CHAPTER-2

SYNTHESIS AND CHARACTERIZATION OF
SUBSTITUTED-2-AMINO BENZENETHIOLS
AND 4-AMINO-1,2,4-TRIAZOLE-3-THIOLS
PART-A

SYNTHESIS AND CHARACTERIZATION OF
SUBSTITUTED-2-AMINOBNENZENETHIOLS
The Current chapter is focused on the synthetic methodology of substituted 2-aminobenzothiazoles and 2-aminobenzenethiols. Synthetic procedure involves the synthesis of 2-aminobenzenethiols from 2-aminobenzothiazoles. The latter were prepared by treatment of substituted aniline with potassium thiocyanate and bromine in glacial acetic acid.

The structure of all the synthesized 2-aminobenzenethiols have been established on the basis of spectroscopic data.
Wide spread applications of benzothiazines, triazolothiadiazines and phenothiazines in medicinal, industrial, biological and agricultural fields have stimulated our interest to synthesize 2-aminobenzothiazoles and 2-aminobenzenethiols which have been used as synthetic intermediates for the synthesis of a variety of pharmacologically important heterocyclic compounds. The aryl pharmacophore of benzenethiols and substituted triazolothiols exhibits a wide range of biological and pharmacological activities, such as anticonvulsant, antituberculosis, antiproferative, antitumor, antimicrobial, analgesic, vasodilator etc.\textsuperscript{1-16}.

In the present investigation we have synthesized a number of 2-aminobenzothiazoles and 2-aminobenzenethiols. The various methods have been reported in the literature for the synthesis of these compounds. Some important methods have been presented briefly:

(1) **HERZ METHOD**

Richard Herz\textsuperscript{17} has reported a method for the preparation of 2-aminobenzenethiols, which is now known as Herz reaction. In this
method aryl amine (I) was treated with sulfur monochloride (II) to afford thiazathiolium chloride (III) (which is also called as Herz compound\textsuperscript{18}), which on alkaline hydrolysis provides sodium salt of 2-aminobenzenthiol. In this method, the replacement of chloride ion by hydroxyl group is followed by the cleavage of five membered ring of intermediate (IV) during hydrolysis to yield sodium salt of 2-aminobenzenethiols\textsuperscript{19-23} (V) (scheme 2.1).

For the hydrolysis of Herz compound a number of methods have been reported, but sodium hydroxide is normally used. Hydrolysis by making alkaline with sodium carbonate and subsequent heating with sodium hydrogen sulphite have also furnished good results. In some cases the Herz compound was first converted into corresponding hydroxide\textsuperscript{24} and then subjected to hydrolysis after recrystallization.
The Herz reaction has some limitations because it has been noted that anilines which are unsubstituted in para-position undergo chlorination at para-position by sulphur monochloride during the course of reaction. This is the reason that Farrington and Warburton failed to isolate o-aminothiophenol from aniline by the Herz reaction, but obtained only 2-amino-5-chlorothiophenol (scheme 2.2).
Koing and Weinberg were also unsuccessful in preparing 2-amino-3-methylbenzenethiol but obtained 2-amino-5-chloro-3-methylbenzenethiol (scheme 2.3).

Therefore, the preparation of 2-aminobenzenethiols by Herz method, requires the para-position of arylamine to be occupied by such a group which cannot be substituted by chloro group. The chloro group does not replace the group such as ethoxy, phenoxy, methyl, methoxy, dimethylamino, bromo etc. during Herz reaction. However, some groups such as sulfonic acid, arsonic, carbonyl etc. at 5-position are relatively replaced\(^\text{26}\).

**(2) THIOCYANOGENATION**

Another widely used method for the preparation of 2-aminobenzenethiol includes the hydrolytic cleavage of benzothiazoles. This method also has some limitations when para position in aniline is free. The thiocyanogenation at both ortho and para position to the amino
group during the course of reaction is the serious drawback of this method. In some cases intermediates do not undergo cyclisation (scheme 2.4).

(Scheme: 2.4)

(3) REDUCTION OF BIS-(o-NITROPHENYL) DISULFIDES

It involves two steps. In the first step, bis-(o-nitrophenyl) disulfides is obtained by the reaction of halonitrobenzene with sodium polysulfide. The second step involves the reduction of bis-(o-nitrophenyl) disulfides with zinc and acetic acid or zinc and
hydrochloric acid to provide zinc salt of 2-aminobenzenethiol\textsuperscript{27-31} (scheme 2.5).

\[
\begin{align*}
\text{R} & \quad \text{NO}_2 \\
\text{S} & \quad \text{Na}_2\text{S.9H}_2\text{O} \\
\text{S} & \quad \text{Zn/HCl} \quad \text{or} \quad \text{Zn/AcOH} \\
\text{R} & \quad \text{NH}_3^+\text{Cl}^- \\
\end{align*}
\]

(Scheme: 2.5)

The reduction of diphenyl sulphides has also been reported with Sn/HCl\textsuperscript{32-34} and In/NH\textsubscript{4}Cl in ethanol\textsuperscript{35} (scheme 2.6).

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{NO}_2 \\
\text{S} & \quad \text{Na}_2\text{S.9H}_2\text{O} \\
\text{S} & \quad \text{Sn/HCl} \quad \text{or} \quad \text{In/NH}_4\text{Cl} \\
\text{F}_3\text{C} & \quad \text{NH}_2 \\
\end{align*}
\]

(Scheme: 2.6)
This method cannot be applied for the synthesis of nitroderivatives of 2-aminobenzenethiols because of simultaneous reduction of the nitro group during reduction of disulphide derivative into o-aminobenzenethiol.

(4) HYDROLYSIS OF 2-AMINOBENZOTHIAZOLES

This method involves two steps. In the first step substituted aminobenzothiazole is prepared and than the latter hydrolysed to get 2-aminobenzenethiol. Various methods are reported for synthesis of 2-aminobenzothiazoles out of which some important are discussed here.

(a) Synthesis of 2-aminobenzothiazoles

(i). 2-Aminobenzothiazoles have been prepared\(^\text{36}\) by treating cyclohexanone with thiourea and iodine at 100° C (scheme 2.7).

(ii). In recently used method\(^\text{37}\), benzene thiourea derivative on treatment with bromine and chloroform in ice cold solution followed by neutralization with sulphurous acid and ammonia solution provide 2-aminobenzothiazole (scheme 2.8).
(iii). Jordan et.al have been prepared 2-aminobenzothiazoles in quantitative yields by using organic ammoniumtribromide (OATB) (benzyltrimethyl-ammonium tribromide) as an alternative electrophilic bromine source in place of bromine and chloroform\textsuperscript{38} (scheme 2.9).

\[
\text{R}^+ \text{NH} - \text{C} = \text{NH}_2 \xrightarrow{\text{OATB} (1 \text{ mole equiv}) \text{ AcOH}} \text{R}^+ \text{S} - \text{C} - \text{NH}_2 \text{NH}_2^- \text{HBr}
\]

(Scheme: 2.9)
(iv). Huang et al. have been prepared 2-aminobenzothiazoles recently by means of copper and palladium-catalyzed intramolecular C-S bond formation\(^{39}\) (scheme 2.10).

(Scheme: 2.10)

(b) **Hydrolysis of 2-aminobenzothiazoles**

Synthesized 2-aminobenzothiazoles were hydrolysed to 2-aminobenzenethiol in second step by aqueous potassium hydroxide.

(Scheme: 2.11)

(5) **OTHER METHODS**

There are some other methods reported recently for synthesis of 2-aminobenzenethiols as explained by schemes (2.12)\(^{40}\) and (2.13)\(^{41}\)

(Scheme: 2.12)
In the present investigation, a modified method having two steps instead of time consuming and low yielding three step\textsuperscript{42} method is used for the synthesis of 2-aminobenzenethiols required for the synthesis of 1,4-benzothiazine and phenothiazine derivatives.

**EXPERIMENTAL**

All the melting points are uncorrected. The purity of the compounds was checked on thin layer of silica gel in various non-aqueous solvent systems. Infrared spectra of all the synthesized compounds have been scanned in KBr on Shimadzu FTIR Affinity-1 and their NMR spectra scanned on Varian Gemini 400 spectrometer (300 MHz) using TMS as an internal standard.

1. **Preparation of substituted 2-aminobenzothiazoles**

A mixture of potassium thiocyanate (60 mmol) and substituted aniline (60 mmol) was added to a precooled (5\(^\circ\)C) glacial acetic acid (125 ml) and placed into freezing mixture. Now a bromine solution (20 mmol Br\(_2\) in 20 ml glacial acetic acid) was added drop by drop with
constant stirring so that temperature does not rise above 5°C and continue the stirring for additional 2.5 h. The separated out solid hydrochloride salt was filtered, washed with 5 ml acetic acid and dried. The hydrochloride salt was dissolve in hot water and neutralized with ammonia solution. Finally the solid was filtered, washed with water and crystallized to get substituted 2-aminobenzothiazole.

2. Preparation of 2-aminobenzenethiol

Substituted 2-aminobenzothiazole was refluxed with an aqueous solution of potassium hydroxide (5 times by weight of benzothiazole) until evolution of ammonia ceased. The refluxed solution was neutralized with glacial acetic acid. The separated yellowish semisolid 2-aminobenzenethiol was extracted with solvent ether. The evaporation of solvent ether and crystallization from methanol afforded the desired 2-aminobenzenethiol (scheme 2.14).

![Scheme: 2.14](image-url)
In present investigation following 2-aminobenzenethiols have been synthesized:

1. 2-Amino-5-chlorobenzenethiol
2. 2-Amino-5-methylbenzenethiol
3. 2-Amino-5-methoxybenzenethiol
4. 2-Amino-5-ethoxybenzenethiol
5. 2-Amino-5-bromobenzenethiol

Physical and spectral data of the synthesized 2-aminobenzenethiols

(1). 2-Amino-5-chlorobenzenethiol

Molecular Formula : C₆H₆NSCl

Yield : 35%, M.P. 110°C

IR (KBr, ν max, cm⁻¹) : 3350, 3295 (N-H str.), 2470 (S-H str.), 735 (C-Cl str.).

¹H NMR (CDCl₃) δ : 7.15-6.75 (3H, m, Ar-H), 4.35 (2H, s, NH₂), 2.75 (1H, s, SH).
(2). 2-Amino-5-methylbenzenethiol

Molecular Formula : C$_7$H$_9$NS

![Molecule structure](attachment:2-Amino-5-methylbenzenethiol.png)

Yield : 62%, M.P. 90-92$^\circ$C.

IR (KBr, $\nu_{max}$, cm$^{-1}$) : 3420, 3340 (N-H str.), 2510 (S-H str.), 1420, 1360 (C-H bending).

$^1$H NMR (CDCl$_3$) $\delta$ : 7.25-6.65 (3H, m, Ar-H), 4.30 (2H, s, NH$_2$), 2.30 (3H, s, CH$_3$), 2.50 (1H, s, SH).

(3). 2-Amino-5-methoxy benzenethiol

Molecular Formula : C$_7$H$_9$NOS

![Molecule structure](attachment:2-Amino-5-methoxy benzenethiol.png)

Yield : 55% , M.P. 105$^\circ$C.

IR (KBr, $\nu_{max}$, cm$^{-1}$) : 3365-3285 (N-H str.), 2370 (S-H str.), 1410, 1350 (C-H bending), 1270 (O-C str.).

$^1$H NMR (CDCl$_3$) $\delta$ : 7.35-6.90 (3H, m, Ar-H), 4.65 (2H, s, NH$_2$), 3.50 (3H, s, CH$_3$), 2.30 (1H, s, SH).
(4).  2-Amino-5-ethoxy benzenethiol

Molecular Formula : C₈H₁₁NOS

Yield : 45%, M.P. 104°C
IR (KBr, \( \nu_{\text{max}}, \text{cm}^{-1} \)) : 3350-3285 (N-H str.), 2345 (S-H str.), 1400-1370 (C-H bending), 1310 (O-C str.).
\(^1\)H NMR (CDCl₃) : 7.25-6.85 (3H, m, Ar-H) 4.55 (2H, s, NH₂), 3.80 (2H, q, CH₂ at C₅), 1.35 (3H, t, CH₃ at C₅) 2.25 (1H, s, SH).

(5).  2-Amino-5-bromobenzenethiol

Molecular Formula : C₆H₆NSBr

Yield : 32%, M.P. 111-113°C
IR (KBr, \( \nu_{\text{max}}, \text{cm}^{-1} \)) : 3400, 3290 (N-H str.), 2475 (S-H str.), 810 (C-Br str.).
\(^1\)H NMR (CDCl₃) : 7.30-6.80 (3H, m, Ar-H), 4.45 (2H, s, NH₂), 2.85 (1H, s, SH).
SPECTRAL ANALYSIS

The structures of synthesized substituted 2-aminobenzenethiols have been confirmed by spectral analysis. In IR spectra, two sharp bands in the region 3450-3300 cm\(^{-1}\) and 3330-3240 cm\(^{-1}\) are assigned to asymmetric and symmetric vibrations of primary amino group respectively. Weak band due to S-H stretching vibration is observed in the region 2450-2530 cm\(^{-1}\). The IR bands due to C-Cl, C-Br are observed at 735 and 810 cm\(^{-1}\) respectively.

\(^1\)H NMR spectra of synthesized compounds exhibits singlet at \(\delta\) 4.30-4.70 due to NH\(_2\) protons. Multiplet due to aromatic protons appeared in the region \(\delta\) 7.50-6.60. The singlet observed at \(\delta\) 2.25-2.85 is attributed to SH proton.
Fig. 1: IR spectrum of substituted-2-aminobenzethiol
Fig. 2: $^1$H NMR spectrum of substituted-2-aminobenzenethiol
REFERENCES


25. W. Koing, Ber., 61, 2067 (1928).
PART-B

SYNTHESIS AND CHARACTERIZATION OF 4-AMINO-1,2,4-TRIAZOLE-3-TIOLS
This chapter deals with synthesis and spectral studies of 4-amino-1,2,4-triazole-3-thiol. Triazolothiols have been prepared by environmentally benign solvent free method using microwave irradiation.

The purity of synthesized compounds has been checked by thin layer chromatography. IR and NMR spectral studies have also been included.
Heterocycles bearing a symmetrical triazole or 1,2,4-triazole scaffold are the structural element of many drugs that have diverse pharmacological activities. The triazole nucleus is an important part of the therapeutically interesting drugs. The 1,2,4-triazole derivatives are being used extensively in medicine, namely alprazolam (tranquilizer), estazolam (hypnotic, sedative, and tranquilizer), rilmazafone (hypnotic, anxiolytic, used in the case of neurotic insomnia), benatradin (diuretic), trapidil (hypotensive), trazodone (antidepressant, anxiolytic), etoperidone (antidepressant), nefazodone (antidepressant, 5-HT2A-antagonist), anastrozole (antineoplastic, nonsteroidal aromatase inhibitor), letrozole (antineoplastic, aromatase inhibitor), ribavirin (antiviral), fluconazole, itraconazole, terconazole (antifungal), and so forth\(^1\).

The biological profile of triazole derivatives is very extensive\(^2-4\). Compounds bearing a symmetrical triazole moiety are reported to show a broad spectrum of pharmacological activities such as antibacterial\(^5-8\), antifungal\(^9-15\), antimicrobial\(^16-20\), antimycobacterial\(^21-22\), antioxidant\(^23\),
analgesic\textsuperscript{24-25}, antipyretic\textsuperscript{26}, anticancer\textsuperscript{27-32}, anticonvulsant\textsuperscript{33-34}, antiinflammatory\textsuperscript{35-39}, CNS stimulants, sedatives, antianxiety etc.

In addition to these important biological applications, mercapto-1,2,4-triazoles have been reported to have their importance in the preparative organic chemistry and have been used to synthesize structurally diverse therapeutically interesting compounds such as, triazolothiadiazines and triazolobenzothiadiazines.

In the present investigation we have synthesized the intermediate 5-substituted-4-amino-1,2,4-triazole-3-thiols required for synthesis of thiadiazine derivatives. Different synthetic methods have been reported in the literature for the synthesis of 5-substituted-4-amino-1,2,4-triazole-3-thiol. Some recently reported important methods have been presented briefly.

(1) **FROM 2-MERCAPTO-1,3,4-OXADIAZOLES**

5-Substituted-4-amino-1,2,4-triazole-3-thiols were prepared by the reaction of 5-substituted-2-mercapto-1,3,4-oxadiazoles with hydrazine hydrate. The reaction is considered to proceed\textsuperscript{40-43} with the recyclization of 5-substituted-1,3,4-oxadiazole-2-thiol (scheme 2.15).
(2) FROM THIOCARBOHYDRAZIDES

The condensation of thiocarbohydrazides with aliphatic and aromatic carboxylic acids is the widely used method\textsuperscript{44-48} for the preparation of 5-alkyl/aryl-4-amino-1,2,4-triazole-3-thiols. The reaction was improved by using carboxylic acids at their melting points (scheme 2.16).

(Scheme: 2.15)

(3) FROM CARBOXYLIC ACID HYDRAZIDES

In this method, the condensation of carboxylic acid hydrazides with carbon disulphide in ethanolic KOH yields potassium-3-aryldithiocarbazates and the latter was directly converted to 4-amino-1,2,4-triazole-3-thiol by the reaction with an excess of hydrazine\textsuperscript{49}. The methylation of 3-aryldithiocarbazates with methyl iodide provided the
S-alkylated derivatives that also cyclised to 4-amino-1,2,4-triazole-3-thiol with hydrazine (scheme 2.17).

The increasing importance of 1,2,4-triazoles as agrochemicals inspired us to synthesize a new series viz 5-substituted-4-amino-1,2,4-triazole-3-thiol. In the present investigation entirely new solvent free environment friendly microwave assisted method is used for the synthesis of substituted 4-amino-1,2,4-triazole-3-thiols. The conventional method is also used to compare the results.

**EXPERIMENTAL**

Melting points of all the synthesized compounds were determined on open aluminum block and are uncorrected. Purity was checked by thin layer chromatography using Merck silica gel G-60. IR spectra were recorded in KBr on Shimizu Affinity-1 FTIR spectrophotometer. $^1$H
NMR spectra were recorded on Varian Gemini 400 spectrometer (300 MHz) using TMS as an internal standard.

**CONVENTIONAL METHOD**

1. **Synthesis of Arylhydrazides**

   Hydrazine hydrate (10 mmol) was added to the esters of substituted aromatic acids (10 mmol) and refluxed the solution for 30 min. To the refluxing mixture, 20 ml of ethanol was added as a solvent in order to homogenize the contents. The resulting mixture was further allowed to reflux for 6 hrs. Excess ethanol was distilled out and the contents were allowed to cool. The crystals formed were filtered, washed thoroughly with water and dried.

2. **Synthesis of 5-(4-Substitutedphenyl)-1,3,4-oxadiazole-2-thiols**

   To a solution of aryl hydrazide 1 (10 mmol) in ethanol (30 ml), potassium hydroxide (10 mmol) in absolute ethanol (50 ml) and carbon disulfide (20 mmol) were added and refluxed for about 5 hrs. till evolution of hydrogen sulfide ceased. The reaction mixture was cooled at room temperature and diluted with water. On acidification with dilute hydrochloric acid, the required oxadiazole derivative was precipitated out. It was filtered, washed thoroughly with cold water and recrystallized from ethanol.
3. **Synthesis of 4-Amino-1,2,4-triazole-3-thiols**

A mixture of compound 2 (10 mmol) and hydrazine hydrate (10 mmol) in dry pyridine (15 ml) was refluxed for about 4 hrs. The reaction mixture was cooled at room temperature and neutralized with dilute hydrochloric acid. The solid precipitated out was filtered, washed thoroughly with cold water and recrystallized from ethanol (scheme 2.18).

![Chemical structure](image)

(Scheme: 2.18)

**MICROWAVE ASSISTED METHOD**

4-Amino-5-substituted-1,2,4-triazole-3-thiols were prepared in three steps by new environmentally benign solvent free methods using microwave irradiation. The conventional methods for synthesis of these intermediates require hazardous chemicals like pyridine etc and long heating systems. The yield obtained from microwave methods was better as compared to conventional method.
1. **Synthesis of Arylhydrazides**

   A mixture of esters of substituted aromatic acids (10 mmol) and hydrazine hydrate (10 mmol) exposed to microwave irradiations intermittently at 30 seconds for four minutes in microwave oven. After completion of reaction, the contents were allowed to cool at room temperature. The crystals separated out were filtered, washed thoroughly with water and dried to get aryl hydrazide (I).

2. **Synthesis of 5-(4-Substitutedphenyl)-1,3,4-oxadiazole-2 thiols**

   A mixture of aryl hydrazide I (10 mmol) and potassium hydroxide (10 mmol) was well grinded to make a fine homogeneous powder. To this powder carbondisulfide (20 mmol) was added and exposed to microwave irradiations intermittently at 20 seconds for two minutes. The reaction mixture was cooled and neutralized with dilute hydrochloric acid. The solid separated out on neutralization was filtered, washed with cold water and dried. There is no need to purify the product 1,3,4-oxadiazole-2-thiol derivatives (II) for further reaction.

3. **Synthesis of 4-Amino-1,2,4-triazole-3-thiols**

   A mixture of compound 2 (10 mmol) and hydrazine hydrate (10 mmol) was exposed to microwave irradiations intermittently at 30 seconds for 4.5 minutes. After completion of reaction as monitored by
TLC, the hot reaction mixture was cooled at room temperature and neutralized with dilute hydrochloric acid. The solid separated out was filtered, washed thoroughly with water and crystallized from ethanol (scheme 2.19).

Following 4-amino-1,2,4-triazole-3-thiols have been synthesized

1. 4-Amino-5-(4-methoxyphenyl)-1,2,4-triazole-3-thiol
2. 4-Amino-5-(4-flurophenyl)-1,2,4-triazole-3-thiol
3. 4-Amino-5-(4-chlorophenyl)-1,2,4-triazole-3-thiol
4. 4-Amino-5-(4-bromophenyl)-1,2,4-triazole-3-thiol
5. 4-Amino-5-(4-nitrophenyl)-1,2,4-triazole-3-thiol
(1). 4-Amino-5-(4-methoxyphenyl)-1,2,4-triazole-3-thiol

Molecular Formula: C₉H₁₀N₄OS

Yield: 68%, M.P. 204 °C.

IR (KBr, νmax, cm⁻¹): 3335, 3280 (N-H), 2570 (S-H), 1610 (C=N), 3010 (C-H, Ar).

¹H NMR (CDCl₃) δ: 5.45 (2H, s, NH₂), 12.50 (1H, s, SH), 7.45-7.80 (4H, m, H-Ar), 3.80 (3H, s, OCH₃).

(2). 4-Amino-5-(4-fluorophenyl)-1,2,4-triazole-3-thiol

Molecular Formula: C₈H₇FN₄S

Yield: 65%, M.P. 139°C.

IR (KBr, νmax, cm⁻¹): 3420, 3315(N-H), 2590 (S-H), 1615 (C=N), 2980 (C-H, Ar).

¹H NMR (CDCl₃) δ: 5.40 (2H, s, NH₂), 12.15 (1H, s, SH), 6.75-7.30 (4H, m, H-Ar).
(3). 4-Amino-5-(4-chlorophenyl)-1,2,4-triazole-3-thiol

Molecular Formula: C₈H₇ClN₄S

Yield: 70%, M.P. 212 °C.

IR (KBr, v_max, cm⁻¹): 3350, 3270 (N-H), 2560 (S-H), 1545 (C=N), 695 (C-Cl).

¹H NMR (CDCl₃) δ: 5.75 (2H, s, NH₂), 12.5 (1H, s, SH), 7.60-8.10 (4H, m, Ar-H).

(4). 4-Amino-5-(4-bromophenyl)-1,2,4-triazole-3-thiol

Molecular Formula: C₈H₇BrN₄S

Yield: 70%, M.P. 205 °C.

IR (KBr, v_max, cm⁻¹): 3350, 3260 (N-H), 2559 (S-H), 1545 (C=N), 1340 (C-N, Ar), 640 (C-Br).

¹H NMR (CDCl₃) δ: 5.70 (2H, s, NH₂), 13.0 (1H, s, SH), 7.70 (4H, m, Ar-H).
(5).  4-Amino-5-(4-nitrophenyl)-1,2,4-triazole-3-thiol

Molecular Formula: C₈H₇N₅O₂S

Yield: 62%, M.P. 213 °C.

IR (KBr, νmax, cm⁻¹): 3345, 3275 (N-H), 2560 (S-H), 1555 (C=N), 1385 (C-NO₂).

¹H NMR (CDCl₃) δ: 5.20 (2H, s, NH₂), 12.5 (1H, s, SH), 8.00-8.25 (4H, m, Ar-H).

SPECTRAL ANALYSIS

The structures of synthesized compounds have been confirmed by their spectral characteristics. In IR spectra, the position of characteristic absorption bands for NH₂, C=N and SH groups are in accordance with their assigned structures. The two sharp absorption bands in the regions 3310-3250 cm⁻¹ are observed due to the asymmetric and symmetric stretching vibrations of the primary amino group. An absorption band in the region 1540-1620 cm⁻¹ is observed due to C=N stretching vibrations.

In the ¹H NMR spectra characteristic peaks for protons in NH₂ and SH groups are in accordance with the structure of synthesized 1,2,4-
triazoles. The signal for the S-H proton on triazole ring was observed in these compounds as a singlet at 11.50-13.00 ppm and signal for the NH₂ was observed as a singlet between 5.20-5.80 ppm.

![Chemical structures]

The absence of absorption band /peak corresponding to N-H and presence of S-H absorption confirm the thiol form (1) of triazole ring.
Fig. 3: IR Spectra of 5-substituted-4-amino-1,2,4-triazole-3-thiol
REFERENCES


