Synthesis and Spectral Studies of Substituted 2-Aminobenzenethiols
The current chapter throws light on synthetic procedures of substituted 2-aminobenzenethiols. The synthesis of 2-aminobenzenethiols involve either thiocyanogenation of substituted anilines (if the para position to amino group of substituted aniline is occupied) or the alkaline hydrolytic cleavage of substituted 2-aminobenzothiazoles which in turn were prepared by the cyclization of substituted phenylthioureas by bromine in acetic acid / chloroform (if para position to amino group of substituted aniline is unoccupied). These phenylthioureas were prepared by the treatment of substituted anilines with ammonium thiocyanate in hydrochloric acid.

The purity of the synthesized 2-aminobenzenethiols were checked by thin layer chromatography using silica gel "G" as adsorbent, in various non-aqueous solvent systems. Spectral analysis has been used for structural assignments of all the synthesized 2-aminobenzenethiols.
The chemistry of 2-aminobenzenethiols such as oxidation and reaction with π-deficient compounds has been utilized in the synthesis of several interesting products. Due to the adjacency of the –NH₂ and -SH groups, 2-aminobenzenethiols can readily forms a number of attractive heterocycles which can be biologically active. These bioactive heterocycles can be used to exploit chemical diversity and to create a drug like screening library from which possible leading candidates can be sort out.

It was known that the oxidation of thiol yields the corresponding disulphide, this conversion is the useful transformation and is of importance both from a biological and a practical point of view. Thus we have used 2-aminobenzenethiols as starting material to synthesize attractive thiazine scaffolds which are phenothiazines, benzothiazines and their corresponding derivatives as these are directly associated with important applications in everyday life such as pharmaceuticals, insecticides, pesticides etc.
Most of the methods for the preparation of 2-aminobenzenethiols either lack generality or are inefficient, giving low yields or hard to purify mixtures of products. Further, preparation and purification of these compounds is complicated by their inherent lack of stability. Different methods available in the literature used for the synthesis of 2-aminobenzenethiols are discussed in the succeeding sections:

1. **Herz Method**

   The condensation of substituted aromatic amines (a) (with occupied para position) with sulfur monochloride (b) results in the formation of thiazothiolum chloride (c; Herz compound) which on alkaline hydrolysis yields sodium salt of the corresponding 2-aminobenzenethiol.\(^1\text{-}^4\)

   The mechanism involves replacement of chlorine by hydroxyl group during hydrolysis of Herz compound\(^5\text{-}^6\) and opening of five membered ring in the presence of an alkali to produce sodium salt of 2-aminobenzenethiol (Scheme 2.1).
Scheme-2.1

Generally, sodium hydroxide is used to hydrolyse Herz compound (c) into respective 2-aminobenzenethiol but hydrolysis has also been carried out by sodium carbonate and sodium hydrogen sulphite.\(^7\)

The major drawbacks which make this method undesirable for present investigation are:
1. This method fails to synthesize desired 2-aminobenzenethiols from the aromatic amines having free para position, as it does chlorination at unoccupied para position. In an attempt Farrington and Warburton failed to isolate 2-aminobenzenethiol from aniline having free para position using Herz method because the formation of 2-amino-5-chlorobenzenethiol was favoured over 2-aminobenzenethiol. Similarly, Koning and Weinberg failed to obtain 2-amino-3-methylbenzenethiol from o-toluidine because 2-amino-5-chloro-3-methylbenzenethiol was favoured as product using Herz method. Therefore, in order to synthesize desired 2-aminobenzenethiols via this method, para-position of arylamines should remain occupied and that too by such groups which cannot be replaced by chlorine e.g. bromo, chloro, ethoxy, methoxy, dimethylamine, methyl, phenoxy etc. rather than groups like arsenic, nitro, sulfonic acid etc. which can be easily replaced by chlorine during the course of Herz reaction resulting undesired products.

2. Unsubstituted 2-aminobenzenethiol cannot be synthesized by this method.
3. In some cases, the hydrolysis of Herz compound remains unsuccessful.

2. **Reduction of bis-(o-nitrophenyl) disulfides**

   This is a two step method:

   1. First step is characterized by reaction of substituted o-halonitrobenzenes with sodium polysulfide\(^{16}\) (obtained from the reaction of sodium sulfide nonahydrate and sulfur) to produce bis-(o-nitrophenyl) disulfides.

   2. Second step involves reduction of above synthesized bis-(o-nitrophenyl) disulfides with tin and hydrochloric acid or zinc and acetic acid to produce hydrochloride or zinc salt of 2-aminobenzenethiols (Scheme-2.2).

"Scheme-2.2"
Several workers in due course of time reported preparation of substituted 2-aminobenzenethiols using this method. Onda et al.\textsuperscript{17} synthesized the zinc salt of 2-amino-4-bromobenzenethiol, but they could not isolate free amine. Hodgson and Wilson\textsuperscript{18} reported the synthesis of sodium salt of 2-amino-4-chlorobenzenethiol by the direct reaction of 2,5-dichloronitrobenzene with sodium disulfide in water, but the compound was not analysed. Later, the formation of same compound was reported by the reduction of diphenyldisulfide derivative with zinc and acetic acid by Pollack and coworkers.\textsuperscript{19} Lankelma and Knauf\textsuperscript{20} reduced diphenyldisulfide derivatives by tin and hydrochloric acid and found that free amine was readily oxidised by air. Cauquil \textit{et al.}\textsuperscript{21,22} prepared the sodium salt of 2-amino-4-bromobenzenethiol by reduction of 2,5-dibromonitrobenzene with sodium disulfide.

This method too has some major limitations which reduced our interest toward its utilization in present research. The limitations faced by this method are:

(i) Due to the presence of metallic chloride it is difficult to isolate substituted 2-aminobenzenethiols from them instead of the fact
that substituted 2-aminobenzenethiol hydrochlorides are formed in high yield.

(ii) Nitro substituted 2-aminobenzenethiols can not be obtained via this method because during the reduction of diphenyl derivative in the second step nitro group too get reduced into amino group.

(iii) Desired substituted $o$-halonitrobenzenes are not commercially available so they have to be prepared in the laboratory which is a tedious and time consuming task.

3. Thiocyanogenation

This method involves thiocyanogenation of arylamines which results in the production of 2-aminobenzothiazoles. Thiocyanogen gas which is generated in situ by the reaction of cupric chloride and sodium thiocyanate or bromine and ammonium/potassium thiocyanate$^{23-26}$ carried out thiocyanogenation. Lastly, on alkaline hydrolysis 2-aminobenzothiazoles yields 2-aminobenzenethiols$^{27}$ (Scheme 2.3).
Like Herz method, arylamines having unoccupied para position to an amino group cannot synthesize 2-aminobenzenethiols via this method too because thiocyanogenation simultaneously occurs at both ortho and para positions to amino group during the reaction. Therefore, only those arylamines which have a substitute at para position can produce 2-aminobenzenethiols by the hydrolytic cleavage of 2-aminobenzothiazoles.
As this method has lesser limitations rather than other reported methods hence in the present investigation it is used to synthesize substituted 2-aminobenzenethiols with occupied para position to amino group. Still the problem looms to synthesize 2-aminobenzenethiols having free para position to the amino group in a good yield.

Therefore, a modified method has been employed which involves following steps:

1. The first step involves the reaction of arylamine 1(a-b) with ammonium thiocyanate in hydrochloric acid to form phenylthioureas 2(a-b).

2. In second step, subsequent cyclization of phenylthioureas 2(a-b) by bromine in chloroform takes place to produce 2-aminobenzothiazoles 3(a-b). Further on alkaline hydrolysis followed by neutralization with glacial acetic acid these substituted 2-aminobenzothiazoles result in the formation of corresponding 2-aminobenzenethiols\textsuperscript{28-58} 4(a-b) (Scheme 2.4).
This method proved to be one of the best methods for the synthesis of substituted 2-aminobenzenethiols with free para-position to the amino group.

In the present work, 2-amino-3-chlorobenzenethiol (4a) and 2-amino-3-flouro-6-methylbenzenethiol (4b) have been synthesized (using this method) by alkaline hydrolysis of 2-amino-4-
chlorobenzothiazole (3a) and 2-amino-4-flouro-7-methylbenzothiazole (3b) respectively which in turn, was prepared by the cyclization of their corresponding phenylthioureas (2-Chlorophenylthiourea (2a) and 2-Flouro-5-methylphenylthiourea (2b) respectively) by bromine in chloroform. These phenylthioureas (2a-b) were in turn, synthesized by the treatment of 2-chloro aniline (1a) and 2-flouro-5-methyl aniline (1b) respectively with ammonium thiocyanate in hydrochloric acid.

**Experimental**

All the melting points were determined in open capillary tubes and are uncorrected. IR spectra were recorded in KBr and CCl₄ on SHIMADZU 8400 S FT-IR spectrophotometer. ¹H NMR spectra were measured on JEOL AL-300 FT NMR spectrometer in CDCl₃/DMSO-d₆ at an frequency of 300.40 MHz using TMS as an internal standard (chemical shifts are measured in δ ppm). Mass spectra were obtained on JEOL SX 102 / DA-600 using Argon/Xenon as FAB gas. The purity of compounds were checked by TLC using silica gel "G" as adsorbent in various non aqueous solvent systems and visualizing these by UV light or in an Iodine chamber. Elemental analysis of these compounds was also done.
(A) Preparation of 2-aminobenzothiazole

(i) Synthesis of substituted phenylthiourea 2(a-b)

In a 250 ml R.B flask 0.1 mole of substituted aniline [2-chloro aniline (1a) / 2-flouro-5-methyl aniline (1b)] and a mixture of concentrated hydrochloric acid (9ml) and water (25ml) were taken and fitted with a reflux condenser. The contents were heated for about half an hour till solution of aniline hydrochloride was formed. Then, it was cooled down to room temperature and 0.1 mole of ammonium thiocyanate was added. The reaction mixture was refluxed for 4-5 hours. The solid separated out on cooling, was filtered, washed with water, dried and crystallized from ethanol. The physical and analytical data of synthesized substituted phenylthiourea 2(a-b) is summarized in Table 2.1.

(ii) Synthesis of substituted 2-aminobenzothiazole 3(a-b)

In a two necked 500 ml R.B. flask containing 100 ml chloroform and equipped with a mechanical stirrer and dropping funnel 0.1 mole of synthesized substituted phenylthiourea 2(a-b) was taken. Bromine (0.1 mole) in chloroform (100 ml) was added dropwise to this reaction mixture with constant stirring over a period of 45 minutes and the temperature was maintained below 5°C. After complete addition of bromine solution, the stirring was continued for a period of 4 hours.
The reaction mixture was then refluxed till the evolution of hydrogen bromide vapours ceased (about 4 hrs.). Resulting solid was dried, treated with sulfur dioxide water and filtered. The filtrate was neutralized with aqueous ammonia and the precipitate obtained was filtered, washed well with water and crystallized from ethanol. The physical and analytical data of 2-aminobenzothiazole 3(a-b) is summarized in Table 2.2.

(B) Preparation of 2-aminobenzothiazoles 3(c-e) in single step for para substituted aniline (Thiocyanogenation)

In a two necked round bottom flask equipped with a mechanical stirrer and dropping funnel mixture of 0.1 mole of substituted aniline 1(c-e) and 0.2 mole of ammonium thiocyanate in glacial acetic acid (100 ml) was taken. To this mixture bromine (0.1 mole) in acetic acid was added dropwise with stirring for a period of two hours. The temperature of the reaction mixture was maintained below 5°C. After complete addition of bromine, the stirring was kept continuous for a period of three hours. Solid separated out was filtered and dried. The resulting solid was dissolved in hot water and filtered. Filtrate was neutralized with sodium carbonate solution. The precipitate obtained was filtered, washed well with water, dried and crystallized from
ethanol (Scheme 2.5). The physical and analytical data of substituted 2-aminobenzothiazoles 3(c-e) are summarized in Table-2.2.

By thiocyanogenation, 2-amino-6-methylbenzothiazole (3c), 2-amino-4-bromo-6-methylbenzothiazole (3d) and 2-amino-6-(4’-chloro)phenoxybenzothiazole (3e) had been synthesized, which on alkaline hydrolysis, gave 2-amino-5-methylbenzenethiol (4c), 2-amino-3-bromo-5-methylbenzenethiol (4d) and 2-amino-5-(4’chloro)phenoxybenzenethiol (4e) respectively.

(C) Preparation of substituted 2-aminobenzenethiols 4(a-e)

In a 500 ml R.B. flask, a mixture of substituted 2-aminobenzothiazole (3a-e; 0.1 mole), potassium hydroxide (5 times by
weight of 2-aminobenzothiazole) and water (10 times by weight of 2-aminobenzothiazole) were taken and refluxed until the evolution of ammonia gas ceased (about 25-30 hours). The contents were filtered, diluted with ice cold water and neutralised with acetic acid with vigorous stirring. The temperature of the solution was maintained below 5°C otherwise a decomposed greenish mass is formed instead of 2-aminobenzenethiol (Scheme 2.4 & 2.5). After complete neutralization, the yellowish precipitate was obtained which, in turn, was extracted 2-3 times with solvent ether. Etheral layer on evaporation afforded yellow solid mass, which on recrystallization from ethanol yielded desired 2-aminobenzenethiol 4(a-e). The physical and analytical data of substituted 2-aminobenzenethiols are summarized in Table 2.3.

All the synthesized substituted 2-aminobenzenethiols are listed below:

4 a  2-amino-3-chlorobenzenethiol

4 b  2-amino-3-flouro-6-methylbenzenethiol

4 c  2-amino-5-methylbenzenethiol

4 d  2-amino-3-bromo-5-methylbenzenethiol

4 e  2-amino-5-(4’chloro)phenoxybenzenethiol
Spectral Analysis

Infrared Spectra

All the synthesized substituted 2-aminobenzenethiols exhibit two sharp peaks due to stretching vibrations of primary amino group in the region 3480-3462 cm\(^{-1}\) and 3240-3220 cm\(^{-1}\). Due to S–H stretching vibrations a weak band is observed in the region 2588-2570 cm\(^{-1}\). Compounds 4(b-d) show two bands due to asymmetric and symmetric stretching vibrations of CH\(_3\) group in the region 2951-2923 cm\(^{-1}\) and 2868-2850 cm\(^{-1}\) respectively. In compounds 4b, 4a&c and 4d a band due to C-F, C-Cl and C-Br is observed in the region 1244 cm\(^{-1}\), 746-735 cm\(^{-1}\) and 615 cm\(^{-1}\) respectively. Compound 4e exhibited two peaks at 1288 cm\(^{-1}\) and 1192 cm\(^{-1}\) which can be assigned to C-O-C asymmetric and symmetric stretching vibrations. The infrared spectral data of the synthesized substituted 2-aminobenzenethiols 4(a-e) are summarized in Table 2.4.

\(^1\)H NMR Spectra (Nuclear Magnetic Resonance Spectra)

All synthesized substituted 2-aminobenzenethiols exhibit singlet at \(\delta\) 4.36-4.22 ppm due to NH\(_2\) protons. The singlet observed at \(\delta\) 1.55-1.38 ppm is attributed to SH proton. Multiplet due to aromatic protons appeared in the region \(\delta\) 7.28-6.26 ppm. Compounds 4(b-d) exhibit a
singlet at $\delta$ 2.37-2.23 ppm due to CH$_3$ protons. The $^1$H NMR spectral data of synthesized substituted 2-aminobenzenethiols (4a-e) are summarized in Table 2.5.

**Mass spectra**

The molecular ion peaks are observed in accordance with the molecular weights.
REFERENCES

1. Cassella and Co., Ger. Pat., (i) 367, 346; Frdl., 14, 918 (1922), (ii) 367, 345; Frdl., 14, 914 (1922), (iii) 367, 344; Frdl., 14, 912 (1922), (iv) 364, 822; Frdl., 14, 920 (1922).


11. W. Koning, Ber., 61, 2067 (1928).
Table 2.1: Physical and analytical data of substituted phenylthiourea 2(a-b)

![Chemical Structure]

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Table 2.2: Physical and analytical data of substituted 2-aminobenzothiazoles 3(a-e)

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Table 2.3: Physical and analytical data of substituted 2-aminobenzenethiols 4(a-e)

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Table 2.4: Infrared spectral data of substituted 2-aminobenzenethiols 4(a-e) (in cm\(^{-1}\))

\[
\begin{align*}
\text{A} &= \text{NH}_2 \text{ asymmetric and symmetric stretching vibrations.} \\
\text{B} &= \text{S-H stretching vibrations.} \\
\text{C} &= \text{C-H asymmetric and symmetric stretching vibrations of CH}_3 \text{ group.} \\
\text{D} &= \text{C-F stretching vibrations} \\
\text{E} &= \text{C-Cl stretching vibrations} \\
\text{F} &= \text{C-Br stretching vibrations} \\
\text{G} &= \text{C-O-C stretching vibrations} \\
\end{align*}
\]

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<th>S. No.</th>
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<th>B</th>
<th>C</th>
<th>D</th>
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\[
\begin{align*}
\text{A} &= \text{NH}_2 \text{ asymmetric and symmetric stretching vibrations.} \\
\text{B} &= \text{S-H stretching vibrations.} \\
\text{C} &= \text{C-H asymmetric and symmetric stretching vibrations of CH}_3 \text{ group.} \\
\text{D} &= \text{C-F stretching vibrations} \\
\text{E} &= \text{C-Cl stretching vibrations} \\
\text{F} &= \text{C-Br stretching vibrations} \\
\text{G} &= \text{C-O-C stretching vibrations} \\
\end{align*}
\]
Table 2.5: $^{1}$H NMR spectral data of substituted 2-aminobenzenethiols 4(a-e) (δ ppm)

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