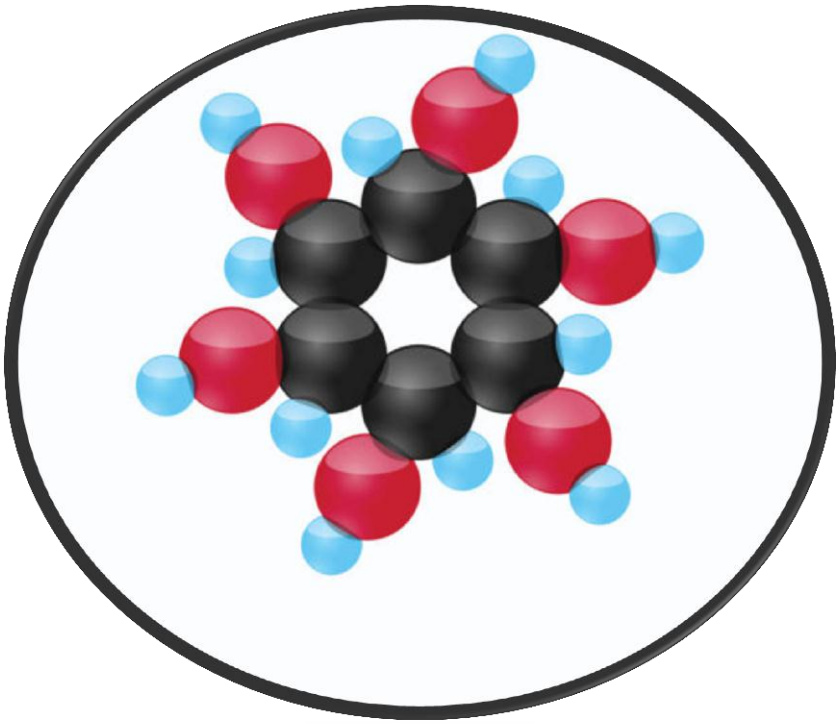
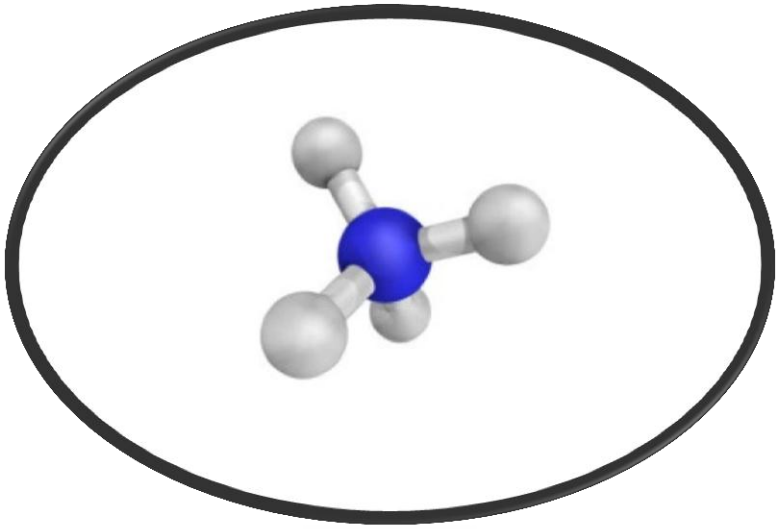
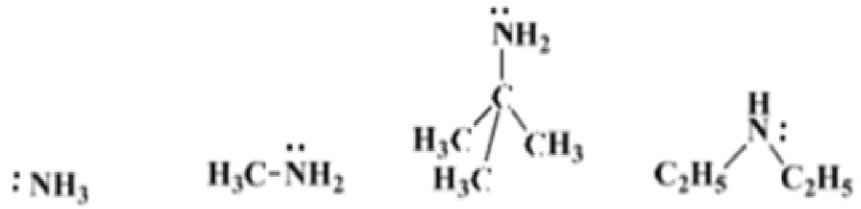


AMINES

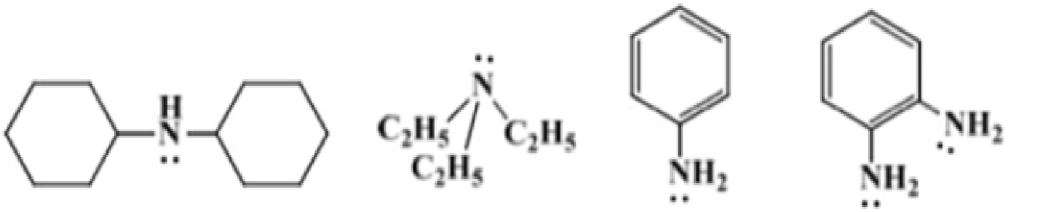


Identification of Amines

Amines are basic organic compounds that are considered as derivatives of ammonia. They are classified as primary, secondary, or tertiary according to the number of groups attached to the nitrogen atom: RNH_2, R_2NH, or R_3N respectively where R is any alkyl or aryl group.



ammonia — methylamine — *t*-butylamine — diethylamine

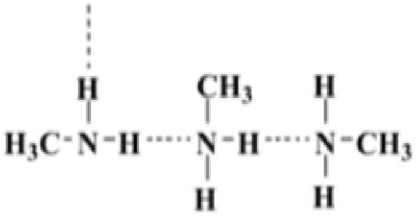


dicyclohexylamine — triethylamine — aniline — *o*-phenylenediamine

N,N-dimethylaniline — diphenylamine — *p,p*-diaminodiphenylamine

Physical properties

Like ammonia, amines are polar compounds and all of them can form intermolecular hydrogen bonds except tertiary amines.



They have lower boiling points than alcohols or carboxylic acids of the same molecular weight but higher boiling points than non polar

compounds. Methylamine is gas while *o*-phenylenediamine and *p,p*-diaminodiphenylmethane are solids. The others are liquids.

All amines are capable of forming hydrogen bonds with water, thus those with six carbon atoms or less are quite soluble in water. They are soluble in organic solvents as ether, alcohol and benzene.

All of them have fish like odour except the methylamines and ethylamines which smell just like ammonia.

Aromatic amines are colourless when pure, but they are easily oxidized by air becoming coloured. They are generally very toxic and can be absorbed through the skin.

Chemical reaction

All classes of amines (primary, secondary, and tertiary) have an unshared pair of electrons on the nitrogen atom, just like ammonia. That is why they are similar to ammonia in their chemical behavior (mainly basicity and neocleophilicity).

1. Ramini and Simon tests (Sodium nitroprusside tests).

(*conventional Ramini and Simon tests*)

In Ramini test the amine reacts with acetone and the product interacts with sodium nitroprusside ($Na_2[Fe(NO)(CN)_5].2H_2O$) that is dissolved in 50 % aqueous methanolic solution to produce a coloured complex. In Simon test acetone is replaced by 2.5 *M* acetaldehyde solution. These two tests distinguish between primary and secondary aliphatic amines.

To distinguish between aromatic amines (primary, secondary and tertiary) the ***modified Ramini and Simon tests*** are applied. These tests use the same reagents and procedure of the conventional tests but the modifications are the replacement of the methanolic solution of sodium nitroprusside by a solution of sodium nitroprusside in dimethylsulfoxide (modified sodium nitroprusside reagent) and the use of a saturated aqueous solution of zinc chloride instead of water.

Procedure

- **Ramini test**

To 1 mL of methanolic sodium nitroprusside solution add 1 mL of distilled water, 5 drops of acetone, and about 30 mg of the amine. In most cases the characteristic colour appears in a few seconds, although in some cases 2 minutes may be necessary.

- **Simon test**

Follow the above procedure exactly but use 5 drops of 2.5 *M* acetaldehyde solution instead of acetone. Up to 2 minutes may be needed for the colour to develop.

- **Modified Ramini test**

To 1 mL of the modified sodium nitroprusside reagent add 1 mL of saturated aqueous zinc chloride solution, 5 drops of acetone, and about 30 mg of the amine. Primary and secondary aromatic amines produce orange-red to red-brown colours within a period of few seconds to 5 minutes. Tertiary aromatic amines give a colour that changes from orange-red to green over a period of about 5 minutes.

- **Modified Simon test**

Follow the above procedure exactly but use 5 drops of 2.5 *M* acetaldehyde solution instead of acetone. Primary aromatic amines give an orange-red to red-brown colour within 5 minutes; secondary aromatic amines give a colour changing from red to purple within 5 minutes; tertiary aromatic amines give a colour that changes from orange-red to green over a period of about 5 minutes.

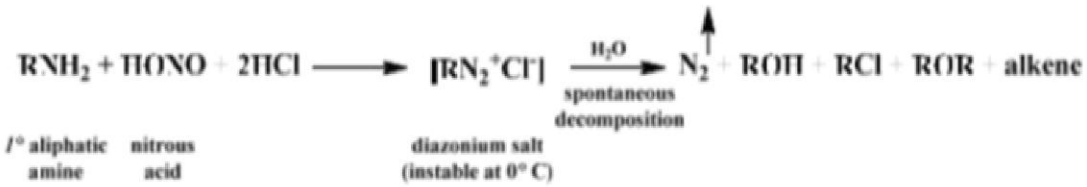
Examples are outlined in the following table:

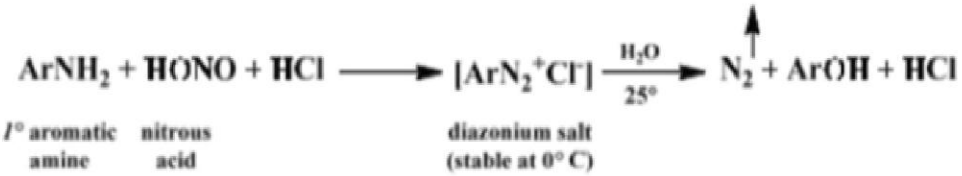
Amine	Ramini test	Simon test	Modified Ramini test	Modified Simon test
tert-butylamine	deep red	red-brown		
dicyclohexylamine	deep red	violet with precipitate		
diethylamine	red-brown	deep blue		
aniline			turbid orange, changes to henna colour	brown
o-phenylenediamine			turbid red brown	turbid henna colour
p,p-diaminodiphenylmethane			light brown precipitate	light brown precipitate
N,N-dimethylaniline			brown changes to green	brown changes to green (rapid change)
diphenylamine			orange- red to red brown	pale orange

2. Nitrous acid test.

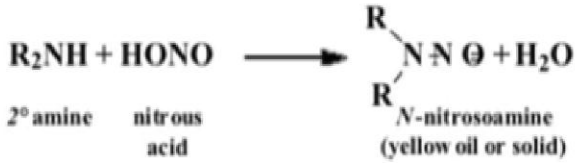
The reaction of amines with nitrous acid (HNO_2) is another test that classifies the amine not only as primary, secondary, or tertiary, but also as aliphatic or aromatic.

Primary aromatic and aliphatic amines react with nitrous acid to form an intermediate diazonium salt. The aliphatic diazonium salts decompose spontaneously by rapid loss of nitrogen, particularly when the original amino group is attached to a secondary or tertiary carbon, while most aromatic diazonium salts are stable at 0°C but lose nitrogen slowly on warming to room temperature.



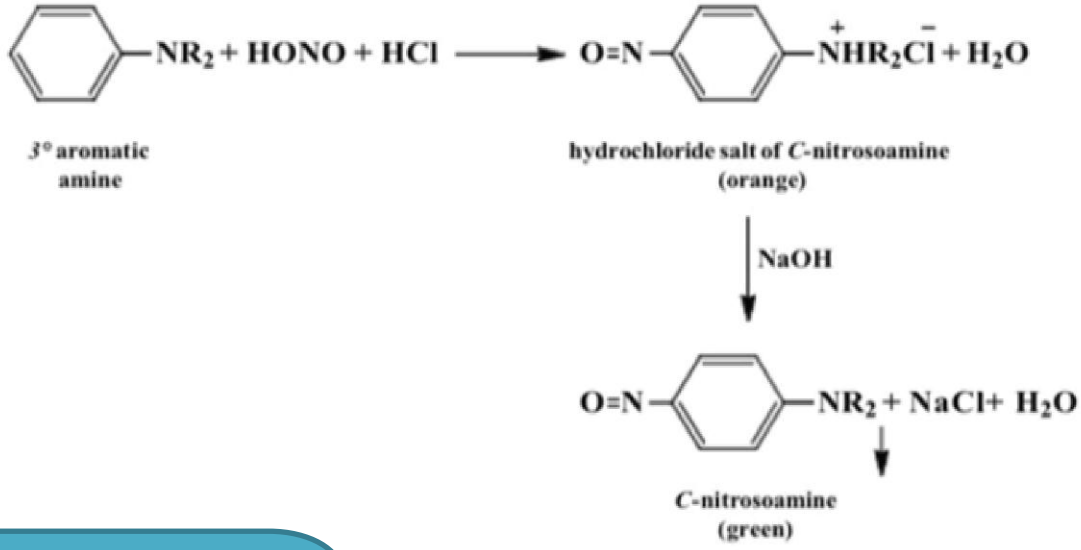


Secondary amines undergo a reaction with nitrous acid to form *N*-nitrosoamines, which are usually yellow oils or solids. These are carcinogenic compounds; therefore, *students are advised not to perform nitrous acid test for secondary amines*.



Tertiary aliphatic amines do not react with nitrous acid, but they form a soluble salt.

Tertiary aromatic amines react with nitrous acid to form the orange-coloured hydrochloride salt of the C-nitrosoamine. Treating the solution with base liberates the blue or green C-nitrosoamine.



Procedure

Nitrous acid is prepared instantaneously by the reaction of sodium nitrite and hydrochloric acid:

In a test tube dissolve 0.5 mL or 0.5 g of the amine in a mixture of 5.mL of concentrated hydrochloric acid and 2.5 mL of water, and cool the solution to 0°C in a beaker of ice. In another test tube dissolve 0.5 g of sodium nitrite in 2.5 mL of water, and add this solution drop wise, with shaking to the cold solution of the amine hydrochloride. Move 2 mL of the final solution to another test tube, warm gently, and examine for evolution of gas.

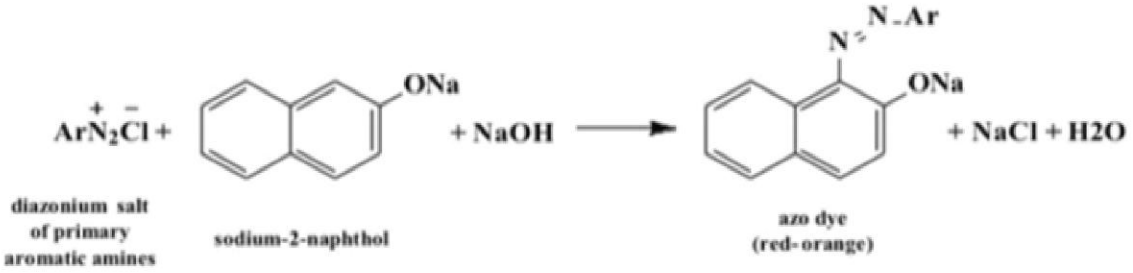
Results

- The observation of rapid bubbling or foaming as the aqueous sodium nitrite solution is added at 0°C indicates the presence of a *primary aliphatic amine*.
- The evolution of gas (bubbling) upon warming to room temperature indicates that the amine is a *primary aromatic amine*, and the solution should be subjected to the coupling reaction (test 3).
- If a pale yellow oil (heavier than water) or low-melting solid, which is the *N*-nitrosoamine, is formed with no evolution of gas, the original amine is a *secondary amine*.
- If a dark-orange solution or an orange crystalline solid is formed, which is the hydrochloride salt of the *C*-nitrosoamine, the amine is *tertiary aromatic*. Treating 2 mL of this solution with few drops of 10 % sodium hydroxide or sodium carbonate solution produces the bright-green or -blue nitrosoamine base.

- If only solubilization of the amine is obtained with no other results, the amine is *tertiary aliphatic*.

3. Coupling reaction.

(a test for primary aromatic amines).



diazonium salt of primary aromatic amines

sodium-2-naphthol

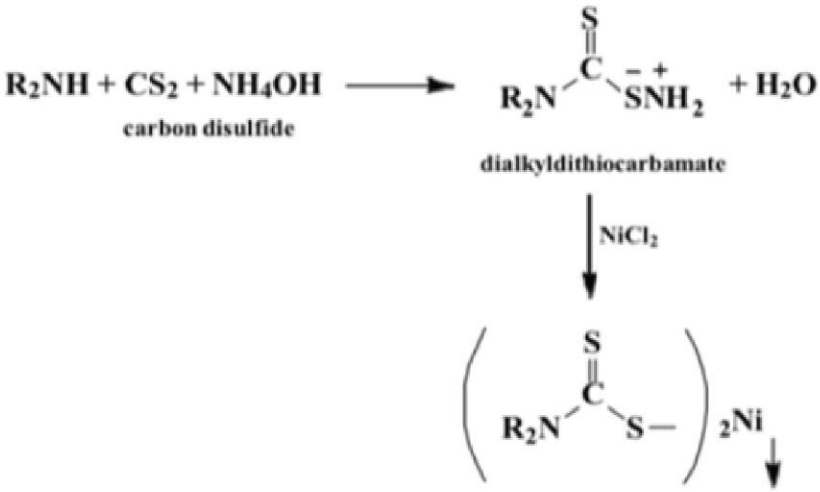
azo dye (red-orange)

Procedure

Dissolve 0.1 g of 2-naphthol in a mixture of 2 mL of 10 % sodium hydroxide solution and 5 mL distilled water. Add 2 mL of the cold diazonium solution and observe the result. The formation of a red- orange dye (red precipitate in case of phenol) with evolution of gas only upon warming indicates that the compound is a primary aromatic amine.

4. Carbon disulfide reagent test

(for secondary aliphatic amines).



Procedure

In a test tube dissolve 50 mg (1-2 drops) of the amine in 5 mL distilled water (or 1-2 drops of concentrated hydrochloric acid if necessary). In another test tube mix o.5- 1 mL of concentrated ammonia solution with 1 mL of nickel chloride in carbon disulfide reagent ($NiCl_2/CS_2$). Add 0.5- 1 mL from the first test tube to the second one. A definite precipitation indicates that the unknown is a secondary amine. A slight turbidity is an indication of a trace of a secondary amine as an impurity.

5. Lignin test *(for primary and secondary aromatic amines).*

This test depends on the action of lignin in the newsprint paper.

Procedure

Dissolve 10- 20 mg of the amine in a few drops of ethanol and moisten a small area of newsprint paper with this solution. Place 2 drops of 6 *N* hydrochloric acid on the moistened spot. The immediate development of a yellow or an orange colour is a positive test for a primary or secondary aromatic amine.