannot engage in hydrogen bonding

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