Chapter - 5

Isomerisation of 1,3,5-thiadiazines into s-triazines
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Abstract

Novel synthesis of a series of 1-substituted-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl) guanyl]-6-substitutedamino-1,2-dihydro-s-triazines (13), 1-substituted-2-thio-(1H)-4-(3-substitutedthiocarbamido-1-yl)-6-(1-substitutedguanidino-3-yl)-1,2-dihydro-s-triazine (14), 1-substituted-2-thio-(1H)-4-[(1-substituted-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-substitutedamino-1,2-dihydro-s-triazines (15), 1-substituted-2-thio-(1H)-4-[(1-substituted-2-thio-(1H)-4-substitutedamino-1,2-dihydro-s-triazin-6-yl)-amino-6-substitutedamino-1,2-dihydro-s-triazines (16), 1-substituted-(2H)-2-thio-4-(3-substitutedthiocarbamido-1-yl)-6-(2-imino-4-thio-5-substitutedbiureto-1-yl)-1,2-dihydro-s-triazines (17), 1,3-Bis-(1-substituted-2-thio-(1H)-6-substitutedamino-1,2-dihydro-s-triazin-4-yl) thiocarbamides (18) and 1-substituted-2-thio-(1H)-4-(1-substitutedthiocarbamido-3-yl)-6-substitutedamino-1,2-dihydro-s-triazines (19) have been successfully carried out.

All compounds i.e. (13), (14), (15), (16), (17), (18) and (19) were synthesized by the isomerisation of 2-substitutedamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-substitutedamino-1,3,5-thiadiazines (6), 2-(1-substitutedguanidino-3-yl)-4-(3-substitutedthiocarbamido-1-yl)-6-substitutedamino-1,3,5-thiadiazines (7), 2-substituted-4-[(4-amino-6-substitutedamino-1,3,5-thiaziaz-2-yl)]-amino-6-substitutedamino-1,3,5-thiadiazines (8), 2-substitutedamino-4-(4-substitutedamino-6-substitutedamino-1,3,5-thiaziaz-2-yl)-6-substitutedamino-1,3,5-thiadiazines (9), 2-(2-imino-4-thio-5-substitutedbiureto-1-yl)-4-(3-substitutedthiocarbamido-1-yl)-6-substitutedamino-1,3,5-thiadiazines (10), 1,3-Bis-(2-substitutedamino-6-substitutedamino-1,3,5-thiaziaz-4-yl) thiocarbamides (11) and 2-substitutedamino-4-(1-substitutedthiocarbamido-3-yl)-6-substitutedamino-1,3,5-thiadiazines (12) respectively by refluxing respective thiadiazine in 5% aqueous ethanolic sodium bicarbonate medium. The structures of all these synthesized compounds were justified on the basis of chemical characteristics, elemental analysis, IR and PMR spectral analysis.
Introduction

The literature survey reveals that the heterocyclic compounds containing nitrogen and nitrogen and sulphur have gain immense importance in human life due to their variety of applications in agricultural, medicinal, pharmacological and industrial. It has also found that the heterocyclic compounds containing s-triazine in the nucleus have been successfully tested against several pathogens and it was found that they possess potential therapeutical value\(^1\) for several diseases. So, these compounds possess their own importance in medical faculty, industrial and agricultural field. Some s-triazine acts as antibacterial\(^2-5\), antiinflammatory\(^6\), blood pressure depresant\(^7\), antidiabetic\(^8\), hypoglycaemic agent\(^9\), muscle relaxant\(^10\), antitumor\(^11\) and some cure cancer\(^12\). Some of them are used in industries such as finishing and brightening agents\(^13\). They are also used as herbicidals,\(^14-19\) sea water algicidal\(^20\), fungicidal,\(^21-23\) and insecticidals.\(^24\) Some triazino compounds shows remarkable antimicrobial activity.\(^25\) As a part of research work presently being undertaken in this laboratory in the synthesis of novel series of s-triazenes containing biureto, thio, phenyl, methyl, phenylamino, guanidino, thiocarbamido groups in the s-triazine nucleus. So it was thought interesting to make isomerisation of all thiadiazines (synthesized in Chapter-4) into s-triazenes in presence of aqueous ethanolic sodium bicarbonate medium.

This chapter is divided in three section viz. Section-A, Section-B and Section-C.
Results and Discussion

Section - A:

In view of medicinal, pharmacological, agricultural and industrial importance of s-triazine we explore direct synthetic procedure for 1-substituted-2-thio-(1H)-4-(2-imino-4-thio-biureto-5-yl)-6-substitutedamino-1,2-dihydro-s-triazine (13), 1-substituted-2-thio-(1H)-4-(3-substitutedthiocarbamido-1-yl)-6-(1-substitutedguanidino-3-yl)-1,2-dihydro-s-triazine (14), 1-substituted-2-thio-(1H)-4-[(1-substituted-2-thio(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-substitutedamino-1,2-dihydro-s-triazine (15) and 1-substituted-2-thio-(1H)-4-(1-substituted-2-thio-(1H)-4-substitutedamino-1,2-dihydro-s-triazin-6-yl)-amino-6-substitutedamino-1,2-dihydro-s-triazine (16).

The compounds (13) and (14) were synthesized by the isomerisation of (6) and (7) in 5% aqueous ethanolic sodium bicarbonate solution respectively in Class (i) Scheme Va and Scheme Vb, while compounds (15) and (16) were synthesized by the isomerisation of (8) and (9) in 5% aqueous ethanolic sodium bicarbonate solution respectively in Class (ii) as shown in Scheme Vc and Scheme Vd respectively.
\[ \text{SCHEME - Va} \]

\[
\begin{align*}
\text{R-NH-C} & \quad \text{C-NH-C-NH-C-NH}_2 \\
\text{S} & \quad \text{S} \\
\text{N} & \quad \text{N} - \text{R}_1 \\
\end{align*}
\]

Isomerisation \[ \text{Aqueous ethanolic sodium bicarbonate} \]

Where,
\[ \text{R} = \text{phenyl, } p\text{-chlorophenyl, } p\text{-tolyl, ethyl, methyl, } \text{t-butyl} \]
\[ \text{R}_1 = \text{phenyl, } p\text{-chlorophenyl, ethyl, } \text{t-butyl} \]

\[ (6) \]

\[ \text{SCHEME - Vb} \]

\[
\begin{align*}
\text{R-NH-C-NH} & \quad \text{C-NH-C-NH-R'} \\
\text{S} & \quad \text{S} \\
\text{N} & \quad \text{N} - \text{R}_1 \\
\end{align*}
\]

Isomerisation \[ \text{Aqueous ethanolic sodium bicarbonate} \]

Where, \[ \text{R} = \text{phenyl, } p\text{-chlorophenyl, } p\text{-tolyl, ethyl, methyl, } \text{t-butyl} \]
\[ \text{R}_1 = \text{phenyl, ethyl} \]
\[ \text{R}' = \text{phenyl, allyl} \]

\[ (7) \]
SCHEME - Vc

Where,
R = phenyl, \( p \)-chlorophenyl, \( p \)-tolyl, ethyl, methyl, \( t \)-butyl
R\(_1\) = phenyl, \( p \)-chlorophenyl, ethyl, \( t \)-butyl

SCHEME - Vd

Where,
R = phenyl, \( p \)-chlorophenyl, \( p \)-tolyl, ethyl, methyl, \( t \)-butyl
R\(_1\) = phenyl;
R' = phenyl, allyl
Synthesis of 1-substituted-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl) guanyl]-6-substitutedamino-1,2-dihydro-s-triazine (13) and 1-Substituted-2-thio-(1H)-4-(3-substitutedthiocarbamido-1-yl)-6-(1-substitutedguanidino-3-yl)-1,2-dihydro-s-triazine (14)

[A] : Synthesis of 1-phenyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl) guanyl]-6-phenylimino-1,2-dihydro-s-triazine [13a(i)]

2-Phenylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-phenylimino-1,3,5-thiadiazine [6a(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath. During heating the reactant went into solvent. After distillation of excess solvent, the pale yellow crystals were isolated. It was recrystallized from glacial acetic acid to get [13a(i)], yield 62%, m.p. 185°C.

The probable reaction mechanism of the formation of [13a(i)] may be stated as follows.

\[
\begin{align*}
\text{Aqueous ethanolic} & \quad \text{sodium bicarbonate} \\
\text{Isomerisation} & \quad \text{Isomerisation}
\end{align*}
\]

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Properties of [13a(i)] :

1. It was pale yellow crystalline solid having m.p. 185°C.

2. It gave positive test for nitrogen and sulphur.

3. It was found to be desulphurizable when boiled with alkaline plumbite solution.

4. It was soluble in benzene, DMSO, DMF and acetic acid.

5. The benzene solution of compound when treated with pure and dry carbon disulphide a yellow colour was developed.\textsuperscript{26-27} This indicates the presence of basic imino group (=NH) in the compound.

6. It formed picrate m.p. 145°C.

7. Elemental analysis:

<table>
<thead>
<tr>
<th>Elements</th>
<th>Found</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>51.49</td>
<td>51.52</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3.09</td>
<td>4.04</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>28.14</td>
<td>28.28</td>
</tr>
<tr>
<td>Sulphur</td>
<td>16.12</td>
<td>16.16</td>
</tr>
</tbody>
</table>

8. From analytical data, the molecular formula was found to be $\text{C}_{17}\text{H}_{16}\text{N}_{8}\text{S}_{2}$.

9. **IR Spectrum**: The IR spectrum of compound [13a(i)] was carried out in KBr pellets and is reproduced on Plate No. IR-5.1. The important absorption can be correlated as follows.
Absorption observed (cm⁻¹) | Assignment | Absorption expected (cm⁻¹)
--- | --- | ---
3373.9 | N–H stretching | 3500-3100²⁸-³¹
3150.0 | C–H (Ar) stretching | 3150-3000³²
1669.0 | C≡N stretching | 1789-1471³³
1572.4 | >C=NH (imino) grouping | 1789-1471³³
1181.3 | C–N stretching | 1340-1250³⁴
995.8 | N > C = S grouping | 1200-1050³⁵-³⁶
596.6 | C–S stretching | 800-600³⁷

10. **PMR**: The PMR spectrum²⁹,³²,³³,³⁶ of compound [13a(i)] was carried out in DMSO-\(d_6\) and CDCl₃ and reproduced on Plate No. PMR-5.1. This spectrum distinctly displayed signals due to Ar–NH protons at \(\delta\) 8.19-8.23 ppm, Ar–H protons at \(\delta\) 6.6-7.2 ppm, and NH₂ protons at \(\delta\) 5.9-6.107 ppm. The signals at \(\delta\) 3.25-3.47 ppm is due to moisture in DMSO-\(d_6\).

From the above properties and spectral analysis the compound [13a(i)] was assigned the structure as 1-phenyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl)guanyl]-6-phenylamino-1,2-dihydro-s-triazine.

\[
\begin{align*}
\text{NH} &\quad \text{C} &\quad \text{C} &\quad \text{NH} \\
\text{C} &\quad \text{C} &\quad \text{NH} &\quad \text{S} &\quad \text{NH}
\end{align*}
\]

[13a(i)]
Similarly, the other triazines, [13a(ii)] to [13f(iv)] were synthesized by the isomerisation of other thiadiazines [6a(ii)] to [6f(iv)] in 5% aqueous ethanolic sodium bicarbonate solution and the related products were isolated in good yield [Table No. 5.1]. Similarly, [14a(i)] to [14f(ii)] and (14g) to (14/) were synthesized by the isomerisation of [7a(i)] to [7f(ii)] and (7g) to (7/) thiadiazines in 5% aqueous ethanolic sodium bicarbonate solution to isolate related products with good yield and enlisted in Table No. 5.2.

[B] : Synthesis of 1-phenyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl) guanyl]-6-ethylamino-1,2-dihydro-s-triazine [13b(i)].

2-Ethylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-phenylimino-1,3,5-thiadiazine [6b(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath. During heating the reactant went into solvent. After distillation of excess solvent, the ivory crystals were isolated. It was recrystallised from glacial acetic acid to get [13b(i)], yield 63%, m.p. 182°C.

Properties of [13b(i)] :
1. It was ivory crystalline solid having m.p. 182°C.
2. It gave positive test for nitrogen and sulphur.
3. It was found to be desulphurizable when boiled with alkaline plumbite solution.
4. It was soluble in acetic acid, benzene, DMSO and DMF.
5. The benzene solution of compound when treated with pure and dry carbon disulphide a yellow colour was developed. This indicates the presence of basic imino group (=NH) in the compound.
6. It formed picrate m.p. 173°C.
Table - 5.1

<table>
<thead>
<tr>
<th>S. N.</th>
<th>2-Substitutedamino-4-(2-imino-4-thioiureto-5-yl-carbamido)-6-substitutedamino-1,3,5-thiadiazine (6)</th>
<th>1-Substituted-2-thio-(1H)-4-[2-imino-4-thioiureto-5-yl]-6-substitutedamino-1,2-dihydro-s-triazine (13)</th>
<th>Yield (%)</th>
<th>m.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>2-Phenylamino-4-( ...........)- 6-phenylmino-1,3,5-thiadiazine [6a(i)]</td>
<td>1-Phenyl-2-thio-(1H)-4-[. ........]-6-phenylamino-1,2-dihydro-s-triazine [13a(i)]</td>
<td>62</td>
<td>185</td>
</tr>
<tr>
<td>1</td>
<td>2-Phenylamino-4-( ...........)- 6-p-chlorophenylmino-1,3,5-thiadiazine [6a(ii)]</td>
<td>1-p-Chlorophenyl-2-thio-(1H)-4-[. ........]-6-phenylamino-1,2-dihydro-s-triazine [13a(ii)]</td>
<td>59</td>
<td>191</td>
</tr>
<tr>
<td>2</td>
<td>2-Phenylamino-4-( ...........)- 6-ethylmino-1,3,5-thiadiazine [6a(iii)]</td>
<td>1-Ethyl-2-thio-(1H)-4-[. ........]-6-phenylamino-1,2-dihydro-s-triazine [13a(iii)]</td>
<td>71</td>
<td>179</td>
</tr>
<tr>
<td>3</td>
<td>2-Phenylamino-4-( ...........)- 6-t-butylimino-1,3,5-thiadiazine [6a(iv)]</td>
<td>1-t-Butyl-2-thio-(1H)-4-[. ........]-6-phenylamino-1,2-dihydro-s-triazine [13a(iv)]</td>
<td>69</td>
<td>167</td>
</tr>
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<td>4</td>
<td>2-Ethylamino-4-( ...........)- 6-phenylmino-1,3,5-thiadiazine [6b(i)]</td>
<td>1-Phenyl-2-thio-(1H)-4-[. ........]-6-ethylamino-1,2-dihydro-s-triazine [13b(i)]</td>
<td>63</td>
<td>182</td>
</tr>
<tr>
<td>5</td>
<td>2-Ethylamino-4-( ...........)- 6-p-chlorophenylmino-1,3,5-thiadiazine [6b(ii)]</td>
<td>1-p-Chlorophenyl-2-thio-(1H)-4-[. ........]-6-ethylamino-1,2-dihydro-s-triazine [13b(ii)]</td>
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</tr>
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<td>6</td>
<td>2-Ethylamino-4-( ...........)- 6-ethylmino-1,3,5-thiadiazine [6b(iii)]</td>
<td>1-Ethyl-2-thio-(1H)-4-[. ........]-6-ethylamino-1,2-dihydro-s-triazine [13b(iii)]</td>
<td>69</td>
<td>174</td>
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<td>7</td>
<td>2-Ethylamino-4-( ...........)- 6-t-butylimino-1,3,5-thiadiazine [6b(iv)]</td>
<td>1-t-Butyl-2-thio-(1H)-4-[. ........]-6-ethylamino-1,2-dihydro-s-triazine [13b(iv)]</td>
<td>71</td>
<td>159</td>
</tr>
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<tr>
<td>9</td>
<td>2-p-Chlorophenylamino-4-(---)-6-phenylamino-1,3,5-thiadiazine [6c(i)]</td>
<td>1-Phenyl-2-thio-(1H)-4-[..-]-6-p-chlorophenylamino-1,2-dihydro-s-triazine [13c(i)]</td>
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<td>10</td>
<td>2-p-Chlorophenylamino-4-(---)-6-p-chlorophenylimino-1,3,5-thiadiazine [6c(ii)]</td>
<td>1-p-Chlorophenyl-2-thio-(1H)-4-[..-]-6-p-chlorophenylimino-1,2-dihydro-s-triazine [13c(ii)]</td>
<td>57</td>
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<td>11</td>
<td>2-p-Chlorophenylamino-4-(---)-6-ethylamino-1,3,5-thiadiazine [6c(iii)]</td>
<td>1-Phenyl-2-thio-(1H)-4-[..-]-6-ethylamino-1,2-dihydro-s-triazine [13c(iii)]</td>
<td>58</td>
<td>195</td>
</tr>
<tr>
<td>12</td>
<td>2-p-Chlorophenylamino-4-(---)-6-t-butyldimino-1,3,5-thiadiazine [6c(iv)]</td>
<td>1-t-Butyl-2-thio-(1H)-4-[..-]-6-p-chlorophenylimino-1,2-dihydro-s-triazine [13c(iv)]</td>
<td>71</td>
<td>181</td>
</tr>
<tr>
<td>13</td>
<td>2-p-Tolylamino-4-(---)-6-phenylamino-1,3,5-thiadiazine [6d(i)]</td>
<td>1-Phenyl-2-thio-(1H)-4-[..-]-6-p-tolylamino-1,2-dihydro-s-triazine [13d(i)]</td>
<td>79</td>
<td>194</td>
</tr>
<tr>
<td>14</td>
<td>2-p-Tolylamino-4-(---)-6-p-chlorophenylimino-1,3,5-thiadiazine [6d(ii)]</td>
<td>1-p-Chlorophenyl-2-thio-(1H)-4-[..-]-6-p-tolylamino-1,2-dihydro-s-triazine [13d(ii)]</td>
<td>65</td>
<td>209</td>
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<td>15</td>
<td>2-p-Tolylamino-4-(---)-6-ethylamino-1,3,5-thiadiazine [6d(iii)]</td>
<td>1-Ethyl-2-thio-(1H)-4-[..-]-6-p-tolylamino-1,2-dihydro-s-triazine [13d(iii)]</td>
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<td>191</td>
</tr>
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<td>16</td>
<td>2-p-Tolylamino-4-(---)-6-t-butyldimino-1,3,5-thiadiazine [6d(iv)]</td>
<td>1-t-Butyl-2-thio-(1H)-4-[..-]-6-p-tolylamino-1,2-dihydro-s-triazine [13d(iv)]</td>
<td>72</td>
<td>172</td>
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<td>17</td>
<td>2-Methylamino-4-(---)-6-phenylamino-1,3,5-thiadiazine [6e(i)]</td>
<td>1-Phenyl-2-thio-(1H)-4-[..-]-6-methylamino-1,2-dihydro-s-triazine [13e(i)]</td>
<td>65</td>
<td>171</td>
</tr>
<tr>
<td>18</td>
<td>2-Methylamino-4-(---)-6-p-chlorophenylimino-1,3,5-thiadiazine [6e(ii)]</td>
<td>1-p-Chlorophenyl-2-thio-(1H)-4-[..-]-6-methylamino-1,2-dihydro-s-triazine [13e(ii)]</td>
<td>71</td>
<td>169</td>
</tr>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
<td>(5)</td>
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<td>-----</td>
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<td>-----</td>
<td>-----</td>
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</tr>
<tr>
<td>19</td>
<td>2-Methylamino-4-( ...........) - 6-ethylimino-1,3,5-thiadiazine [6e(iii)]</td>
<td>1-Ethyl-2-thio-(1H)-4-[.. .......] -6-methylamino-1,2-dihydro-s-triazine [13e(iii)]</td>
<td>62</td>
<td>164</td>
</tr>
<tr>
<td>20</td>
<td>2-Methylamino-4-( ...........) - 6-&lt;t-thylamino-1,3,5-thiadiazine [6e(iv)]</td>
<td>1-&lt;t-Butyl-2-thio-(1H)-4-[.. .......] -6-methylamino-1,2-dihydro-s-triazine [13e(iv)]</td>
<td>68</td>
<td>174</td>
</tr>
<tr>
<td>21</td>
<td>2-&lt;t-Butylamino-4-( ...........) - 6-phenylamino-1,3,5-thiadiazine [6f(i)]</td>
<td>1-Phenyl-2-thio-(1H)-4-[.. .......] -6-t-butylamino-1,2-dihydro-s-triazine [13f(i)]</td>
<td>65</td>
<td>181</td>
</tr>
<tr>
<td>22</td>
<td>2-t-Butylamino-4-( ...........) - 6-p-chlorophenylamino-1,3,5-thiadiazine [6f(ii)]</td>
<td>1-p-Chlorophenyl-2-thio-(1H)-4-[.. .......] -6-t-butylamino-1,2-dihydro-s-triazine [13f(ii)]</td>
<td>69</td>
<td>178</td>
</tr>
<tr>
<td>23</td>
<td>2-t-Butylamino-4-( ...........) - 6-ethylimino-1,3,5-thiadiazine [6f(iii)]</td>
<td>1-Ethyl-2-thio-(1H)-4-[.. .......] -6-t-butylamino-1,2-dihydro-s-triazine [13f(iii)]</td>
<td>71</td>
<td>152</td>
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<td>24</td>
<td>2-t-Butylamino-4-( ...........) - 6-t-butylamino-1,3,5-thiadiazine [6f(iv)]</td>
<td>1-t-Butyl-2-thio-(1H)-4-[.. .......] -6-t-butylamino-1,2-dihydro-s-triazine [13f(iv)]</td>
<td>73</td>
<td>168</td>
</tr>
</tbody>
</table>

*Gave satisfactory C, H, N and S analysis.*
7. Elemental analysis:

<table>
<thead>
<tr>
<th>Elements</th>
<th>Found</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>44.35</td>
<td>44.83</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.42</td>
<td>4.60</td>
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<tr>
<td>Nitrogen</td>
<td>33.05</td>
<td>32.18</td>
</tr>
<tr>
<td>Sulphur</td>
<td>18.22</td>
<td>18.39</td>
</tr>
</tbody>
</table>

8. From analytical data, the molecular formula was found to be $C_{13}H_{16}N_8S_2$.

9. **IR Spectrum**: The IR spectrum of compound [13b(i)] was carried out in KBr pellets and is reproduced on Plate No. IR-5.2. The important absorption can be correlated as follows.

<table>
<thead>
<tr>
<th>Absorption observed (cm$^{-1}$)</th>
<th>Assignment</th>
<th>Absorption expected (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3387.3</td>
<td>N–H stretching</td>
<td>3500-3100$^{28,31}$</td>
</tr>
<tr>
<td>3147.7</td>
<td>C–H (Ar) stretching</td>
<td>3150-3000$^{32}$</td>
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<tr>
<td>1666.3</td>
<td>C=N stretching</td>
<td>1789-1471$^{33}$</td>
</tr>
<tr>
<td>1305.3</td>
<td>C–N stretching</td>
<td>1340-1250$^{34}$</td>
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<tr>
<td>1178.0</td>
<td>$N\overset{N}{\searrow}C=S$ grouping</td>
<td>1200-1050$^{35,36}$</td>
</tr>
<tr>
<td>746.9</td>
<td>C–S stretching</td>
<td>800-600$^{37}$</td>
</tr>
</tbody>
</table>

10. **PMR**: The PMR spectrum$^{29,32,33,36}$ of compound [13b(i)] was carried out in DMSO-$d_6$ and CDCl$_3$ and reproduced on Plate No. PMR-5.2. This spectrum distinctly displayed signals due to Ar–H protons at $\delta$ 8.15 ppm, triazino NH protons at $\delta$ 6.69 ppm, NH$_2$ protons at $\delta$ 5.83 ppm,
-CH₂ protons at δ 3.31 ppm and -CH₃ protons at δ 2.52-2.54 ppm. The signals at δ 1.24 ppm is due to moisture in DMSO-d₆ and δ 0.844-0.869 ppm are due to DMSO.

From the above properties and spectral analysis the compound [13b(i)] was assigned the structure as 1-phenyl-2-thio-(1H)-4-[{(2-imino-4-thiobiureto-5-yl) guanyl]-6-ethylamino-1,2-dihydro-s-triazine.

\[
\begin{align*}
\text{Synthesis of 1-substituted-2-thio-(1H)-4-[(1-substituted-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-substitutedamino-1,2-dihydro-s-triazine (15) and} \\
\text{1-Substituted-2-thio-(1H)-4-(1-substituted2-thio-(1H)-4-substitutedamino-1,2-dihydro-s-triazin-6-yl)amino-6-substitutedamino-1,2-dihydro-s-triazine (16)}
\end{align*}
\]

\[\text{[A] : Synthesis of 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-phenylamino-1,2-dihydro-s-triazine [15a(i)]}
\]

2-Phenylamino-4-[(4-amino-6-phenylimino-1,3,5-thiadiaz-2-yl)]-amino-6-phenylimino-1,3,5-thiadiazine [8a(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and refluxed for 2 hr on water bath. During heating the reactant went into solvent. After distillation of excess solvent, the pale brown crystals were isolated. It was recrystallized from glacial acetic acid to get [15a(i)], yield 72%, m.p. 257°C.

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### Table - 5.2*

<table>
<thead>
<tr>
<th>S. N.</th>
<th>2-(1-Substitutedguanidino-3-yl)-4-(3-substitutedthiocarbamido-1-yl) -6-substitutedimino-1,3,5-thiadiazine (7)</th>
<th>1-Substituted-2-thio-(1H)-4-(3-substitutedthiocarbamido-1-yl)-6-(1-substitutedguanidino-3-yl)-1,2-dihydro-s-triazine (14)</th>
<th>Yield (%)</th>
<th>m.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
<td>(5)</td>
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<tr>
<td>25</td>
<td>2-(1-Phenylguanidino-3-yl)-4-(3-phenylthio...1-yl)-6-phenylimino-1,3,5-thiadiazine [7a(i)]</td>
<td>1-Phenyl-2-thio-(1H)-4-(3-phenylthio...1-yl)-6-(1-phenylguanidino-3-yl) s-triazine [14a(i)]</td>
<td>61</td>
<td>258</td>
</tr>
<tr>
<td>26</td>
<td>2-(1-Phenylguanidino -3-yl)-4-(3-phenylthio...1-yl)-6-ethylmino-1,3,5-thiadiazine [7a(ii)]</td>
<td>1-Ethyl-2-thio-(1H)-4-(3-phenylthio...1-yl)-6-(1-phenylguanidino-3-yl) s-triazine [14a(ii)]</td>
<td>59</td>
<td>246</td>
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<tr>
<td>27</td>
<td>2-(1-p-chlorophenylguanidino-3-yl)-4-(3-phenylthio...1-yl)-6-phenylimino-1,3,5-thiadiazine [7b(i)]</td>
<td>1-Phenyl-2-thio-(1H)-4-(3-phenylthio...1-yl)-6-(1-p-chlorophenylguanidino-3-yl) s-triazine [14b(i)]</td>
<td>65</td>
<td>249</td>
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<tr>
<td>28</td>
<td>2-(1-p-chlorophenylguanidino-3-yl)-4-(3-phenylthio...1-yl)-6-ethylmino-1,3,5-thiadiazine [7b(ii)]</td>
<td>1-Ethyl-2-thio-(1H)-4-(3-phenylthio...1-yl)-6-(1-p-chlorophenylguanidino-3-yl) s-triazine [14b(ii)]</td>
<td>69</td>
<td>244</td>
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<tr>
<td>29</td>
<td>2-(1-p-Tolylguanidino-3-yl)-4-(3-phenylthio...1-yl)-6-phenylimino-1,3,5-thiadiazine [7c(i)]</td>
<td>1-Phenyl-2-thio-(1H)-4-(3-phenylthio...1-yl)-6-(1-p-tolylguanidino-3-yl) s-triazine [14c(i)]</td>
<td>72</td>
<td>262</td>
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<td>30</td>
<td>2-(1-p-Tolylguanidino-3-yl)-4-(3-phenylthio...1-yl)-6-ethylmino-1,3,5-thiadiazine [7c(ii)]</td>
<td>1-Ethyl-2-thio-(1H)-4-(3-phenylthio...1-yl)-6-(1-p-tolylguanidino-3-yl) s-triazine [14c(ii)]</td>
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<td>31</td>
<td>2-(1-Ethylguanidino-3-yl)-4-(3-phenylthio...1-yl)-6-phenylimino-1,3,5-thiadiazine [7d(i)]</td>
<td>1-Phenyl-2-thio-(1H)-4-(3-phenylthio...1-yl)-6-(1-ethylguanidino-3-yl) s-triazine [14d(i)]</td>
<td>73</td>
<td>256</td>
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<td>(1)</td>
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<tr>
<td>32</td>
<td>2-(1-Ethylguanidino-3-y1)-4-(3-phenylthio...1-yl) -6-ethylmino-1,3,5-thiadiazine [7d(ii)]</td>
<td>1-Ethyl-2-thio-(1H)-4-(3-phenylthio......1-yl)- -6-(1-ethylguanidino-3-y1)...... s-triazine [14d(ii)]</td>
<td>66</td>
<td>231</td>
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<td>33</td>
<td>2-(1-Methylguanidino -3-y1)-4-(3-phenylthio... ...1-yl)-6-phenylmino-1,3,5-thiadiazine [7e(ii)]</td>
<td>1-Phenyl-2-thio-(1H)-4-(3-phenylthio......1-yl)- -6-(1-methylguanidino-3-y1)...... s-triazine [14e(ii)]</td>
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<td>221</td>
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<tr>
<td>34</td>
<td>2-(1-Methylguanidino -3-y1)-4-(3-phenylthio... ...1-yl)-6-ethylmino-1,3,5-thiadiazine [7e(i)]</td>
<td>1-Ethyl-2-thio-(1H)-4-(3-phenylthio......1-yl)- -6-(1-methylguanidino-3-y1)...... s-triazine [14e(i)]</td>
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<td>209</td>
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<tr>
<td>35</td>
<td>2-(1-i-Butylguanidino-3-y1)-4-(3-phenylthio... ...1-yl)-6-phenylmino-1,3,5-thiadiazine [7f(i)]</td>
<td>1-Phenyl-2-thio-(1H)-4-(3-phenylthio......1-yl)- -6-(1-i-butylguanidino-3-y1)...... s-triazine [14f(i)]</td>
<td>70</td>
<td>219</td>
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<td>36</td>
<td>2-(1-i-Butylguanidino -3-y1)-4-(3-phenylthio... ...1-yl)-6-ethylmino-1,3,5-thiadiazine [7f(ii)]</td>
<td>1-Ethyl-2-thio-(1H)-4-(3-phenylthio......1-yl)- -6-(1-i-butylguanidino-3-y1)...... s-triazine [14f(ii)]</td>
<td>71</td>
<td>252</td>
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<td>37</td>
<td>2-(1-Phenylguanidino -3-y1)-4-(3-allylthio...1-yl) -6-phenylmino-1,3,5-thiadiazine (7g)</td>
<td>1-Phenyl-2-thio-(1H)-4-(3-allylthio......1-yl)- -6-(1-phenylguanidino-3-y1)...... s-triazine (14g)</td>
<td>69</td>
<td>268</td>
</tr>
<tr>
<td>38</td>
<td>2-(1-p-Chlorophenylguanidino -3-y1)-4-(3-allylthio...1-yl)-6-phenylmino-1,3,5-thiadiazine (7h)</td>
<td>1-Phenyl-2-thio-(1H)-4-(3-allylthio......1-yl)- -6-(1-p-chlorophenylguanidino-3-y1)...... s-triazine (14h)</td>
<td>68</td>
<td>257</td>
</tr>
<tr>
<td>39</td>
<td>2-(1-p-TolyIguanidino-3-y1)-4-(3-allylthio...1-yl) -6-phenylmino-1,3,5-thiadiazine (7i)</td>
<td>1-Phenyl-2-thio-(1H)-4-(3-allylthio......1-yl)- -6-(1-p-tolyIguanidino-3-y1)...... s-triazine (14i)</td>
<td>65</td>
<td>252</td>
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<td>40</td>
<td>2-(1-Ethylguanidino-3-y1)-4-(3-allylthio...1-yl) -6-phenylmino-1,3,5-thiadiazine (7j)</td>
<td>1-Phenyl-2-thio-(1H)-4-(3-allylthio......1-yl)- -6-(1-ethylguanidino-3-y1)...... s-triazine (14j)</td>
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<td>231</td>
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<tr>
<td>41</td>
<td>2-(1-Methylguanidino-3-y1)-4-(3-allylthio...1-yl) -6-phenylmino-1,3,5-thiadiazine (7k)</td>
<td>1-Phenyl-2-thio-(1H)-4-(3-allylthio......1-yl)- -6-(1-methylguanidino-3-y1)...... s-triazine (14k)</td>
<td>73</td>
<td>219</td>
</tr>
<tr>
<td>42</td>
<td>2-(1-i-Butylguanidino-3-y1)-4-(3-allylthio...1-yl) -6-phenylmino-1,3,5-thiadiazine (7i)</td>
<td>1-Phenyl-2-thio-(1H)-4-(3-allylthio......1-yl)- -6-(1-i-butylguanidino-3-y1)...... s-triazine (14i)</td>
<td>62</td>
<td>223</td>
</tr>
</tbody>
</table>

*Gave satisfactory C, H, N and S analysis
The probable reaction mechanism of the formation of [15a(i)] may be stated as follows.

\[
\begin{align*}
\text{Isomerisation} & \quad \text{Aqueous ethanolic sodium bicarbonate} \\
\end{align*}
\]

Properties of [15a(i)] :

1. It was pale brown crystalline solid having m.p. 257°C.
2. It gave positive test for nitrogen and sulphur.
3. It was found to be desulphurizable when boiled with alkaline plumbite solution.
4. It was soluble in benzene, DMF, acetic acid and DMSO.
5. Diazotization Test :- It gave positive diazotization test indicating the presence of primary aromatic amino (-NH₂) group.
6. It formed picrate m.p. 230°C.
7. Elemental analysis:

<table>
<thead>
<tr>
<th>Elements</th>
<th>Found</th>
<th>Calculated</th>
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</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>57.73</td>
<td>57.95</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3.62</td>
<td>3.82</td>
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<tr>
<td>Nitrogen</td>
<td>25.15</td>
<td>25.36</td>
</tr>
<tr>
<td>Sulphur</td>
<td>12.70</td>
<td>12.87</td>
</tr>
</tbody>
</table>

8. From analytical data, the molecular formula was found to be $C_{24}H_{19}N_9S_2$.

9. **IR Spectrum**: The IR spectrum of compound [15a(i)] was carried out in KBr pellets and is reproduced on Plate No. IR-5.3. The important absorption can be correlated as follows.

<table>
<thead>
<tr>
<th>Absorption observed (cm$^{-1}$)</th>
<th>Assignment</th>
<th>Absorption expected (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3356.6</td>
<td>N–H stretching</td>
<td>3500–3100$^{28,31}$</td>
</tr>
<tr>
<td>3131.3</td>
<td>C–H (Ar) stretching</td>
<td>3150–3000$^{32}$</td>
</tr>
<tr>
<td>1688.4</td>
<td>C=N stretching</td>
<td>1789–1471$^{33}$</td>
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<tr>
<td>1635.4</td>
<td>&gt;C=NH (imino) grouping</td>
<td>1789–1471$^{33}$</td>
</tr>
<tr>
<td>1294.7</td>
<td>C–N stretching</td>
<td>1340–1250$^{34}$</td>
</tr>
<tr>
<td>1197.7</td>
<td>$\text{N} \overset{\equiv}{\cdots} \text{C} = \text{S}$ grouping</td>
<td>1200–1050$^{35,36}$</td>
</tr>
<tr>
<td>777.9</td>
<td>C–S stretching</td>
<td>800–600$^{37}$</td>
</tr>
</tbody>
</table>
10. **PMR**: The PMR spectrum\(^{29,32,33,36}\) of compound [15a(i)] was carried out in DMSO-\(d_6\) and CDCl\(_3\) and reproduced on Plate No. PMR-5.3. This spectrum distinctly displayed signals due to Ar–NH protons at \(\delta\) 7.87-8.60 ppm, Ar–H protons at \(\delta\) 6.8-7.2 ppm, and NH\(_2\) protons at \(\delta\) 5.9-6.1 ppm. The signals at \(\delta\) 3.21-3.42 ppm is due to moisture in DMSO-\(d_6\), \(\delta\) 2.51-2.53 ppm are due to moisture in DMSO and at \(\delta\) 1.24 ppm is due to DMSO.

From the above properties and spectral analysis the compound [15a(i)] was assigned the structure as 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-amino-1,2-hydro-s-triazin-6-yl)]-amino-6-phenylamino-1,2-dihydro-s-triazine.

Similarly, the other s-triazines [15a(ii)] to [15f(iv)] were synthesized by the isomerisation of other thiadiazines [8a(ii)] to [8f(iv)] in 5% aqueous ethanolic sodium bicarbonate solution and the related products were isolated in good yield [Table No. 5.3]. Similarly, (16a) to (16f) were synthesized by the isomerisation of (9a) to (9g) thiadiazines in 5% aqueous ethanolic sodium bicarbonate solution to isolate related products with good yield and enlisted in Table No. 5.4.
### Table - 5.3

<table>
<thead>
<tr>
<th>S. N.</th>
<th>2-Substituted-4-[(4-amino-6-substitutedimino-1,3,5-thiadiaz-2-yl)]-amino-6-substitutedimino-1,3,5-thiadiazine (8)</th>
<th>1-Substituted-2-thio-(1H)-4-[(1-substituted-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-substitutedamino-1,2-dihydro-s-triazine (15)</th>
<th>Yield (%)</th>
<th>m.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
<td>(5)</td>
</tr>
<tr>
<td>43</td>
<td>2-Phenylamino-4-[(4-amino-6-phenylimino-1,3,5-thiadiaz-2-yl)]-amino-6-phenylimino-1,3,5-thiadiazine [8a(i)]</td>
<td>1-Phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-6-yl)]-amino-6-phenylamino-3-yl)..... s-triazine[15a(i)]</td>
<td>72</td>
<td>257</td>
</tr>
<tr>
<td>44</td>
<td>2-Phenylamino-4-[(4-amino-6-p-chlorophenylimino-2-yl)]-amino-6-p-chlorophenylimino-1,3,5-thiadiazine [8a(ii)]</td>
<td>1-p-Chlorophenyl-2-thio-(1H)-4-[(1-p-chlorophenyl-2-thio-(1H)-6-yl)]-amino-6-phenylamino-3-yl)..... s-triazine[15a(ii)]</td>
<td>73</td>
<td>274</td>
</tr>
<tr>
<td>45</td>
<td>2-Phenylamino-4-[(4-amino-6-ethylimino-2-yl)]-amino-6-ethylimino-1,3,5-thiadiazine [8a(iii)]</td>
<td>1-Ethyl-2-thio-(1H)-4-[(1-ethyl-2-thio-(1H)-6-yl)]-amino-6-phenylamino-3-yl)..... s-triazine[15a(iii)]</td>
<td>79</td>
<td>241</td>
</tr>
<tr>
<td>46</td>
<td>2-Phenylamino-4-[(4-amino-6-tert-butyliino-2-yl)]-amino-6-tert-butyliino-1,3,5-thiadiazine [8a(iv)]</td>
<td>1-tert-Butyl-2-thio-(1H)-4-[(1-tert-butyliino-2-thio-(1H)-6-yl)]-amino-6-phenylamino-3-yl)..... s-triazine[15a(iv)]</td>
<td>81</td>
<td>243</td>
</tr>
<tr>
<td>47</td>
<td>2-Ethylamino-4-[(4-amino-6-phenylimino-2-yl)]-amino-6-phenylimino-1,3,5-thiadiazine [8b(i)]</td>
<td>1-Phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-6-yl)]-amino-6-ethylamino-3-yl)..... s-triazine[15b(i)]</td>
<td>69</td>
<td>232</td>
</tr>
<tr>
<td>48</td>
<td>2-Ethylamino-4-[(4-amino-6-p-chlorophenylimino-2-yl)]-amino-6-p-chlorophenylimino-1,3,5-thiadiazine [8b(ii)]</td>
<td>1-p-Chlorophenyl-2-thio-(1H)-4-[(1-p-chlorophenyl-2-thio-(1H)-6-yl)]-amino-6-ethylamino-3-yl)..... s-triazine[15b(ii)]</td>
<td>72</td>
<td>261</td>
</tr>
<tr>
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<td>1</td>
<td>2</td>
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<td>-----------------------------------------------------</td>
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</tr>
<tr>
<td>49</td>
<td>2-Ethylamino-4-[(4-amino-6-ethylimino-2-yl)-amino-6-ethylimino-1,3,5-thiadiazine [8b(iii)]</td>
<td>1-Ethyl-2-thio-(1H)-4-[(1-ethyl-2-thio-(1H)-6-yl)]-amino-6-ethylamino-3-yl... s-triazine [15b(iii)]</td>
<td>68</td>
<td>235</td>
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<tr>
<td>50</td>
<td>2-Ethylamino-4-[(4-amino-6-t-butylimino-2-yl)-amino-6-t-butylimino-1,3,5-thiadiazine [8b(iv)]</td>
<td>1-t-Butyl-2-thio-(1H)-4-[(1-t-butyl-2-thio-(1H)-6-yl)]-amino-6-ethylamino-3-yl... s-triazine [15b(iv)]</td>
<td>77</td>
<td>247</td>
</tr>
<tr>
<td>51</td>
<td>2-p-Chlorophenylamino-4-[(4-amino-6-phenylimino-2-yl)-amino-6-phenylamino-1,3,5-thiadiazine [8c(i)]</td>
<td>1-Phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-6-yl)]-amino-6-p-chlorophenylamino-3-yl... s-triazine [15c(i)]</td>
<td>62</td>
<td>267</td>
</tr>
<tr>
<td>52</td>
<td>2-p-Chlorophenylamino-4-[(4-amino-6-p-chlorophenylimino-2-yl)-amino-6-p-chlorophenylamino-1,3,5-thiadiazine [8c(ii)]</td>
<td>1-p-Chlorophenyl-2-thio-(1H)-4-[(1-p-chlorophenyl-2-thio-(1H)-6-yl)]-amino-6-p-chlorophenylamino-3-yl... s-triazine [15c(ii)]</td>
<td>75</td>
<td>271</td>
</tr>
<tr>
<td>53</td>
<td>2-p-Chlorophenylamino-4-[(4-amino-6-ethylimino-2-yl)-amino-6-ethylamino-1,3,5-thiadiazine [8c(iii)]</td>
<td>1-Ethyl-2-thio-(1H)-4-[(1-ethyl-2-thio-(1H)-6-yl)]-amino-6-p-chlorophenylamino-3-yl... s-triazine [15c(iii)]</td>
<td>77</td>
<td>249</td>
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<td>54</td>
<td>2-p-Chlorophenylamino-4-[(4-amino-6-t-butylimino-2-yl)-amino-6-t-butylimino-1,3,5-thiadiazine [8c(iv)]</td>
<td>1-t-Butyl-2-thio-(1H)-4-[(1-t-butyl-2-thio-(1H)-6-yl)]-amino-6-p-chlorophenylamino-3-yl... s-triazine [15c(iv)]</td>
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<td>55</td>
<td>2-p-Tolylamino-4-[(4-amino-6-phenylimino-2-yl)-amino-6-phenylimino-1,3,5-thiadiazine [8d(i)]</td>
<td>1-Phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-6-yl)]-amino-6-p-tolylamino-3-yl... s-triazine [15d(i)]</td>
<td>69</td>
<td>251</td>
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<tr>
<td>56</td>
<td>2-p-Tolylamino-4-[(4-amino-6-p-chlorophenylimino-2-yl)-amino-6-p-chlorophenylimino-1,3,5-thiadiazine [8d(ii)]</td>
<td>1-p-Chlorophenyl-2-thio-(1H)-4-[(1-p-chlorophenyl-2-thio-(1H)-6-yl)]-amino-6-p-tolylamino-3-yl... s-triazine [15d(ii)]</td>
<td>66</td>
<td>279</td>
</tr>
<tr>
<td>57</td>
<td>2-p-Tolylamino-4-[(4-amino-6-ethylimino-2-yl)-amino-6-ethylamino-1,3,5-thiadiazine [8d(iii)]</td>
<td>1-Ethyl-2-thio-(1H)-4-[(1-ethyl-2-thio-(1H)-6-yl)]-amino-6-p-tolylamino-3-yl... s-triazine [15d(iii)]</td>
<td>71</td>
<td>221</td>
</tr>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
<td>(5)</td>
</tr>
<tr>
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<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>58</td>
<td>2-$p$-Tolylamino-4-[(4-amino-6-$t$-butylimino-...</td>
<td>1-$t$-Butyl-2-thio-(1H)-4-[(1-$t$-butyl-2-thio-(1H)-...</td>
<td>73</td>
<td>219</td>
</tr>
<tr>
<td></td>
<td>2-yl)-amino-6-$t$-butylimino-1,3,5-...</td>
<td>...6-yl)]-amino-6-$p$-tolylamino-3-yl)] s-triazine</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>thiazidazine [8d(iv)]</td>
<td>[15d(iv)]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>2-Methylamino-4-[(4-amino-6-phenylimino-...</td>
<td>1-Phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-...</td>
<td>74</td>
<td>231</td>
</tr>
<tr>
<td></td>
<td>2-yl)-amino-6-phenylimino-1,3,5-...</td>
<td>6-yl)]-amino-6-methylamino-3-yl)] s-triazine</td>
<td></td>
<td></td>
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<td>thiazidazine [8e(ii)]</td>
<td>[15e(i)]</td>
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<td>60</td>
<td>2-Methylamino-4-[(4-amino-6-$p$-chlorophenylimino...</td>
<td>1-$p$-Chlorophenyl-2-thio-(1H)-4-[(1-$p$-chlorophenyl...</td>
<td>67</td>
<td>251</td>
</tr>
<tr>
<td></td>
<td>2-yl)-amino-6-$p$-chlorophenylimino-1,3,5-...</td>
<td>2-thio-(1H)-6-yl)]-amino-6-methylamino-3-yl)...</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>thiazidazine [8e(ii)]</td>
<td>...s-triazine [15e(ii)]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>61</td>
<td>2-Methylamino-4-[(4-amino-6-ethylimino-...</td>
<td>1-Ethyl-2-thio-(1H)-4-[(1-ethyl-2-thio-(1H)-...</td>
<td>61</td>
<td>221</td>
</tr>
<tr>
<td></td>
<td>2-yl)-amino-6-ethylimino-1,3,5-...</td>
<td>6-yl)]-amino-6-methylamino-3-yl)] s-triazine</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>thiazidazine [8e(iii)]</td>
<td>[15e(iii)]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>62</td>
<td>2-$t$-Butylamino-4-[(4-amino-6-$t$-butylimino-...</td>
<td>1-$t$-Butyl-2-thio-(1H)-4-[(1-$t$-butyl-2-thio-(1H)-...</td>
<td>65</td>
<td>247</td>
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<tr>
<td></td>
<td>2-yl)-amino-6-$t$-butylimino-1,3,5-...</td>
<td>...6-yl)]-amino-6-methylamino-3-yl)] s-triazine</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>thiazidazine [8e(iv)]</td>
<td>[15e(iv)]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>63</td>
<td>2-$t$-Butylamino-4-[(4-amino-6-phenylimino-...</td>
<td>1-Phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-...</td>
<td>73</td>
<td>242</td>
</tr>
<tr>
<td></td>
<td>2-yl)-amino-6-phenylimino-1,3,5-...</td>
<td>6-yl)]-amino-6-$t$-butylamino-3-yl)] s-triazine</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>thiazidazine [8f(i)]</td>
<td>[15f(i)]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>64</td>
<td>2-$t$-Butylamino-4-[(4-amino-6-$p$-chlorophenylimino...</td>
<td>1-$p$-Chlorophenyl-2-thio-(1H)-4-[(1-$p$-chlorophenyl...</td>
<td>61</td>
<td>272</td>
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<td></td>
<td>2-yl)-amino-6-$p$-chlorophenylimino-1,3,5-...</td>
<td>2-thio-(1H)-6-yl)]-amino-6-$t$-butylamino-3-yl)...</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>thiazidazine [8f(ii)]</td>
<td>...s-triazine [15f(ii)]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>2-$t$-Butylamino-4-[(4-amino-6-ethylimino-...</td>
<td>1-Ethyl-2-thio-(1H)-4-[(1-ethyl-2-thio-(1H)-...</td>
<td>72</td>
<td>224</td>
</tr>
<tr>
<td></td>
<td>2-yl)-amino-6-ethylimino-1,3,5-...</td>
<td>6-yl)]-amino-6-$t$-butylamino-3-yl)] s-triazine</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>thiazidazine [8f(iii)]</td>
<td>[15f(iii)]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>66</td>
<td>2-$t$-Butylamino-4-[(4-amino-6-$t$-butylimino-...</td>
<td>1-$t$-Butyl-2-thio-(1H)-4-[(1-$t$-butyl-2-thio-(1H)-...</td>
<td>75</td>
<td>239</td>
</tr>
<tr>
<td></td>
<td>2-yl)-amino-6-$t$-butylimino-1,3,5-...</td>
<td>...6-yl)]-amino-6-$t$-butylamino-3-yl)] s-triazine</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>thiazidazine [8f(iv)]</td>
<td>[15f(iv)]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Gave satisfactory C, H, N and S analysis.*
[B] : Synthesis of 1-phenyl-2-thio-(1H)-4-[[1-phenyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-ethylamino-1,2-dihydro-s-triazine [15b(i)].

2-Ethylamino-4-[[4-amino-6-phenylimino-1,3,5-thiadiaz-2-yl)]-amino-6-phenylimino-1,3,5-thiadiazine [8b(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath. During heating the reactant went into solvent. After distillation of excess solvent, the brown crystals were isolated. It was recrystallized from glacial acetic acid to get [15b(i)], yield 69%, m.p. 232°C.

Properties of [15b(i)] :

1. It was brown crystalline solid having m.p. 232°C.
2. It gave positive test for nitrogen and sulphur.
3. It was found to be desulphurizable when boiled with alkaline plumbite solution.
4. It was soluble in benzene, DMF, acetic acid and acetone.
5. Diazotization Test :- It gave positive diazotization test indicating the presence of primary aromatic amino (–NH₂) group.
6. It formed picrate m.p. 228°C.
7. Elemental analysis :

<table>
<thead>
<tr>
<th>Elements</th>
<th>Found</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>53.32</td>
<td>53.45</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.09</td>
<td>4.24</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>28.01</td>
<td>28.06</td>
</tr>
<tr>
<td>Sulphur</td>
<td>14.19</td>
<td>14.25</td>
</tr>
</tbody>
</table>

8. From analytical data, the molecular formula was found to be $C_{26}H_{19}N_9S_2$. 

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9. **IR Spectrum**: The IR spectrum of compound [15b(i)] was carried out in KBr pellets and is reproduced on Plate No. IR-5.4. The important absorption can be correlated as follows.

<table>
<thead>
<tr>
<th>Absorption observed (cm⁻¹)</th>
<th>Assignment</th>
<th>Absorption expected (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3428.4</td>
<td>N-H stretching</td>
<td>3500-3100²⁸⁻³¹</td>
</tr>
<tr>
<td>3150.0</td>
<td>C-H (Ar) stretching</td>
<td>3150-3000³²</td>
</tr>
<tr>
<td>2752.4</td>
<td>C-H stretching</td>
<td>3000-2840³²</td>
</tr>
<tr>
<td>1641.7</td>
<td>C=N stretching</td>
<td>1789-1471³³</td>
</tr>
<tr>
<td>1570.2</td>
<td>&gt;C=NH (imino) grouping</td>
<td>1789-1471³³</td>
</tr>
<tr>
<td>1254.2</td>
<td>C-N stretching</td>
<td>1340-1250³⁴</td>
</tr>
<tr>
<td>1091.8</td>
<td>N &gt; C = S grouping</td>
<td>1200-1050³⁵⁻³⁶</td>
</tr>
<tr>
<td>721.6</td>
<td>C-S stretching</td>
<td>800-600³⁷</td>
</tr>
</tbody>
</table>

10. **PMR**: The PMR spectrum²⁹⁻³²,³³,³⁶ of compound [15b(i)] was carried out in DMSO-\(d_6\) and CDCl₃ and reproduced on Plate No. PMR-5.4. This spectrum distinctly displayed signals due to Ar-NH protons at \(\delta 8.32\) ppm, Ar-H protons at \(\delta 7.93-7.96\) ppm, triazino NH protons at \(\delta 7.60\) ppm, \(-\text{CH}_2\) protons at \(\delta 4.45-4.68\) ppm and \(-\text{CH}_3\) protons at \(\delta 0.87-1.49\) ppm. The signals at \(\delta 3.25\) ppm is due to moisture in DMSO-\(d_6\) and at \(\delta 2.01-2.04\) ppm are due to DMSO.

From the above properties and spectral analysis the compound [15b(i)] was assigned the structure as 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-ethylamino-1,2-dihydro-s-triazine.
Table - 5.4*

<table>
<thead>
<tr>
<th>S. N.</th>
<th>2-Substitutedamino-4-(4-substitutedamino-6-substitutedimino-1,3,5-thiadiaz-2-yl)-6-substitutedimino-1,3,5-thiadiazine (9)</th>
<th>1-Substituted-2-thio-(1H)-4-(1-substituted-2-thio-(1H)-4-substitutedamino-1,2-dihydro-s-triazin-6-yl)amino-6-substitutedamino-1,2-dihydro-s-triazine(16)</th>
<th>Yield (%)</th>
<th>m.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
<td>(5)</td>
</tr>
<tr>
<td>67</td>
<td>2-Phenylamino-4-(4-phenylamino-6-phenylimino-1,3,5-thiadiaz-2-yl)-6-phenylimino-1,3,5-thiadiazine (9a)</td>
<td>1-Phenyl-......(1-phenyl-2-......4-phenylimino-6-yl)amino-6-phenylamino......... s-triazine (16a)</td>
<td>69</td>
<td>262</td>
</tr>
<tr>
<td>68</td>
<td>2-Phenylamino-4-(4-p-chlorophenylamino-6-phenylimino-1,3,5-thiadiaz-2-yl)-6-phenylimino-1,3,5-thiadiazine (9b)</td>
<td>1-Phenyl-......(1-phenyl-2-......4-p-chlorophenylamino-6-yl)-amino-6-phenylamino......... s-triazine (16b)</td>
<td>62</td>
<td>254</td>
</tr>
<tr>
<td>69</td>
<td>2-Phenylamino-4-(4-p-tolylamino-6-phenylimino-1,3,5-thiadiaz-2-yl)-6-phenylimino-1,3,5-thiadiazine (9c)</td>
<td>1-Phenyl-......(1-phenyl-2-......4-p-tolylamino-6-yl)-amino-6-phenylamino......... s-triazine (16c)</td>
<td>68</td>
<td>259</td>
</tr>
<tr>
<td>70</td>
<td>2-Phenylamino-4-(4-ethylamino-6-phenylimino-1,3,5-thiadiaz-2-yl)-6-phenylimino-1,3,5-thiadiazine (9d)</td>
<td>1-Phenyl-......(1-phenyl-2-......4-ethylamino-6-yl)-amino-6-phenylamino......... s-triazine (16d)</td>
<td>71</td>
<td>261</td>
</tr>
<tr>
<td>71</td>
<td>2-Phenylamino-4-(4-methylamino-6-phenylimino-1,3,5-thiadiaz-2-yl)-6-phenylimino-1,3,5-thiadiazine (9e)</td>
<td>1-Phenyl-......(1-phenyl-2-......4-methylamino-6-yl)-amino-6-phenylamino......... s-triazine (16e)</td>
<td>73</td>
<td>274</td>
</tr>
<tr>
<td>72</td>
<td>2-Phenylamino-4-(4-t-butylamino-6-phenylimino-1,3,5-thiadiaz-2-yl)-6-phenylimino-1,3,5-thiadiazine (9f)</td>
<td>1-Phenyl-......(1-phenyl-2-......4-t-butylamino-6-yl)-amino-6-phenylamino......... s-triazine (16f)</td>
<td>65</td>
<td>271</td>
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</table>

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Chapter 5
<table>
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<th>(4)</th>
<th>(5)</th>
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<td>73</td>
<td>2-Allylamino-4-(4-phenylamino-6-phenylamino-1,3,5-thiadiaz-2-yl)-6-phenylamino-1,3,5-thiadiazine (9g)</td>
<td>1-Phenyl-......(1-phenyl-2-......4-phenylamino-6-yl)-amino-6-allylamino......... s-triazine (16g)</td>
<td>61</td>
<td>275</td>
</tr>
<tr>
<td>74</td>
<td>2-Allylamino-4-(4-p-chlorophenylamino-6-phenylamino-1,3,5-thiadiaz-2-yl)-6-phenylamino-1,3,5-thiadiazine (9h)</td>
<td>1-Phenyl-......(1-phenyl-2-......4-p-chlorophenylamino-6-yl)-amino-6-allylamino......... s-triazine (16h)</td>
<td>69</td>
<td>269</td>
</tr>
<tr>
<td>75</td>
<td>2-Allylamino-4-(4-p-tolylamino-6-phenylamino-1,3,5-thiadiaz-2-yl)-6-phenylamino-1,3,5-thiadiazine (9i)</td>
<td>1-Phenyl-......(1-phenyl-2-......4-p-tolylamino-6-yl)-amino-6-allylamino......... s-triazine (16i)</td>
<td>72</td>
<td>253</td>
</tr>
<tr>
<td>76</td>
<td>2-Allylamino-4-(4-ethylamino-6-phenylamino-1,3,5-thiadiaz-2-yl)-6-phenylamino-1,3,5-thiadiazine (9j)</td>
<td>1-Phenyl-......(1-phenyl-2-......4-ethylamino-6-yl)-amino-6-allylamino......... s-triazine (16j)</td>
<td>65</td>
<td>241</td>
</tr>
<tr>
<td>77</td>
<td>2-Allylamino-4-(4-methylamino-6-phenylamino-1,3,5-thiadiaz-2-yl)-6-phenylamino-1,3,5-thiadiazine (9k)</td>
<td>1-Phenyl-......(1-phenyl-2-......4-methylamino-6-yl)-amino-6-allylamino......... s-triazine (16k)</td>
<td>63</td>
<td>227</td>
</tr>
<tr>
<td>78</td>
<td>2-Allylamino-4-(4-t-butylamino-6-phenylamino-1,3,5-thiadiaz-2-yl)-6-phenylamino-1,3,5-thiadiazine (9l)</td>
<td>1-Phenyl-......(1-phenyl-2-......4-t-butylamino-6-yl)-amino-6-allylamino......... s-triazine (16l)</td>
<td>72</td>
<td>231</td>
</tr>
</tbody>
</table>

*Gave satisfactory C, H, N and S analysis.
Section - B :

In view of medicinal, pharmacological, agricultural and industrial importance of s-triazine, we explore direct procedure of 1-substituted-\((2H)\)-2-thio-4-(3-substitutedthiocarbamido-1-yl)-6-(2-imino-4-thio-5-substitutedbiureto-1-yl)-1,2-dihydro-s-triazine (17) and 1,3-Bis-(1-substituted-2-thio-(1H)-6-substitutedamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide (18).

The compound (17) and (18) were synthesized by the isomerisation of 2-(2-imino-4-thio-5-substitutedbiureto-1-yl)-4-(3-substitutedthiocarbamido-1-yl)-6-substitutedamino-1,3,5-thiadiazine (10) and 1,3-Bis-(2-substitutedamino-6-substitutedamino-1,3,5-thiadiaz-4-yl) thiocarbamide (11) in 5% aqueous ethanolic sodium bicarbonate solution as shown in Scheme Ve and Scheme Vf respectively.
SCHEME - Ve

\[
\begin{align*}
R-NH-C-NH-C-NH-C-NH-C-NH-R \\
S & S & S & NH & S \\
N-R_1
\end{align*}
\] (10)

Isomerisation

Aqueous ethanolic sodium bicarbonate

\[
\begin{align*}
R-NH-C-NH-C-NH-C-NH-C-NH-C-NH-R \\
S & S & S & NH & S \\
N-R_1
\end{align*}
\] (17)

Where,

\[\begin{align*}
R &= \text{phenyl, } p\text{-chlorophenyl, } \\
& \text{p-tolyl, ethyl, methyl, } \\
& t\text{-butyl}
\end{align*}\]

\[\begin{align*}
R_1 &= \text{phenyl, } p\text{-chlorophenyl, ethyl}
\end{align*}\]

SCHEME - Vf

\[
\begin{align*}
R-NH-C-NH-C-NH-C-NH-C-NH-R \\
S & S & S & NH & S \\
N-R_1
\end{align*}
\] (11)

Isomerisation

Aqueous ethanolic sodium bicarbonate

\[
\begin{align*}
R-NH-C-NH-C-NH-C-NH-C-NH-R \\
S & S & S & NH & S \\
N-R_1
\end{align*}
\] (18)

Where,

\[\begin{align*}
R &= \text{phenyl, } p\text{-chlorophenyl, } \\
& \text{p-tolyl, ethyl, methyl, } \\
& t\text{-butyl}
\end{align*}\]

\[\begin{align*}
R_1 &= \text{phenyl, } p\text{-chlorophenyl, ethyl}
\end{align*}\]
Synthesis of 1-substituted-(2H)-2-thio-4-(3-substitutedthiocarbamido-1-yl)-6-(2-imino-4-thio-5-substitutedbiureto-1-yl)-1,2-dihydro-s-triazine (17)

Synthesis of 1-ethyl-(2H)-2-thio-4-(3-phenylthiocarbamido-1-yl)-6-(2-imino-4-thio-5-phenylbiureto-1-yl)-1,2-dihydro-s-triazine [17a(iii)]

2-(2-imino-4-thio-5-phenylbiureto-1-yl)-4-[(3-phenylthio carbamido-1-yl)-6-ethylimino-1,3,5-thiadiazine [10a(iii)] (0.05 M) and was suspended in 5% aqueous ethanolic sodium bicarbonate solution and refluxed for 2 hr on water bath. During heating the reactant went into solvent. After distillation of excess solvent, the yellow crystalline solid were isolated. It was recrystallized from glacial acetic acid to get [17a(iii)], yield 71%, m.p. 243°C.

The probable reaction mechanism of the formation of [17a(iii)] may be stated as follows.
Properties of [17a(iii)] :

1. It was lemon yellow crystalline solid having m.p. 243°C.
2. It gave positive test for nitrogen and sulphur.
3. It was found to be desulphurizable when boiled with alkaline plumbite solution.
4. It was soluble in acetone, DMSO, benzene and acetic acid.
5. The benzene solution of compound when treated with pure and dry carbon disulphide a yellow colour was developed.\textsuperscript{26-27} This indicates the presence of basic imino group (=NH) in the compound.
6. It formed picrate m.p. 210°C.
7. Elemental analysis :

<table>
<thead>
<tr>
<th>Elements</th>
<th>Found</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>49.63</td>
<td>49.68</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.29</td>
<td>4.35</td>
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<tr>
<td>Nitrogen</td>
<td>26.08</td>
<td>26.09</td>
</tr>
<tr>
<td>Sulphur</td>
<td>19.79</td>
<td>19.88</td>
</tr>
</tbody>
</table>

8. From analytical data, the molecular formula was found to be $\text{C}_{20}\text{H}_{21}\text{N}_{9}\text{S}_{3}$.
9. \textbf{IR Spectrum} : The IR spectrum of compound [17a(iii)] was carried out in KBr pelletes and is reproduced on Plate No. IR-5.5. The important absorption can be correlated as follows.
<table>
<thead>
<tr>
<th>Absorption observed  (cm$^{-1}$)</th>
<th>Assignment</th>
<th>Absorption expected  (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3435.6</td>
<td>N–H stretching</td>
<td>3500-3100$^{28,31}$</td>
</tr>
<tr>
<td>2922.6</td>
<td>C–H stretching</td>
<td>3000-2840$^{32}$</td>
</tr>
<tr>
<td>1687.8</td>
<td>C=O stretching</td>
<td>1789-1471$^{33}$</td>
</tr>
<tr>
<td>1648.2</td>
<td>&gt;C=NH (imino) grouping</td>
<td>1789-1471$^{33}$</td>
</tr>
<tr>
<td>1508.5</td>
<td>C–H bending</td>
<td>1560-1375$^{32}$</td>
</tr>
<tr>
<td>1294.5</td>
<td>C–N stretching</td>
<td>1340-1250$^{34}$</td>
</tr>
<tr>
<td>1193.6</td>
<td>N &gt; C = S grouping</td>
<td>1200-1050$^{35,36}$</td>
</tr>
<tr>
<td>776.9</td>
<td>C–S stretching</td>
<td>800-600$^{17}$</td>
</tr>
</tbody>
</table>

10. **PMR**: The PMR spectrum$^{29,32,33,36}$ of compound [17a(iii)] was carried out in DMSO-$d_6$ and CDCl$_3$, and reproduced on Plate No. PMR-5.5. This spectrum distinctly displayed signals due to Ar–NH protons at $\delta$ 8.25-8.61 ppm, triazino NH protons at $\delta$ 7.89 ppm, Ar–H protons at $\delta$ 6.0-6.85 ppm, –CH$_2$ protons at $\delta$ 3.21-3.38 ppm and –CH$_3$ protons at $\delta$ 0.84-1.50 ppm. The signals at $\delta$ 2.53 ppm is due to moisture in DMSO and at $\delta$ 2.1 ppm is due to DMSO.

From the above properties and spectral analysis the compound [17a(iii)] was assigned the structure as 1-ethyl-(2H)-2-thio-4-(3-phenylthiocarbamido-1-yl)-6-(2-imino-4-thio-5-phenylbiureto-1-yl)-1,2-dihydro-s-triazine.
Similarly, the other triazines, [17a(i)] to [17f(iii)] were synthesized by isomerisation of other thiadiazines, [10a(i)] to [10f(iii)] in 5% aqueous ethanolic sodium bicarbonate solution and the related products were isolated in good yield and enlisted in Table No. 5.5.

Synthesis of 1,3-bis-(1-substituted-2-thio-(1H)-6-substitutedamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide (18):

Synthesis of 1,3-bis-(1-phenyl-2-thio-(1H)-6-phenylamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide [18a(i)].

1,3-Bis-(2-phenylamino-6-phenylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11a(i)] (0.05 M) and was suspended in 5% aqueous ethanolic sodium bicarbonate solution and refluxed for 2 hr on water bath. During heating the reactant went into solvent. After distillation of excess solvent, the ivory crystalline solid were isolated. It was recrystallized from glacial acetic acid to get [18a(i)], yield 61%, m.p. 294°C.

The probable reaction mechanism of the formation of [18a(i)] may be stated as follows.
<table>
<thead>
<tr>
<th>S. N.</th>
<th>2-(2-Imino-4-thio-5-Substitutedbiureto-1-yl)-4-(3-substitutedthiocarbamido-1-yl)-6-substitutedimino-1,3,5-thiadiazine (10)</th>
<th>1-Substituted-(2H)-2-thio-4-(3-substitutedthiocarbamido-1-yl)-6-(2-imino-4-thio-5-substitutedbiureto-1-yl)-1,2-dihydro-s-triazine (17)</th>
<th>Yield (%)</th>
<th>m.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
<td>(5)</td>
</tr>
<tr>
<td>79</td>
<td>2-(2-imino .........5-phenylbiureto-1-yl)-4-(3-phenyl .........1-yl)-6-phenylimino-1,3,5-thiadiazine [10a(i)]</td>
<td>1-Phenyl-......(3-phenyl-......1-yl)-6-(2-imino-......5-phenylbiureto-1-yl) ....... s-triazine [17a(i)]</td>
<td>65</td>
<td>236</td>
</tr>
<tr>
<td>80</td>
<td>2-(2-imino .........5-phenylbiureto-1-yl)-4-(3-phenyl .........1-yl)-6-p-chlorophenylimino-1,3,5-thiadiazine [10a(ii)]</td>
<td>1-p-Chlorophenyl-......(3-phenyl-......1-yl)-6-(2-imino-......5-phenylbiureto-1-yl) ....... s-triazine [17a(ii)]</td>
<td>69</td>
<td>261</td>
</tr>
<tr>
<td>81</td>
<td>2-(2-imino .........5-phenylbiureto-1-yl)-4-(3-phenyl .........1-yl)-6-ethylimino-1,3,5-thiadiazine [10a(iii)]</td>
<td>1-Ethyl-......(3-phenyl-......1-yl)-6-(2-imino-......5-phenylbiureto-1-yl) ....... s-triazine [17a(iii)]</td>
<td>71</td>
<td>243</td>
</tr>
<tr>
<td>82</td>
<td>2-(2-imino .........5-p-chlorophenylbiureto-1-yl)-4-(3-p-chlorophenyl .........1-yl)-6-phenylimino-1,3,5-thiadiazine [10b(i)]</td>
<td>1-Phenyl-......(3-p-chlorophenyl-......1-yl)-6-(2-imino-......5-p-chlorophenylbiureto-1-yl) ....... s-triazine [17b(i)]</td>
<td>67</td>
<td>255</td>
</tr>
<tr>
<td>83</td>
<td>2-(2-imino .........5-p-chlorophenylbiureto-1-yl)-4-(3-p-chlorophenyl .........1-yl)-6-p-chlorophenylimino-1,3,5-thiadiazine [10b(ii)]</td>
<td>1-p-Chlorophenyl-......(3-p-chlorophenyl-......1-yl)-6-(2-imino-......5-p-chlorophenylbiureto-1-yl) ....... s-triazine [17b(ii)]</td>
<td>72</td>
<td>258</td>
</tr>
<tr>
<td>84</td>
<td>2-(2-imino .........5-p-chlorophenylbiureto-1-yl)-4-(3-p-chlorophenyl .........1-yl)-6-ethylimino-1,3,5-thiadiazine [10b(iii)]</td>
<td>1-Ethyl-......(3-p-chlorophenyl-......1-yl)-6-(2-imino-......5-p-chlorophenylbiureto-1-yl) ....... s-triazine [17b(iii)]</td>
<td>71</td>
<td>241</td>
</tr>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
<td>(5)</td>
</tr>
<tr>
<td>------</td>
<td>------------------------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------------------------</td>
<td>-----</td>
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<tr>
<td>85</td>
<td>2-(2-imino.....5-p-tolylbiureto-1-yl)-4-(3-p-tolyl.....1-yl)-6-phenylimino-1,3,5-thiadiazine [10c(i)]</td>
<td>1-Phenyl.....(3-p-tolyl.....1-yl)-6-(2-imino.....5-p-tolylbiureto-1-yl) ...... s-triazine [17c(i)]</td>
<td>68</td>
<td>251</td>
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<tr>
<td>86</td>
<td>2-(2-imino.....5-p-tolylbiureto-1-yl)-4-(3-p-tolyl.....1-yl)-6-p-chlorophenylimino-1,3,5-thiadiazine [10c(ii)]</td>
<td>1-p-Chlorophenyl.....(3-p-tolyl.....1-yl)-6-(2-imino.....5-p-tolylbiureto-1-yl) ...... s-triazine [17c(ii)]</td>
<td>62</td>
<td>259</td>
</tr>
<tr>
<td>87</td>
<td>2-(2-imino.....5-p-tolylbiureto-1-yl)-4-(3-p-tolyl.....1-yl)-6-ethyliminono-1,3,5-thiadiazine [10c(iii)]</td>
<td>1-Ethyl.....(3-p-tolyl.....1-yl)-6-(2-imino.....5-p-tolylbiureto-1-yl) ...... s-triazine [17c(iii)]</td>
<td>71</td>
<td>241</td>
</tr>
<tr>
<td>88</td>
<td>2-(2-imino.....5-ethylbiureto-1-yl)-4-(3-ethyl.....1-yl)-6-phenylimino-1,3,5-thiadiazine [10d(i)]</td>
<td>1-Phenyl.....(3-ethyl.....1-yl)-6-(2-imino.....5-ethylbiureto-1-yl) ...... s-triazine [17d(i)]</td>
<td>65</td>
<td>241</td>
</tr>
<tr>
<td>89</td>
<td>2-(2-imino.....5-ethylbiureto-1-yl)-4-(3-ethyl.....1-yl)-6-p-chlorophenylimino-1,3,5-thiadiazine [10d(ii)]</td>
<td>1-p-Chlorophenyl.....(3-ethyl.....1-yl)-6-(2-imino.....5-ethylbiureto-1-yl) ...... s-triazine [17d(ii)]</td>
<td>69</td>
<td>249</td>
</tr>
<tr>
<td>90</td>
<td>2-(2-imino.....5-ethylbiureto-1-yl)-4-(3-ethyl.....1-yl)-6-ethyliminono-1,3,5-thiadiazine [10d(iii)]</td>
<td>1-Ethyl.....(3-ethyl.....1-yl)-6-(2-imino.....5-ethylbiureto-1-yl) ...... s-triazine [17d(iii)]</td>
<td>71</td>
<td>219</td>
</tr>
<tr>
<td>91</td>
<td>2-(2-imino.....5-methylbiureto-1-yl)-4-(3-methyl.....1-yl)-6-phenylimino-1,3,5-thiadiazine [10e(i)]</td>
<td>1-Phenyl.....(3-methyl.....1-yl)-6-(2-imino.....5-methylbiureto-1-yl) ...... s-triazine [17e(i)]</td>
<td>73</td>
<td>223</td>
</tr>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
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<tr>
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<td>----------------------------------------------------------------------</td>
<td>----------------------------------------------------------------------</td>
<td>-----</td>
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</tr>
<tr>
<td>92</td>
<td>2-(2-imino .........5-methylbiureto-1-yl)-4-(3-methyl .......1-yl)-6-p-chlorophenylimino-1,3,5-thiadiazine [10e(ii)]</td>
<td>1-p-Chlorophenyl-......(3-methyl-........1-yl)-6-(2-imino-......5-methylbiureto-1-yl) ..... s-triazine [17e(ii)]</td>
<td>63</td>
<td>235</td>
</tr>
<tr>
<td>93</td>
<td>2-(2-imino .........5-methylbiureto-1-yl)-4-(3-methyl .......1-yl)-6-ethylimino-1,3,5-thiadiazine [10e(iii)]</td>
<td>1-Ethyl-......(3-methyl-........1-yl)-6-(2-imino-......5-methylbiureto-1-yl) ..... s-triazine [17e(iii)]</td>
<td>74</td>
<td>217</td>
</tr>
<tr>
<td>94</td>
<td>2-(2-imino .........5-t-butylbiureto-1-yl)-4-(3-t-butyl .......1-yl)-6-phenylimino-1,3,5-thiadiazine [10f(ii)]</td>
<td>1-Phenyl-......(3-t-butyl-........1-yl)-6-(2-imino-......5-t-butylbiureto-1-yl) ..... s-triazine [17f(i)]</td>
<td>61</td>
<td>252</td>
</tr>
<tr>
<td>95</td>
<td>2-(2-imino .........5-t-butylbiureto-1-yl)-4-(3-t-butyl .......1-yl)-6-p-chlorophenylimino-1,3,5-thiadiazine [10f(ii)]</td>
<td>1-p-Chlorophenyl-......(3-t-butyl-........1-yl)-6-(2-imino-......5-t-butylbiureto-1-yl) ..... s-triazine [17f(ii)]</td>
<td>76</td>
<td>257</td>
</tr>
<tr>
<td>96</td>
<td>2-(2-imino .........5-t-butylbiureto-1-yl)-4-(3-t-butyl .......1-yl)-6-ethylimino-1,3,5-thiadiazine [10f(iii)]</td>
<td>1-Ethyl-......(3-t-butyl-........1-yl)-6-(2-imino-......5-t-butylbiureto-1-yl) ..... s-triazine [17f(iii)]</td>
<td>65</td>
<td>267</td>
</tr>
</tbody>
</table>

*Gave satisfactory C, H, N and S analysis.*
Properties of [18a(i)] :

1. It was ivory crystalline solid having m.p. 294°C.

2. It gave positive test for nitrogen and sulphur.

3. It was found to be desulphurizable when boiled with alkaline plumbite solution.

4. It was soluble in acetone, DMSO, DMF and acetic acid.

5. It formed picrate m.p. 257°C.

6. Elemental analysis :

<table>
<thead>
<tr>
<th>Elements</th>
<th>Found</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>58.42</td>
<td>58.86</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3.57</td>
<td>3.80</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>22.02</td>
<td>22.15</td>
</tr>
<tr>
<td>Sulphur</td>
<td>15.10</td>
<td>15.19</td>
</tr>
</tbody>
</table>

7. From analytical data, the molecular formula was found to be C_{31}H_{24}N_{10}S_{3}.
8. **IR Spectrum**: The IR spectrum of compound [18a(i)] was carried out in KBr pelletes and is reproduced on Plate No. IR-5.6. The important absorption can be correlated as follows.

<table>
<thead>
<tr>
<th>Absorption observed (cm⁻¹)</th>
<th>Assignment</th>
<th>Absorption expected (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3359.5</td>
<td>N–H stretching</td>
<td>3500-3100²⁸-³¹</td>
</tr>
<tr>
<td>2924.7</td>
<td>C–H (Ar) stretching</td>
<td>3150-3000³²</td>
</tr>
<tr>
<td>1642.2</td>
<td>C=N stretching</td>
<td>1789-1471³³</td>
</tr>
<tr>
<td>1506.1</td>
<td>&gt;C=NH (imino) grouping</td>
<td>1789-1471³³</td>
</tr>
<tr>
<td>1294.3</td>
<td>C–N stretching</td>
<td>1340-1250³⁴</td>
</tr>
<tr>
<td>1173.7</td>
<td>N &gt; C = S grouping</td>
<td>1200-1050³⁵-³⁶</td>
</tr>
<tr>
<td>778.2</td>
<td>C–S stretching</td>
<td>800-600³⁷</td>
</tr>
</tbody>
</table>

From the above properties and spectral analysis the compound [18a(i)] was assigned the structure as 1,3-bis-(1-phenyl-2-thio-(1H)-6-phenylamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide.

![Structural formula of 18a(i)](image)

Similarly, the other s-triazines, [18a(ii)] to [18f(iii)] were synthesised by isomerisation of other thiadiazines [11a(ii)] to [11f(iii)] in 5% ethanolic sodium bicarbonate and the related products were isolated in good yield and enlisted in Table No. 5.6.
<table>
<thead>
<tr>
<th>S. N.</th>
<th>1,3-Bis-(2-substitutedamino-6-substitutedimino-1,3,5-thiadiaz-4-yl) thiocarbamide (11)</th>
<th>1,3-Bis-(1-substituted-2-thio-(1H)-6-substitutedamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide (18)</th>
<th>Yield (%)</th>
<th>m.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>1,3-Bis-(2-phenylamino-6-phenylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11a(i)]</td>
<td>1,3-Bis-(1-phenyl-2-thio-(1H)-6-phenylimino-1,2-dihydro-s-triazin-4-yl) thiocarbamide [18a(i)]</td>
<td>61</td>
<td>294</td>
</tr>
<tr>
<td>97</td>
<td>1,3-Bis-(2-phenyl-6-p-chlorophenylimino-4-yl) thiocarbamide [11a(ii)]</td>
<td>1,3-Bis-(1-p-chlorophenyl-6-phenylimino-4-yl) thiocarbamide [18a(ii)]</td>
<td>67</td>
<td>251</td>
</tr>
<tr>
<td>98</td>
<td>1,3-Bis-(2-phenyl-6-ethyylimino-4-yl) thiocarbamide [11a(iii)]</td>
<td>1,3-Bis-(1-ethyl-6-phenylimino-4-yl) thiocarbamide [18a(iii)]</td>
<td>73</td>
<td>259</td>
</tr>
<tr>
<td>99</td>
<td>1,3-Bis-(2-p-chlorophenyl-6-phenylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11b(i)]</td>
<td>1,3-Bis-(1-phenyl-2-thio-(1H)-6-p-chlorophenyl-4-yl) thiocarbamide [18b(i)]</td>
<td>71</td>
<td>241</td>
</tr>
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<td>100</td>
<td>1,3-Bis-(2-p-chlorophenyl-6-p-chlorophenylimino-4-yl) thiocarbamide [11b(ii)]</td>
<td>1,3-Bis-(1-p-chlorophenyl-6-p-chlorophenylimino-4-yl) thiocarbamide [18b(ii)]</td>
<td>69</td>
<td>259</td>
</tr>
<tr>
<td>101</td>
<td>1,3-Bis-(2-p-chlorophenyl-6-ethylimino-4-yl) thiocarbamide [11b(iii)]</td>
<td>1,3-Bis-(1-ethyl-6-p-chlorophenylimino-4-yl) thiocarbamide [18b(iii)]</td>
<td>62</td>
<td>261</td>
</tr>
<tr>
<td>102</td>
<td>1,3-Bis-(2-p-tolylamino-6-phenylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11c(i)]</td>
<td>1,3-Bis-(1-phenyl-6-p-tolylamino-4-yl) thiocarbamide [18c(i)]</td>
<td>73</td>
<td>249</td>
</tr>
<tr>
<td>103</td>
<td>1,3-Bis-(2-p-tolyl-6-p-chlorophenylimino-4-yl) thiocarbamide [11c(ii)]</td>
<td>1,3-Bis-(1-p-chlorophenyl-6-p-tolylamino-4-yl) thiocarbamide [18c(ii)]</td>
<td>76</td>
<td>242</td>
</tr>
<tr>
<td>104</td>
<td>1,3-Bis-(2-p-tolyl-6-ethylimino-4-yl) thiocarbamide [11c(iii)]</td>
<td>1,3-Bis-(1-ethyl-6-p-tolylamino-4-yl) thiocarbamide [18c(iii)]</td>
<td>68</td>
<td>244</td>
</tr>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
<td>(5)</td>
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<td>-----</td>
<td>----------------------------------------------------------------------</td>
<td>----------------------------------------------------------------------</td>
<td>-----</td>
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</tr>
<tr>
<td>106</td>
<td>1,3-Bis-(2-ethylamino-6-phenylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11d(i)]</td>
<td>1,3-Bis-(1-phenyl-6-ethylamino-4-yl) thiocarbamide [18d(ii)]</td>
<td>70</td>
<td>259</td>
</tr>
<tr>
<td>107</td>
<td>1,3-Bis-(2-ethyl-6-p-chlorophenylimino-4-yl) thiocarbamide [11d(ii)]</td>
<td>1,3-Bis-(1-p-chlorophenyl-6-ethylamino-4-yl) thiocarbamide [18d(ii)]</td>
<td>79</td>
<td>262</td>
</tr>
<tr>
<td>108</td>
<td>1,3-Bis-(2-ethyl-6-ethylamino-4-yl) thiocarbamide [11d(iii)]</td>
<td>1,3-Bis-(1-ethyl-6-ethylamino-4-yl) thiocarbamide [18d(iii)]</td>
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<td>109</td>
<td>1,3-Bis-(2-methylamino-6-phenylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11e(i)]</td>
<td>1,3-Bis-(1-phenyl-6-methylamino-4-yl) thiocarbamide [18e(i)]</td>
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<td>237</td>
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<td>1,3-Bis-(2-methyl-6-p-chlorophenylimino-4-yl) thiocarbamide [11e(ii)]</td>
<td>1,3-Bis-(1-p-chlorophenyl-6-methylamino-4-yl) thiocarbamide [18e(ii)]</td>
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<td>215</td>
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<tr>
<td>111</td>
<td>1,3-Bis-(2-methyl-6-ethylamino-4-yl) thiocarbamide [11e(iii)]</td>
<td>1,3-Bis-(1-ethyl-6-methylamino-4-yl) thiocarbamide [18e(iii)]</td>
<td>65</td>
<td>237</td>
</tr>
<tr>
<td>112</td>
<td>1,3-Bis-(2-t-butylamino-6-phenylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11f(i)]</td>
<td>1,3-Bis-(1-phenyl-6-t-butylamino-4-yl) thiocarbamide [18f(i)]</td>
<td>71</td>
<td>247</td>
</tr>
<tr>
<td>113</td>
<td>1,3-Bis-(2-t-butyl-6-p-chlorophenylimino-4-yl) thiocarbamide [11f(ii)]</td>
<td>1,3-Bis-(1-p-chlorophenyl-6-t-butylamino-4-yl) thiocarbamide [18f(ii)]</td>
<td>73</td>
<td>236</td>
</tr>
<tr>
<td>114</td>
<td>1,3-Bis-(2-t-butyl-6-ethylamino-4-yl) thiocarbamide [11f(iii)]</td>
<td>1,3-Bis-(1-ethyl-6-t-butylamino-4-yl) thiocarbamide [18f(iii)]</td>
<td>63</td>
<td>213</td>
</tr>
</tbody>
</table>

*Gave satisfactory C, H, N and S analysis.
Section - C:

In view of medicinal, pharmacological, agricultural and industrial importance of s-triazines we explore direct method for synthesis of 1-substituted-2-thio-(1H)-4-(1-substitutedthiocarbamido-3-yl)-6-substitutedamino-1,2-dihydro-s-triazine (19).

The compound (19) was synthesised by the isomerisation of 2-substitutedamino-4-(1-substitutedthiocarbamido-3-yl)-6-substitutedimino-1,3,5-thiadiazine (12) in 5% aqueous ethanolic sodium bicarbonate solution as shown in Scheme Vg.

\[
\text{SCHEME - Vg}
\]

\[
\begin{align*}
\text{R-NH-C} & \text{C-NH-C-NH-R} \\
\text{S} & \text{N-R}_1 \\
\text{N} & \text{S} \\
\text{Isomerisation} & \text{Aqueous ethanolic sodium bicarbonate} \\
\rightarrow
\end{align*}
\]

Where,

\[
\begin{align*}
\text{R} &= \text{phenyl, } p\text{-chlorophenyl, } p\text{-tolyl, ethyl, methyl, } t\text{-butyl} \\
\text{R}_1 &= \text{phenyl, } p\text{-chlorophenyl, ethyl}
\end{align*}
\]
Synthesis of 1-substituted-2-thio-(1H)-4-(1-substitutedthiocarbamido-3-yl)-6-substitutedamino-1,2-dihydro-s-triazine (19):

Synthesis of 1-phenyl-2-thio-(1H)-4-(1-phenylthiocarbamidino-3-yl)-6-phenylamino-1,2-dihydro-s-triazine [19a(i)].

2-Phenylamino-4-(1-phenylthiocarbamido-3-yl)-6-phenylimino-1,3,5-thiadiazine [12a(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and refluxed for 2 hr on water bath. During heating the reactant went into solvent. After distillation of excess solvent, the pale yellow needle shape solid were isolated. It was recrystallized from glacial acetic acid to get [19a(i)], yield 71%, m.p. 227°C.

The probable reaction mechanism of the formation of [19a(i)] may be stated as follows.

Properties of [19a(i)]:
1. It was pale yellow needle shape crystalline solid having m.p. 227°C.
2. It gave positive test for nitrogen and sulphur.
3. It was found to be desulphurizable when boiled with alkaline plumbite solution.

4. It was soluble in acetone, DMSO, acetic acid and DMF.

5. It formed picrate m.p. 237°C.

6. Elemental analysis:

<table>
<thead>
<tr>
<th>Elements</th>
<th>Found</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>61.18</td>
<td>61.40</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.08</td>
<td>4.19</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>19.27</td>
<td>19.53</td>
</tr>
<tr>
<td>Sulphur</td>
<td>14.72</td>
<td>14.88</td>
</tr>
</tbody>
</table>

7. From analytical data, the molecular formula was found to be $C_{22}H_{18}N_6S_2$.

8. **IR Spectrum**: The IR spectrum of compound [19a(i)] was carried out in KBr pellets and is reproduced on Plate No. IR-5.7. The important absorption can be correlated as follows.

<table>
<thead>
<tr>
<th>Absorption observed (cm$^{-1}$)</th>
<th>Assignment</th>
<th>Absorption expected (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3338.3</td>
<td>N–H stretching</td>
<td>3500-3100$^{28-31}$</td>
</tr>
<tr>
<td>3149.6</td>
<td>C–H (Ar) stretching</td>
<td>3150-3000$^{32}$</td>
</tr>
<tr>
<td>1688.4</td>
<td>C=\textit{N} stretching</td>
<td>1789-1471$^{33}$</td>
</tr>
<tr>
<td>1634.3</td>
<td>\textit{C}=\textit{NH} (imino) grouping</td>
<td>1789-1471$^{33}$</td>
</tr>
<tr>
<td>1295.2</td>
<td>C–\textit{N} stretching</td>
<td>1340-1250$^{34}$</td>
</tr>
<tr>
<td>1198.6</td>
<td>$\text{N} ; \text{&gt; C = S}$ grouping</td>
<td>1200-1050$^{35-36}$</td>
</tr>
<tr>
<td>777.9</td>
<td>C–S stretching</td>
<td>800-600$^{37}$</td>
</tr>
</tbody>
</table>
9. **PMR**: The PMR spectrum\(^{29,32,33,36}\) of compound [19a(i)] was carried out in DMSO-\(d_6\) and CDCl\(_3\) and reproduced on Plate No. PMR-5.6. This spectrum distinctly displayed signals due to Ar–NH protons at \(\delta\) 8.52 ppm, NH protons at \(\delta\) 8.08-8.16 ppm and Ar–H protons at \(\delta\) 7.80 ppm. The signals at \(\delta\) 3.31 ppm is due to moisture in DMSO-\(d_6\) and at \(\delta\) 2.55-2.56 ppm is due to DMSO.

From the above properties and spectral analysis the compound [19a(i)] was assigned the structure as 1-phenyl-2-thio-(1H)-4-(1-phenyl-thiocarbamido-3-yl)-6-phenylamino-1,2-dihydro-s-triazine.

![Structure of [19a(i)]](image)

Similarly, the other s-triazines, [19a(ii)] to [19f(iii)] were synthesized by isomerisation of other thiadiazines [12a(ii)] to [12f(iii)] in 5% aqueous sodium bicarbonate solution and the related products were isolated in good yield and enlisted in Table No. 5.7.
<table>
<thead>
<tr>
<th>S. N.</th>
<th>2-substituted amino-4-(1-substituted thio-carbamido-3-yl)-6-substituted imino-1,3,5-thiadiazine (12)</th>
<th>1-Substituted-2-thio-(1H)-4-(1-substituted thio-carbamido-3-yl)-6-substituted amino-1,2-dihydro s-triazine (19)</th>
<th>Yield (%)</th>
<th>m.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>2-Phenylamino-4-(1-phenylthiocarbamido-3-yl)-6-phenylimino-1,3,5-thiadiazine [12a(i)]</td>
<td>1-Phenyl .......... 4-(1-phenyl .......... 3-yl)-6-phenyl .......... s-triazine [19a(i)]</td>
<td>71</td>
<td>227</td>
</tr>
<tr>
<td>117</td>
<td>2-Phenyl .......... 4-(1-phenyl .......... 3-yl)-6-ethyl .......... thiadiazine [12a(iii)]</td>
<td>1-Ethyl .......... 4-(1-phenyl .......... 3-yl)-6-phenyl .......... s-triazine [19a(iii)]</td>
<td>79</td>
<td>189</td>
</tr>
<tr>
<td>118</td>
<td>2-p-Chlorophenyl .......... 4-(1-p-chlorophenyl .......... 3-yl)-6-phenyl .......... thiadiazine [12b(i)]</td>
<td>1-Phenyl .......... 4-(1-p-chlorophenyl .......... 3-yl)-6-p-chlorophenyl .......... s-triazine [19b(i)]</td>
<td>73</td>
<td>197</td>
</tr>
<tr>
<td>120</td>
<td>2-p-Chlorophenyl .......... 4-(1-p-chlorophenyl .......... 3-yl)-6-ethyl .......... thiadiazine [12b(iii)]</td>
<td>1-Ethyl .......... 4-(1-p-chlorophenyl .......... 3-yl)-6-p-chlorophenyl .......... s-triazine [19b(iii)]</td>
<td>72</td>
<td>205</td>
</tr>
<tr>
<td>121</td>
<td>2-p-Tolyl .......... 4-(1-p-tolyl .......... 3-yl)-6-6-phenyl .......... thiadiazine [12c(i)]</td>
<td>1-Phenyl .......... 4-(1-p-tolyl .......... 3-yl)-6-p-tolyl .......... s-triazine [19c(i)]</td>
<td>64</td>
<td>213</td>
</tr>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
<td>(5)</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>123</td>
<td>2-&lt;t&gt;p&lt;/t&gt;-Tolyl -4-(1-&lt;t&gt;p&lt;/t&gt;-tolyl -3-yl)-6-ethyl thiadiazine [12c(iii)]</td>
<td>1-Ethyl -4-(1-&lt;t&gt;p&lt;/t&gt;-tolyl -3-yl)-6-p-tolyl s-triazine [19c(iii)]</td>
<td>58</td>
<td>191</td>
</tr>
<tr>
<td>124</td>
<td>2-Ethyl -4-(1-ethyl -3-yl)-6-6-phenyl thiadiazine [12d(ii)]</td>
<td>1-Phenyl -4-(1-ethyl -3-yl)-6-ethyl s-triazine [19d(ii)]</td>
<td>64</td>
<td>187</td>
</tr>
<tr>
<td>125</td>
<td>2-Ethyl -4-(1-ethyl -3-yl)-6-p-chlorophenyl thiadiazine [12d(ii)]</td>
<td>1-p-chlorophenyl -4-(1-ethyl -3-yl)-6-ethyl s-triazine [19d(ii)]</td>
<td>71</td>
<td>182</td>
</tr>
<tr>
<td>126</td>
<td>2-Ethyl -4-(1-ethyl -3-yl)-6-ethyl thiadiazine [12d(iii)]</td>
<td>1-Ethyl -4-(1-ethyl -3-yl)-6-ethyl s-triazine [19d(iii)]</td>
<td>69</td>
<td>179</td>
</tr>
<tr>
<td>127</td>
<td>2-Methyl -4-(1-methyl -3-yl)-6-6-phenyl thiadiazine [12e(i)]</td>
<td>1-Phenyl -4-(1-methyl -3-yl)-6-methyl s-triazine [19e(i)]</td>
<td>72</td>
<td>167</td>
</tr>
<tr>
<td>128</td>
<td>2-Methyl -4-(1-methyl -3-yl)-6-p-chlorophenyl thiadiazine [12e(ii)]</td>
<td>1-p-chlorophenyl -4-(1-methyl -3-yl)-6-methyl s-triazine [19e(ii)]</td>
<td>76</td>
<td>171</td>
</tr>
<tr>
<td>129</td>
<td>2-Methyl -4-(1-methyl -3-yl)-6-ethyl thiadiazine [12e(iii)]</td>
<td>1-Ethyl -4-(1-methyl -3-yl)-6-methyl s-triazine [19e(iii)]</td>
<td>68</td>
<td>168</td>
</tr>
<tr>
<td>130</td>
<td>2-t-Butyl -4-(1-t-butyl -3-yl)-6-6-phenyl thiadiazine [12f(i)]</td>
<td>1-Phenyl -4-(1-t-butyl -3-yl)-6-t-butyl s-triazine [19f(i)]</td>
<td>79</td>
<td>193</td>
</tr>
<tr>
<td>131</td>
<td>2-t-Butyl -4-(1-t-butyl -3-yl)-6-p-chlorophenyl thiadiazine [12f(ii)]</td>
<td>1-p-chlorophenyl -4-(1-t-butyl -3-yl)-6-t-butyl s-triazine [19f(ii)]</td>
<td>74</td>
<td>168</td>
</tr>
<tr>
<td>132</td>
<td>2-t-Butyl -4-(1-t-butyl -3-yl)-6-ethyl thiadiazine [12f(iii)]</td>
<td>1-Ethyl -4-(1-t-butyl -3-yl)-6-t-butyl s-triazine [19f(iii)]</td>
<td>67</td>
<td>177</td>
</tr>
</tbody>
</table>

*Gave satisfactory C, H, N and S analysis.*
Experimental

The melting points of all the synthesized compounds were recorded using hot paraffin bath and are uncorrected. The carbon and hydrogen analysis was carried out on Carlo-Ebra-1106 analyser, nitrogen estimation was carried out on Colman-N-analyser-29. IR spectra were recorded on Perkin Elmer spectrometer in the range 4000-400 cm⁻¹ in Nujol mul as KBr pellets. PMR spectra were recorded on Bruker AC-300F spectrometer with TMS as internal standard using DMSO-d₆ and CDCl₃ as solvent. The purity of the compound was checked on Silica Gel-G plates by TLC with layer thickness of 0.3 mm. All chemicals used were of AR grade (India Make).

Experiment No. 1:

Synthesis of 1-phenyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl) guanyl]-6-phenylamino-1,2-dihydro-s-triazine [13a(i)] :

2-Phenylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-phenylimino-1,3,5-thiadiazine [6a(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded pale yellow crystals of [13a(i)], yield 62%, m.p. 185°C.

Experiment No. 2:

Synthesis of 1-p-chlorophenyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl) guanyl]-6-phenylamino-1,2-dihydro-s-triazine [13a(ii)] :

2-Phenylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-p-chlorophenylimino-1,3,5-thiadiazine [6a(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13a(ii)], yield 59%, m.p. 191°C.
Experiment No. 3:
Synthesis of 1-ethyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl) guanyl]-6-phenylamino-1,2-dihydro-5-triazine [13a(iii)] :

2-Phenylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-ethylamino-1,3,5-thiadiazine [6a(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13a(iii)], yield 71%, m.p. 179°C.

Experiment No. 4:
Synthesis of 1-ethyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl) guanyl]-6-phenylamino-1,2-dihydro-5-triazine [13a(iv)] :

2-Phenylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-ethylamino-1,3,5-thiadiazine [6a(iv)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13a(iv)], yield 69%, m.p. 167°C.

Experiment No. 5:
Synthesis of 1-phenyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl) guanyl]-6-ethylamino-1,2-dihydro-5-triazine [13b(i)] :

2-Ethylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-phenylamino-1,3,5-thiadiazine [6b(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13b(i)], yield 63%, m.p. 182°C.

Experiment No. 6:
Synthesis of 1-p-chlorophenyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl) guanyl]-6-ethylamino-1,2-dihydro-5-triazine [13b(ii)] :

2-Ethylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-p-chlorophenylamino-1,3,5-thiadiazine [6b(ii)] (0.05 M) was suspended in 5%
aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13b(ii)], yield 75%, m.p. 194°C.

Experiment No. 7:

Synthesis of 1-ethyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-y1) guanyl]-6-ethylamino-1,2-dihydro-s-triazine [13b(iii)]:

2-Ethylamino-4-(2-imino-4-thiobiureto-5-y1-carbamidino)-6-ethylimino-1,3,5-thiadiazine [6b(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13b(iii)], yield 69%, m.p. 174°C.

Experiment No. 8:

Synthesis of 1-t-butyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-y1) guanyl]-6-ethylamino-1,2-dihydro-s-triazine [13b(iv)]:

2-Ethylamino-4-(2-imino-4-thiobiureto-5-y1-carbamidino)-6-t-butylimino-1,3,5-thiadiazine [6b(iv)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13b(iv)], yield 71%, m.p. 159°C.

Experiment No. 9:

Synthesis of 1-phenyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-y1) guanyl]-6-p-chlorophenylamino-1,2-dihydro-s-triazine [13c(i)]:

2-p-Chlorophenylamino-4-(2-imino-4-thiobiureto-5-y1-carbamidino)-6-phenylimino-1,3,5-thiadiazine [6c(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13c(i)], yield 65%, m.p. 192°C.
Experiment No. 10:

Synthesis of 1-p-chlorophenyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl)guanyl]-6-p-chlorophenylamino-1,2-dihydro-s-triazine [13c(ii)] :

2-p-Chlorophenylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-p-chlorophenylimino-1,3,5-thiadiazine [6c(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13c(ii)], yield 57%, m.p. 203°C.

Experiment No. 11:

Synthesis of 1-ethyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl)guanyl]-6-p-chlorophenylamino-1,2-dihydro-s-triazine [13c(iii)] :

2-p-Chlorophenylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-ethylimino-1,3,5-thiadiazine [6c(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13c(iii)], yield 58%, m.p. 195°C.

Experiment No. 12:

Synthesis of 1-t-butyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl)guanyl]-6-p-chlorophenylamino-1,2-dihydro-s-triazine [13c(iv)] :

2-p-Chlorophenylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-t-butylimino-1,3,5-thiadiazine [6c(iv)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13c(iv)], yield 71%, m.p. 181°C.
Experiment No. 13:
Synthesis of 1-phenyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl) guanyl]-6-p-tolylamino-1,2-dihydro-s-triazine [13d(i)]:

2-p-Tolylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-phenylamino-1,3,5-thiadiazine [6d(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13d(i)], yield 79%, m.p. 194°C.

Experiment No. 14:
Synthesis of 1-p-chlorophenyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl) guanyl]-6-p-tolylamino-1,2-dihydro-s-triazine [13d(ii)]:

2-p-Tolylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-p-chlorophenylamino-1,3,5-thiadiazine [6d(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13d(ii)], yield 65%, m.p. 209°C.

Experiment No. 15:
Synthesis of 1-ethyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl) guanyl]-6-p-tolylamino-1,2-dihydro-s-triazine [13d(iii)]:

2-p-Tolylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-ethylamino-1,3,5-thiadiazine [6d(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13d(iii)], yield 59%, m.p. 191°C.

Experiment No. 16:
Synthesis of 1-t-butyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl) guanyl]-6-p-tolylamino-1,2-dihydro-s-triazine [13d(iv)]:

2-p-Tolylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-t-butylamino-1,3,5-thiadiazine [6d(iv)] (0.05 M) was suspended in 5% aqueous
ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13d(iv)], yield 72%, m.p. 172°C.

Experiment No. 17 :

Synthesis of 1-phenyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl) guanyl]-6-methylamino-1,2-dihydro-s-triazine [13e(i)] :

2-Methylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-phenylimino-1,3,5-thiadiazine [6e(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13e(i)], yield 65%, m.p. 171°C.

Experiment No. 18 :

Synthesis of 1-p-chlorophenyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl) guanyl]-6-methylamino-1,2-dihydro-s-triazine [13e(ii)] :

2-Methylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-p-chlorophenylimino-1,3,5-thiadiazine [6e(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13e(ii)], yield 71%, m.p. 169°C.

Experiment No. 19 :

Synthesis of 1-ethyl-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl) guanyl]-6-methylamino-1,2-dihydro-s-triazine [13e(iii)] :

2-Methylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-ethylimino-1,3,5-thiadiazine [6e(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13e(iii)], yield 62%, m.p. 164°C.
Experiment No. 20:
Synthesis of 1-ß-butyl-2-thio-(1H)-4-[2-imino-4-thiobiureto-5-yl] guanyl]-6-methylamino-1,2-dihydro-s-triazine [13e(iv)] :

2-Methylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-ß-butylimino-1,3,5-thiadiazine [6e(iv)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13e(iv)], yield 68%, m.p. 174°C.

Experiment No. 21:
Synthesis of 1-phenyl-2-thio-(1H)-4-[2-imino-4-thiobiureto-5-yl] guanyl]-6-ß-butyliTnino-l,2-dihydr0-s-triazine [13f(i)] :

2-ß-Butylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-phenylimino-1,3,5-thiadiazine [6f(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13f(i)], yield 65%, m.p. 181°C.

Experiment No. 22:
Synthesis of 1-p-chlorophenyl-2-thio-(1H)-4-[2-imino-4-thiobiureto-5-yl] guanyl]-6-ß-butyIamino-1,2-dihydr0-s-triazine [13f(ii)] :

2-ß-Butylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-p-chlorophenylimino-1,3,5-thiadiazine [6f(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13f(ii)], yield 69%, m.p. 178°C.

Experiment No. 23:
Synthesis of 1-ethyl-2-thio-(1H)-4-[2-imino-4-thiobiureto-5-yl] guanyl]-6-ß-butyImino-1,2-dihydr0-s-triazine [13f(iii)] :

2-ß-Butylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-ethylimino-1,3,5-thiadiazine [6f(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13f(iii)], yield 68%, m.p. 178°C.
ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13f(iii)], yield 71%, m.p. 152°C.

Experiment No. 24:
Synthesis of 1-t-buty1-2-thio-(1H)-4-[(2-imino-4-thiobiureto-5-yl) guanyl]-6-t-buty1amino-1,2-dihydro-s-triazine [13f(iv)] :

2-t-Buty1amino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-t-buty1imino-1,3,5-thiadiazine [6f(iv)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [13f(iv)], yield 73%, m.p. 168°C.

Experiment No. 25:
Synthesis of 1-phenyl-2-thio-(1H)-4-(3-phenylthiocarbamido-1-yl)-6-(1-phenylguanidino-3-yl)-1,2-dihydro-s-triazine [14a(i)] :

2-(1-Phenylguanidino-3-yl)-4-(3-phenylthiocarbamidino-1-yl)-6-phenylimino-1,3,5-thiadiazine [7a(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [14a(i)], yield 61%, m.p. 258°C.

Experiment No. 26:
Synthesis of 1-ethyl-2-thio-(1H)-4-(3-phenylthiocarbamido-1-yl)-6-(1-phenylguanidino-3-yl)-1,2-dihydro-s-triazine [14a(ii)] :

2-(1-Phenylguanidino-3-yl)-4-(3-phenylthiocarbamidino-1-yl)-6-ethylimino-1,3,5-thiadiazine [7a(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [14a(ii)], yield 59%, m.p. 246°C.
Experiment No. 27:
Synthesis of 1-phenyl-2-thio-(1H)-4-(3-phenylthiocarbamido-1-yl)-6-(1-p-chlorophenylguanidino-3-yl)-1,2-dihydro-s-triazine [14b(i)]:

2-(1-p-chlorophenylguanidino-3-yl)-4-(3-phenylthiocarbamidino-1-yl)-6-phenylimino-1,3,5-thiadiazine [7b(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [14b(i)], yield 65%, m.p. 249°C.

Experiment No. 28:
Synthesis of 1-ethyl-2-thio-(1H)-4-(3-phenylthiocarbamido-1-yl)-6-(1-p-chlorophenylguanidino-3-yl)-1,2-dihydro-s-triazine [14b(ii)]:

2-(1-p-chlorophenylguanidino-3-yl)-4-(3-phenylthiocarbamidino-1-yl)-6-ethylimino-1,3,5-thiadiazine [7b(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [14b(ii)], yield 69%, m.p. 244°C.

Experiment No. 29:
Synthesis of 1-phenyl-2-thio-(1H)-4-(3-phenylthiocarbamido-1-yl)-6-(1-p-tolylguanidino-3-yl)-1,2-dihydro-s-triazine [14c(i)]:

2-(1-p-Tolylguanidino-3-yl)-4-(3-phenylthiocarbamidino-1-yl)-6-phenylimino-1,3,5-thiadiazine [7c(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [14c(i)], yield 72%, m.p. 262°C.

Experiment No. 30:
Synthesis of 1-ethyl-2-thio-(1H)-4-(3-phenylthiocarbamido-1-yl)-6-(1-p-tolylguanidino-3-yl)-1,2-dihydro-s-triazine [14c(ii)]:

2-(1-p-Tolylguanidino-3-yl)-4-(3-phenylthiocarbamidino-1-yl)-6-ethylimino-1,3,5-thiadiazine [7c(ii)] (0.05 M) was suspended in 5% aqueous ethanol...
ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [14c(ii)], yield 69%, m.p. 267°C.

Experiment No. 31:

Synthesis of 1-phenyl-2-thio-(1H)-4-(3-phenylthiocarbamido-1-yl)-6-(1-ethylguanidino-3-yl)-1,2-dihydro-s-triazine [14d(i)]:

2-(1-Ethylguanidino-3-yl)-4-(3-phenylthiocarbamidino-1-yl)-6-phenylimino-1,3,5-thiadiazine [7d(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [14d(i)], yield 73%, m.p. 256°C.

Experiment No. 32:

Synthesis of 1-ethyl-2-thio-(1H)-4-(3-phenylthiocarbamido-1-yl)-6-(1-ethylguanidino-3-yl)-1,2-dihydro-s-triazine [14d(ii)]:

2-(1-Ethylguanidino-3-yl)-4-(3-phenylthiocarbamidino-1-yl)-6-ethylimino-1,3,5-thiadiazine [7d(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [14d(ii)], yield 66%, m.p. 231°C.

Experiment No. 33:

Synthesis of 1-phenyl-2-thio-(1H)-4-(3-phenylthiocarbamido-1-yl)-6-(1-methylguanidino-3-yl)-1,2-dihydro-s-triazine [14e(i)]:

2-(1-Methylguanidino-3-yl)-4-(3-phenylthiocarbamidino-1-yl)-6-phenylimino-1,3,5-thiadiazine [7e(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [14e(i)], yield 65%, m.p. 221°C.
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Experiment No. 34:

Synthesis of 1-ethyl-2-thio-(1H)-4-(3-phenylthiocarbamido-1-yl)-6-(1-methylguanidino-3-yl)-1,2-dihydro-s-triazine [14e(ii)]

2-(1-Methylguanidino-3-yl)-4-(3-phenylthiocarbamidino-1-yl)-6-ethylimino-1,3,5-thiadiazine [7e(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [14e(ii)], yield 77%, m.p. 209°C.

Experiment No. 35:

Synthesis of 1-phenyl-2-thio-(1H)-4-(3-phenylthiocarbamido-1-yl)-6-(1-t-buty1guanidino-3-yl)-1,2-dihydro-s-triazine [14f(i)]

2-(1-t-Butylguanidino-3-yl)-4-(3-phenylthiocarbamidino-1-yl)-6-phenylimino-1,3,5-thiadiazine [7f(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [14f(i)], yield 70%, m.p. 219°C.

Experiment No. 36:

Synthesis of 1-ethyl-2-thio-(1H)-4-(3-phenylthiocarbamido-1-yl)-6-(1-t-buty1guanidino-3-yl)-1,2-dihydro-s-triazine [14f(ii)]

2-(1-t-Butylguanidino-3-yl)-4-(3-phenylthiocarbamidino-1-yl)-6-ethylimino-1,3,5-thiadiazine [7f(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [14f(ii)], yield 71%, m.p. 252°C.

Experiment No. 37:

Synthesis of 1-phenyl-2-thio-(1H)-4-(3-allylthiocarbamido-1-yl)-6-(1-phenylguanidino-3-yl)-1,2-dihydro-s-triazine (14g)

2-(1-Phenylguanidino-3-yl)-4-(3-allylthiocarbamidino-1-yl)-6-phenylimino-1,3,5-thiadiazine (7g) (0.05 M) was suspended in 5% aqueous
ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of (14g), yield 69%, m.p. 268°C.

Experiment No. 38:

Synthesis of 1-phenyl-2-thio-(1H)-4-(3-allylthiocarbamido-1-yl)-6-(1-p-chlorophenylguanidino-3-yl)-1,2-dihydro-s-triazine (14h):

2-(1-p-Chlorophenylguanidino-3-yl)-4-(3-allylthiocarbamidino-1-yl)-6-phenylimino-1,3,5-thiadiazine (7h) (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of (14h), yield 68%, m.p. 257°C.

Experiment No. 39:

Synthesis of 1-phenyl-2-thio-(1H)-4-(3-allylthiocarbamido-1-yl)-6-(1-p-tolylguanidino-3-yl)-1,2-dihydro-s-triazine (14i):

2-(1-p-Tolylguanidino-3-yl)-4-(3-allylthiocarbamidino-1-yl)-6-phenylimino-1,3,5-thiadiazine (7i) (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of (14i), yield 65%, m.p. 252°C.

Experiment No. 40:

Synthesis of 1-phenyl-2-thio-(1H)-4-(3-allylthiocarbamido-1-yl)-6-(1-ethylguanidino-3-yl)-1,2-dihydro-s-triazine (14j):

2-(1-Ethylguanidino-3-yl)-4-(3-allylthiocarbamidino-1-yl)-6-phenylimino-1,3,5-thiadiazine (7j) (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of (14j), yield 71%, m.p. 231°C.
**Experiment No. 41** :

Synthesis of 1-phenyl-2-thio-(1H)-4-(3-allylthiocarbamido-1-yl)-6-(1-methylguanidino-3-yl)-1,2-dihydro-s-triazine (14k) :

2-(1-Methylguanidino-3-yl)-4-(3-allylthiocarbamidino-1-yl)-6-phenylimino-1,3,5-thiadiazine (7k) (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of (14k), yield 73%, m.p. 219°C.

**Experiment No. 42** :

Synthesis of 1-phenyl-2-thio-(1H)-4-(3-allylthiocarbamido-1-yl)-6-(1-t-butylguanidino-3-yl)-1,2-dihydro-s-triazine (14l) :

2-(1-t-Butylguanidino-3-yl)-4-(3-allylthiocarbamidino-1-yl)-6-phenylimino-1,3,5-thiadiazine (7l) (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of (14l), yield 62%, m.p. 223°C.

**Experiment No. 43** :

Synthesis of 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-phenylamino-1,2-dihydro-s-triazine [15a(i)] :

2-Phenylamino-4-[(4-amino-6-phenylimino-1,3,5-thiadiaz-2-yl)]-amino-6-phenylimino-1,3,5-thiadiazine [8a(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15a(i)], yield 72%, m.p. 257°C.
Experiment No. 44:

Synthesis of $1\text{-}p\text{-}\text{chlorophenyl-2-thio-(1H)-4-}[[1\text{-}p\text{-}\text{chlorophenyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl}]\text{-amino-6-phenylamino-1,2-dihydro-s-triazine}}$ [15a(ii)]:

2-Phenylamino-4-[(4-amino-6-p-chlorophenylimino-1,3,5-thiadiaz-2-yl)]-amino-6-p-chlorophenylimino-1,3,5-thiadiazine [8a(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15a(ii)], yield 73%, m.p. 274°C.

Experiment No. 45:

Synthesis of $1\text{-}\text{ethyl-2-thio-(1H)-4-}[[1\text{-}\text{ethyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl}]\text{-amino-6-phenylamino-1,2-dihydro-s-triazine}}$ [15a(iii)]:

2-Phenylamino-4-[(4-amino-6-ethylimino-1,3,5-thiadiaz-2-yl)]-amino-6-ethylimino-1,3,5-thiadiazine [8a(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15a(iii)], yield 79%, m.p. 241°C.

Experiment No. 46:

Synthesis of $1\text{-}\text{t-butyl-2-thio-(1H)-4-}[[1\text{-}t\text{-}\text{butyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl}]\text{-amino-6-phenylamino-1,2-dihydro-s-triazine}}$ [15a(iv)]:

2-Phenylamino-4-[(4-amino-6-t-butylimino-1,3,5-thiadiaz-2-yl)]-amino-6-t-butylimino-1,3,5-thiadiazine [8a(iv)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15a(iv)], yield 81%, m.p. 243°C.
Experiment No. 47 :

Synthesis of 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-ethylamino-1,2-dihydro-s-triazine [15b(i)] :

2-Ethylamino-4-[-(4-amino-6-phenylimino-1,3,5-thiadiaz-2-yl)]-amino-6-phenylimino-1,3,5-thiadiazine [8b(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15b(i)], yield 69%, m.p. 232°C.

Experiment No. 48 :

Synthesis of 1-p-chlorophenyl-2-thio-(1H)-4-[(1-p-chlorophenyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-ethylamino-1,2-dihydro-s-triazine [15b(ii)] :

2-Ethylamino-4-[-(4-amino-6-p-chlorophenylimino-1,3,5-thiadiaz-2-yl)]-amino-6-p-chlorophenylimino-1,3,5-thiadiazine [8b(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15b(ii)], yield 72%, m.p. 261°C.

Experiment No. 49 :

Synthesis of 1-ethyl-2-thio-(1H)-4-[(1-ethyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-ethylamino-1,2-dihydro-s-triazine [15b(iii)] :

2-Ethylamino-4-[-(4-amino-6-ethylimino-1,3,5-thiadiaz-2-yl)]-amino-6-ethylimino-1,3,5-thiadiazine [8b(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15b(iii)], yield 68%, m.p. 235°C.
Experiment No. 50:

Synthesis of $1$-t-butyl-2-thio-(1H)-4-$ [(1$-t$)$-butyl-2-thio-(1H)-4-amino-1,2$-dihydro-s-triazin-6-yl)]$-amino-6-ethylamino$-1,2$-dihydro-s-triazine$ [15b(iv)]$:

$2$-Ethylamino-$4$-$[ (4$-amino-6-t$)butylimino-1,3,5$)$-thiadiaz-2-yl)]$-amino-6-t$-butylimino$-1,3,5$-thiadiazine$ [8b(iv)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15b(iv)], yield 77%, m.p. 247°C.

Experiment No. 51:

Synthesis of $1$-phenyl-2-thio-(1H)-4-$ [(1$-phenyl-2-thio-(1H)-4-amino-1,2$-dihydro-s-triazin-6-yl)]$-amino$-6$-p$-chlorophenylamino$-1,2$-dihydro-s-triazine$ [15c(i)]$:

$2$-p-Chlorophenylamino-$4$-$[ (4$-amino-6-phenylimino-1,3,5$)$-thiadiaz-2-yl)]$-amino$-6$-phenylimino$-1,3,5$-thiadiazine$ [8c(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15c(i)], yield 62%, m.p. 267°C.

Experiment No. 52:

Synthesis of $1$-p-chlorophenyl-2-thio-(1H)-4-$ [(1$-p$)$-chlorophenyl-2-thio-(1H)-4$-amino-1,2$-dihydro-s-triazin-6-yl)]$-amino-6-p$-chlorophenylamino$-1,2$-dihydro$-s$-triazine$ [15c(ii)]$:

$2$-p-Chlorophenylamino-$4$-$[ (4$-amino-6-p$-chlorophenylimino$-1,3,5$)-thiadiaz-2-yl)]$-amino$-6-p$-chlorophenylimino$-1,3,5$-thiadiazine$ [8c(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15c(ii)], yield 75%, m.p. 271°C.
Experiment No. 53:

Synthesis of 1-ethyl-2-thio-(1H)-4-[(1-ethyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-p-chlorophenylamino-1,2-dihydro-s-triazine [15c(iii)]:

2-p-Chlorophenylamino-4-[(4-amino-6-ethylimino-1,3,5-thiadiaz-2-yl)]-amino-6-ethylimino-1,3,5-thiadiazine [8c(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15c(iii)], yield 77%, m.p. 249°C.

Experiment No. 54:

Synthesis of 1-t-butyl-2-thio-(1H)-4-[(1-t-butyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-p-chlorophenylamino-1,2-dihydro-s-triazine [15c(iv)]:

2-p-Chlorophenylamino-4-[(4-amino-6-t-butylimino-1,3,5-thiadiaz-2-yl)]-amino-6-t-butylimino-1,3,5-thiadiazine [8c(iv)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15c(iv)], yield 62%, m.p. 242°C.

Experiment No. 55:

Synthesis of 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-p-tolylamino-1,2-dihydro-s-triazine [15d(i)]:

2-p-Tolylamino-4-[(4-amino-6-phenylimino-1,3,5-thiadiaz-2-yl)]-amino-6-phenylimino-1,3,5-thiadiazine [8d(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15d(i)], yield 69%, m.p. 251°C.
Experiment No. 56:

Synthesis of 1-\textit{p}-chlorophenyl-2-thio-(1H)-4-[(1-\textit{p}-chlorophenyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-\textit{p}-tolylamino-1,2-dihydro-s-triazine [15d(ii)] :

2-\textit{p}-Tolylamino-4-[(4-amino-6-\textit{p}-chlorophenylimino-1,3,5-thiadiaz-2-yl)]-amino-6-\textit{p}-chlorophenylimino-1,3,5-thiadiazine [8d(ii)] (0.05 M) was suspended in 5\% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15d(ii)], yield 66\%, m.p. 279°C.

Experiment No. 57:

Synthesis of 1-ethy1-2-thio-(1H)-4-[(1-ethyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-ethylamino-1,2-dihydro-s-triazine [15d(iii)] :

2-\textit{\beta}-Tolylamino-4-[(4-amino-6-ethylimino-1,3,5-thiadiaz-2-yl)]-amino-6-ethylimino-1,3,5-thiadiazine [8d(iii)] (0.05 M) was suspended in 5\% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15d(iii)], yield 71\%, m.p. 221°C.

Experiment No. 58:

Synthesis of 1-\textit{\beta}-butyl-2-thio-(1H)-4-[(1-\textit{\beta}-butyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-\textit{\beta}-butylamino-1,2-dihydro-s-triazine [15d(iv)] :

2-\textit{\beta}-Tolylamino-4-[(4-amino-6-\textit{\beta}-butylimino-1,3,5-thiadiaz-2-yl)]-amino-6-\textit{\beta}-butylimino-1,3,5-thiadiazine [8d(iv)] (0.05 M) was suspended in 5\% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15d(iv)], yield 73\%, m.p. 219°C.
Experiment No. 59:

Synthesis of 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-methylamino-1,2-dihydro-s-triazine [15e(i)]:

2-Methylamino-4-[(4-amino-6-phenylimino-1,3,5-thiadiaz-2-yl)]-amino-6-phenylimino-1,3,5-thiadiazine [8e(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15e(i)], yield 74%, m.p. 231°C.

Experiment No. 60:

Synthesis of 1-p-chlorophenyl-2-thio-(1H)-4-[(1-p-chlorophenyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-methylamino-1,2-dihydro-s-triazine [15e(ii)]:

2-Methylamino-4-[(4-amino-6-p-chlorophenylimino-1,3,5-thiadiaz-2-yl)]-amino-6-p-chlorophenylimino-1,3,5-thiadiazine [8e(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15e(ii)], yield 67%, m.p. 251°C.

Experiment No. 61:

Synthesis of 1-ethyl-2-thio-(1H)-4-[(1-ethyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-methylamino-1,2-dihydro-s-triazine [15e(iii)]:

2-Methylamino-4-[(4-amino-6-ethylimino-1,3,5-thiadiaz-2-yl)]-amino-6-ethylimino-1,3,5-thiadiazine [8e(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15e(iii)], yield 61%, m.p. 221°C.
Experiment No. 62:

Synthesis of 1-t-butyl-2-thio-(1H)-4-[(1-t-butyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-methylamino-1,2-dihydro-s-triazine [15e(iv)]:

2-Methylamino-4-[(4-amino-6-t-butylimino-1,3,5-thiadiaz-2-yl)]-amino-6-t-butylimino-1,3,5-thiadiazine [8e(iv)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15e(iv)], yield 65%, m.p. 247°C.

Experiment No. 63:

Synthesis of 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-t-butylamino-1,2-dihydro-s-triazine [15f(i)]:

2-t-Butylamino-4-[(4-amino-6-phenylimino-1,3,5-thiadiaz-2-yl)]-amino-6-phenylimino-1,3,5-thiadiazine [8f(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15f(i)], yield 73%, m.p. 242°C.

Experiment No. 64:

Synthesis of 1-p-chlorophenyl-2-thio-(1H)-4-[(1-p-chlorophenyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-t-butylamino-1,2-dihydro-s-triazine [15f(ii)]:

2-t-Butylamino-4-[(4-amino-6-p-chlorophenylimino-1,3,5-thiadiaz-2-yl)]-amino-6-p-chlorophenylimino-1,3,5-thiadiazine [8f(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15f(ii)], yield 61%, m.p. 272°C.
Experiment No. 65:

Synthesis of 1-ethyl-2-thio-(1H)-4-[(1-ethyl-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-t-butyramino-1,2-dihydro-s-triazine [15f(iii)]:

2-t-Butyramino-4-[(4-amino-6-ethyliminio-1,3,5-thiadiaz-2-yl)]-amino-6-ethyliminio-1,3,5-thiadiazine [8f(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15f(iii)], yield 72%, m.p. 224°C.

Experiment No. 66:

Synthesis of 1-t-buty1-2-thio-(1H)-4-[(1-t-buty1-2-thio-(1H)-4-amino-1,2-dihydro-s-triazin-6-yl)]-amino-6-t-butyramino-1,2-dihydro-s-triazine [15f(iv)]:

2-t-Butyramino-4-[(4-amino-6-t-butylinino-1,3,5-thiadiaz-2-yl)]-amino-6-t-butyrimino-1,3,5-thiadiazine [8f(iv)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [15f(iv)], yield 75%, m.p. 239°C.

Experiment No. 67:

Synthesis of 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-phenylamino-1,2-dihydro-s-triazin-6-yl)]-amino-6-phenylamino-1,2-dihydro-s-triazine (16a):

2-Phenylamino-4-(4-phenylamino-6-phenylimino-1,3,5-thiadiaz-2-yl)-6-phenylimino-1,3,5-thiadiazine (9a) (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of (16a), yield 69%, m.p. 262°C.
Experiment No. 68:

Synthesis of 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-p-chlorophenylamino-1,2-dihydro-s-triazin-6-yl)]-amino-6-phenylamino-1,2-dihydro-s-triazine (16b):

2-Phenylamino-4-(4-p-chlorophenylamino-6-phenylimino-1,3,5-thiadiaz-2-yl)-6-phenylimino-1,3,5-thiadiazine (9b) (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of (16b), yield 62%, m.p. 254°C.

Experiment No. 69:

Synthesis of 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-p-tolylamino-1,2-dihydro-s-triazin-6-yl)]-amino-6-phenylamino-1,2-dihydro-s-triazine (16c):

2-Phenylamino-4-(4-p-tolylamino-6-phenylimino-1,3,5-thiadiaz-2-yl)-6-phenylimino-1,3,5-thiadiazine (9c) (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of (16c), yield 68%, m.p. 259°C.

Experiment No. 70:

Synthesis of 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-ethylamino-1,2-dihydro-s-triazin-6-yl)]-amino-6-phenylamino-1,2-dihydro-s-triazine (16d):

2-Phenylamino-4-(4-ethylamino-6-phenylimino-1,3,5-thiadiaz-2-yl)-6-phenylimino-1,3,5-thiadiazine (9d) (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of (16d), yield 71%, m.p. 261°C.
Experiment No. 71:

Synthesis of 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-methylamino-1,2-dihydro-s-triazin-6-yl)]-amino-6-phenylamino-1,2-dihydro-s-triazine (16e):

2-Phenylamino-4-(4-methylamino-6-phenylimino-1,3,5-thiadiaz-2-yl)-6-phenylimino-1,3,5-thiadiazine (9e) (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of (16e), yield 73%, m.p. 274°C.

Experiment No. 72:

Synthesis of 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-β-butylamino-1,2-dihydro-s-triazin-6-yl)]-amino-6-phenylamino-1,2-dihydro-s-triazine (16f):

2-Phenylamino-4-(4-β-butylamino-6-phenylimino-1,3,5-thiadiaz-2-yl)-6-phenylimino-1,3,5-thiadiazine (9f) (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of (16f), yield 65%, m.p. 271°C.

Experiment No. 73:

Synthesis of 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-phenylamino-1,2-dihydro-s-triazin-6-yl)]-amino-6-allylamino-1,2-dihydro-s-triazine (16g):

2-Allylamino-4-(4-phenylamino-6-phenylimino-1,3,5-thiadiaz-2-yl)-6-phenylimino-1,3,5-thiadiazine (9g) (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of (16g), yield 61%, m.p. 275°C.
Experiment No. 74:

Synthesis of 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-p-chlorophenylamino-1,2-dihydro-s-triazin-6-yl)]-amino-6-allylamino-1,2-dihydro-s-triazine (16h):

2-Allylamino-4-(4-p-chlorophenylamino-6-phenylimino-1,3,5-thiadiaz-2-yl)-6-phenylimino-1,3,5-thiadiazine (9h) (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of (16h), yield 69%, m.p. 269°C.

Experiment No. 75:

Synthesis of 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-tolylamino-1,2-dihydro-s-triazin-6-yl)]-amino-6-allylamino-1,2-dihydro-s-triazine (16i):

2-Allylamino-4-(4-tolylamino-6-phenylimino-1,3,5-thiadiaz-2-yl)-6-phenylimino-1,3,5-thiadiazine (9i) (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of (16i), yield 72%, m.p. 253°C.

Experiment No. 76:

Synthesis of 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-ethylamino-1,2-dihydro-s-triazin-6-yl)]-amino-6-allylamino-1,2-dihydro-s-triazine (16j):

2-Allylamino-4-(4-ethylamino-6-phenylimino-1,3,5-thiadiaz-2-yl)-6-phenylimino-1,3,5-thiadiazine (9j) (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of (16j), yield 65%, m.p. 241°C.

Experiment No. 77:

Synthesis of 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-methylamino-1,2-dihydro-s-triazin-6-yl)]-amino-6-allylamino-1,2-dihydro-s-triazine (16k):

2-Allylamino-4-(4-methylamino-6-phenylimino-1,3,5-thiadiaz-2-yl)-6-phenylimino-1,3,5-thiadiazine (9k) (0.05 M) was suspended in 5% aqueous ethanol...
ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of (16k), yield 63%, m.p. 227°C.

Experiment No. 78:

Synthesis of 1-phenyl-2-thio-(1H)-4-[(1-phenyl-2-thio-(1H)-4-5-buty lamino-1,2-dihydro-s-triazin-6-yl)]- amino-6-allylamino-1,2-dihydro-s-triazine (16l) :

2-Allylamino-4-(4/-butylamino-6-phenylimino-1,3,5-thiadiaz-2-yl)-6-phenylimino-1,3,5-thiadiazine (9l) (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of (16l), yield 72%, m.p. 231°C.

Experiment No. 79:

Synthesis of 1-phenyl-(2H)-2-thio-4-(3-phenylthiocarbamido-1-yl)-6-(2-imino-4-thio-5-phenylbiureto-1-yl)-1,2-dihydro-s-triazine [17a(i)] :

2-(2-Imino-4-thio-5-phenylbiureto-1-yl)-4-(3-phenylthio carbamido-1-yl)-6-phenylimino-1,3,5-thiadiazine [10a(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [17a(i)], yield 65%, m.p. 230°C.

Experiment No. 80:

Synthesis of 1-p-chlorophenyl-(2H)-2-thio-4-(3-phenylthiocarbamido-1-yl)-6-(2-imino-4-thio-5-phenylbiureto-1-yl)-1,2-dihydro-s-triazine [17a(ii)] :

2-(2-Imino-4-thio-5-phenylbiureto-1-yl)-4-(3-phenylthio carbamido-1-yl)-6-p-chlorophenylimino-1,3,5-thiadiazine [10a(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [17a(ii)], yield 69%, m.p. 261°C.
Experiment No. 81:

Synthesis of 1-ethyl-(2H)-2-thio-4-(3-phenylthiocarbamido-1-yl)-6-(2-imino-4-thio-5-phenylbiureto-1-yl)-1,2-dihydro-s-triazine [17a(iii)]:

2-(2-Imino-4-thio-5-phenylbiureto-1-yl)-4-(3-phenylthiocarbamido-1-yl)-6-ethylimino-1,3,5-thiadiazine [10a(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [17a(iii)], yield 71%, m.p. 243°C.

Experiment No. 82:

Synthesis of 1-phenyl-(2H)-2-thio-4-(3-p-chlorophenylthiocarbamido-1-yl)-6-(2-imino-4-thio-5-p-chlorophenylbiureto-1-yl)-1,2-dihydro-s-triazine [17b(i)]:

2-(2-Imino-4-thio-5-p-chlorophenylbiureto-1-yl)-4-(3-p-chlorophenylthiocarbamido-1-yl)-6-phenylimino-1,3,5-thiadiazine [10b(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [17b(i)], yield 67%, m.p. 255°C.

Experiment No. 83:

Synthesis of 1-p-chlorophenyl-(2H)-2-thio-4-(3-p-chlorophenylthiocarbamido-1-yl)-6-(2-imino-4-thio-5-p-chlorophenylbiureto-1-yl)-1,2-dihydro-s-triazine [17b(ii)]:

2-(2-Imino-4-thio-5-p-chlorophenylbiureto-1-yl)-4-(3-p-chlorophenylthiocarbamido-1-yl)-6-p-chlorophenylimino-1,3,5-thiadiazine [10b(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [17b(ii)], yield 72%, m.p. 258°C.
Experiment No. 84:

Synthesis of 1-ethyl-(2H)-2-thio-4-(3-p-chlorophenylthiocarbamido-1-yl)-6-(2-imino-4-thio-5-p-chlorophenylbiureto-1-yl)-1,2-dihydro-s-triazine [17b(iii)] :

\[2-(2-Imino-4-thio-5-p-chlorophenylbiureto-1-yl)-4-(3-p-chlorophenylthiocarbamido-1-yl)-6-ethylimino-1,3,5-thiadiazine\] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [17b(iii)], yield 71%, m.p. 241°C.

Experiment No. 85:

Synthesis of 1-phenyl-(2H)-2-thio-4-(3-p-tolylthiocarbamido-1-yl)-6-(2-imino-4-thio-5-p-tolylbiureto-1-yl)-1,2-dihydro-s-triazine [17c(i)] :

\[2-(2-Imino-4-thio-5-p-tolylbiureto-1-yl)-4-(3-p-tolylthiocarbamido-1-yl)-6-phenylimino-1,3,5-thiadiazine\] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [17c(i)], yield 68%, m.p. 251°C.

Experiment No. 86:

Synthesis of 1-p-chlorophenyl-(2H)-2-thio-4-(3-p-tolylthiocarbamido-1-yl)-6-(2-imino-4-thio-5-p-tolylbiureto-1-yl)-1,2-dihydro-s-triazine [17c(ii)] :

\[2-(2-Imino-4-thio-5-p-tolylbiureto-1-yl)-4-(3-p-tolylthiocarbamido-1-yl)-6-p-chlorophenylimino-1,3,5-thiadiazine\] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [17c(ii)], yield 62%, m.p. 259°C.
Experiment No. 87:

Synthesis of 1-ethyl-(2H)-2-thio-4-(3-p-tolylthiocarbamido-1-yl)-6-(2-imino-4-thio-5-p-tolylbiureto-1-yl)-1,2-dihydro-s-triazine [17c(iii)] :

2-(2-Imino-4-thio-5-p-tolylbiureto-1-yl)-4-(3-p-tolylthiocarbamido-1-yl)-6-ethylimino-1,3,5-thiadiazine [10c(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [17c(iii)], yield 71%, m.p. 241°C.

Experiment No. 88:

Synthesis of 1-phenyl-(2H)-2-thio-4-(3-ethylthiocarbamido-1-yl)-6-(2-imino-4-thio-5-ethylbiureto-1-yl)-1,2-dihydro-s-triazine [17d(i)] :

2-(2-Imino-4-thio-5-ethylbiureto-1-yl)-4-(3-ethylthiocarbamido-1-yl)-6-phenylimino-1,3,5-thiadiazine [10d(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [17d(i)], yield 65%, m.p. 241°C.

Experiment No. 89:

Synthesis of 1-p-chlorophenyl-(2H)-2-thio-4-(3-ethylthiocarbamido-1-yl)-6-(2-imino-4-thio-5-ethylbiureto-1-yl)-1,2-dihydro-s-triazine [17d(ii)] :

2-(2-Imino-4-thio-5-ethylbiureto-1-yl)-4-(3-ethylthiocarbamido-1-yl)-6-p-chlorophenylimino-1,3,5-thiadiazine [10d(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [17d(ii)], yield 69%, m.p. 249°C.
Experiment No. 90:

Synthesis of 1-ethyl-(2H)-2-thio-4-(3-ethylthiocarbamido-1-yI)-6-(2-imino-4-thio-5-ethylbiureto-1-yl)-1,2-dihydro-s-triazine [17d(iii)]:

\[2-(2\text{-}\text{Imino}-4\text{-}\text{thio}-5\text{-}\text{ethylbiureto}-1\text{-}\text{yl})-4\text{-}(3\text{-}\text{ethylthiocarbamido}-1\text{-}\text{yl})-6\text{-}\text{ethylimino}-1,3,5\text{-}\text{thiadiazine} \] [10d(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [17d(iii)], yield 71%, m.p. 219°C.

Experiment No. 91:

Synthesis of 1-phenyl-(2H)-2-thio-4-(3-methylthiocarbamido-1-yI)-6-(2-imino-4-thio-5-methylbiureto-1-yl)-1,2-dihydro-s-triazine [17e(i)]:

\[2-(2\text{-}\text{Imino}-4\text{-}\text{thio}-5\text{-}\text{methylbiureto}-1\text{-}\text{yl})-4\text{-}(3\text{-}\text{methylthiocarbamido}-1\text{-}\text{yl})-6\text{-}\text{phenylimino}-1,3,5\text{-}\text{thiadiazine} \] [10e(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [17e(i)], yield 73%, m.p. 223°C.

Experiment No. 92:

Synthesis of 1-p-chlorophenyl-(2H)-2-thio-4-(3-methylthiocarbamido-1-yl)-6-(2-imino-4-thio-5-methylbiureto-1-yl)-1,2-dihydro-s-triazine [17e(ii)]:

\[2-(2\text{-}\text{Imino}-4\text{-}\text{thio}-5\text{-}\text{methylbiureto}-1\text{-}\text{yl})-4\text{-}(3\text{-}\text{methylthiocarbamido}-1\text{-}\text{yl})-6\text{-}p\text{-}\text{chlorophenylimino}-1,3,5\text{-}\text{thiadiazine} \] [10e(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [17e(ii)], yield 63%, m.p. 235°C.
Experiment No. 93:

Synthesis of 1-ethyl-(2H)-2-thio-4-(3-methylthiocarbamido-1-yl)-6-(2-imino-4-thio-5-methylbiureto-1-yl)-1,2-dihydro-s-triazine [17e(iii)]:

2-(2-imino-4-thio-5-methylbiureto-1-yl)-4-(3-methylthio carbamido-1-yl)-6-ethylimino-1,3,5-thiadiazine [10e(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [17e(iii)], yield 74%, m.p. 217°C.

Experiment No. 94:

Synthesis of 1-phenyl-(2H)-2-thio-4-(3-/-butylthiocarbamido-1-yl)-6-(2-imino-4-thio-5-/-butylbiureto-1-yl)-1,2-dihydro-s-triazine [17f(i)]:

2-(2-imino-4-thio-5-/-butylbiureto-1-yl)-4-(3-/-butylthio carbamido-1-yl)-6-phenylimino-1,3,5-thiadiazine [10f(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [17f(i)], yield 61%, m.p. 252°C.

Experiment No. 95:

Synthesis of 1-p-chlorophenyl-(2H)-2-thio-4-(3-/-butylthiocarbamido-1-yl)-6-(2-imino-4-thio-5-/-butylbiureto-1-yl)-1,2-dihydro-s-triazine [17f(ii)]:

2-(2-imino-4-thio-5-/-butylbiureto-1-yl)-4-(3-/-butylthio carbamido-1-yl)-6-p-chlorophenylimino-1,3,5-thiadiazine [10f(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [17f(ii)], yield 76%, m.p. 257°C.
Experiment No. 96:

Synthesis of 1-ethyl-(2H)-2-thio-4-(3-\(\tau\)-butylthiocarbamido-1-yl)-6-(2-imino-4-thio-5-\(\tau\)-butylbiureto-1-yl)-1,2-dihydro-s-triazine [17f(iii)]:

\[2-(2\text{-imino}-4\text{-thio}-5-\tau\text{-butylbiureto}-1\text{-yl})-4-(3-\tau\text{-butylthio carbamido}-1\text{-yl})-6\text{-ethylimino}-1,3,5\text{-thiadiazine} \equiv 10f(iii)\] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [17f(iii)], yield 65%, m.p. 267°C.

Experiment No. 97:

Synthesis of 1,3-bis-(1-phenyl-2-thio-(1H)-6-phenylamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide [18a(i)]:

1,3-Bis-(2-phenylamino-6-phenylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11a(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18a(i)], yield 61%, m.p. 294°C.

Experiment No. 98:

Synthesis of 1,3-bis-(1-p-chlorophenyl-2-thio-(1H)-6-phenylamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide [18a(ii)]:

1,3-Bis-(2-phenylamino-6-p-chlorophenylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11a(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18a(ii)], yield 67%, m.p. 251°C.
Experiment No. 99:
Synthesis of 1,3-bis-(1-ethyl-2-thio-(1H)-6-phenylamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide [18a(iii)]:

1,3-Bis-(2-phenylamino-6-ethylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11a(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18a(iii)], yield 73%, m.p. 259°C.

Experiment No. 100:
Synthesis of 1,3-bis-(1-phenyl-2-thio-(1H)-6-p-chlorophenylamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide [18b(i)]:

1,3-Bis-(2-p-chlorophenylamino-6-phenylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11b(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18b(i)], yield 71%, m.p. 241°C.

Experiment No. 101:
Synthesis of 1,3-bis-(1-p-chlorophenyl-2-thio-(1H)-6-p-chlorophenylamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide [18b(ii)]:

1,3-Bis-(2-p-chlorophenylamino-6-p-chlorophenylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11b(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18b(ii)], yield 69%, m.p. 259°C.

Experiment No. 102:
Synthesis of 1,3-bis-(1-ethyl-2-thio-(1H)-6-p-chlorophenylamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide [18b(iii)]:

1,3-Bis-(2-p-chlorophenylamino-6-ethylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11b(iii)] (0.05 M) was suspended in 5% aqueous ethanolic
sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18b(iii)], yield 62%, m.p. 261°C.

Experiment No. 103:

Synthesis of 1,3-bis-(1-phenyl-2-thio-(1H)-6-p-tolylamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide [18c(i)]:

1,3-Bis-(2-p-tolylamino-6-phenylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11c(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18c(i)], yield 73%, m.p. 249°C.

Experiment No. 104:

Synthesis of 1,3-bis-(1-p-chlorophenyl-2-thio-(1H)-6-p-tolylamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide [18c(ii)]:

1,3-Bis-(2-p-tolylamino-6-p-chlorophenylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11c(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18c(ii)], yield 76%, m.p. 242°C.

Experiment No. 105:

Synthesis of 1,3-bis-(1-ethyl-2-thio-(1H)-6-p-tolylamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide [18c(iii)]:

1,3-Bis-(2-p-tolylamino-6-ethylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11c(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18c(iii)], yield 68%, m.p. 244°C.
Experiment No. 106:

Synthesis of 1,3-bis-(1-phenyl-2-thio-(1H)-6-ethylamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide [18d(i)]:

1,3-Bis-(2-ethylamino-6-phenylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11d(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18d(i)], yield 70%, m.p. 259°C.

Experiment No. 107:

Synthesis of 1,3-bis-(1-p-chlorophenyl-2-thio-(1H)-6-ethylamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide [18d(ii)]:

1,3-Bis-(2-ethylamino-6-p-chlorophenylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11d(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18d(ii)], yield 79%, m.p. 262°C.

Experiment No. 108:

Synthesis of 1,3-bis-(1-ethyl-2-thio-(1H)-6-ethylamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide [18d(iii)]:

1,3-Bis-(2-ethylamino-6-ethylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11d(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18d(iii)], yield 65%, m.p. 231°C.

Experiment No. 109:

Synthesis of 1,3-bis-(1-phenyl-2-thio-(1H)-6-methylamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide [18e(i)]:

1,3-Bis-(2-methylamino-6-phenylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11e(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18e(i)], yield 75%, m.p. 258°C.
bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18e(i)], yield 63%, m.p. 237°C.

**Experiment No. 110 :**

Synthesis of 1,3-bis-(1-\(p\)-chlorophenyl-2-thio-(1H)-6-methylamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide [18e(ii)] :

1,3-Bis-(2-methylamino-6-\(p\)-chlorophenylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11e(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18e(ii)], yield 64%, m.p. 215°C.

**Experiment No. 111 :**

Synthesis of 1,3-bis-(1-ethyl-2-thio-(1H)-6-methylamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide [18e(iii)] :

1,3-Bis-(2-methylamino-6-ethylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11e(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18e(iii)], yield 65%, m.p. 237°C.

**Experiment No. 112 :**

Synthesis of 1,3-bis-(1-phenyl-2-thio-(1H)-6-\(t\)-butylamino-1,2-dihydro-s-triazin-4-yl) thiocarbamide [18f(i)] :

1,3-Bis-(2-\(t\)-butylamino-6-phenylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11f(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18f(i)], yield 71%, m.p. 247°C.
Experiment No. 113:
Synthesis of 1,3-bis-(1-p-chlorophenyl-2-thio-(1H)-6-β-butylamino-1,2-dihydros-triazin-4-yl) thiocarbamide [18f(ii)]:

1,3-Bis-(2-β-butylamino-6-p-chlorophenylimino-1,3,5-thiadiaz-4-y1) thiocarbamide [11f(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18f(ii)], yield 73%, m.p. 236°C.

Experiment No. 114:
Synthesis of 1,3-bis-(1-ethyl-2-thio-(1H)-6-β-butylamino-1,2-dihydros-triazin-4-yl) thiocarbamide [18f(iii)]:

1,3-Bis-(2-β-butylamino-6-ethylimino-1,3,5-thiadiaz-4-yl) thiocarbamide [11f(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [18f(iii)], yield 63%, m.p. 213°C.

Experiment No. 115:
Synthesis of 1-phenyl-2-thio-(1H)-4-(1-phenylthiocarbamido-3-yl)-6-phenylamino-1,2-dihydr0-s-triazine [19a(i)]:

2-Phenylamino-4-(1-phenylthiocarbamido-3-yl)-6-phenylimino-1,3,5-thiadiazine [12a(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [19a(i)], yield 71%, m.p. 227°C.

Experiment No. 116:
Synthesis of 1-p-chlorophenyl-2-thio-(1H)-4-(1-phenylthiocarbamido-3-yl)-6-phenylamino-1,2-dihydr0-s-triazine [19a(ii)]:

2-Phenylamino-4-(1-phenylthiocarbamido-3-yl)-6-p-chlorophenylimino-1,3,5-thiadiazine [12a(ii)] (0.05 M) was suspended in 5% aqueous...
ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [19a(ii)], yield 71%, m.p. 207°C.

Experiment No. 117:

Synthesis of 1-ethyl-2-thio-(1H)-4-(1-phenylthiocarbamido-3-yl)-6-phenylamino-1,2-dihydro-s-triazine [19a(iii)]:

2-Phenylamino-4-(1-phenylthiocarbamido-3-yl)-6-ethyliminono-1,3,5-thiadiazine [12a(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [19a(iii)], yield 79%, m.p. 189°C.

Experiment No. 118:

Synthesis of 1-phenyl-2-thio-(1H)-4-(1-p-chlorophenylthiocarbamido-3-yl)-6-p-chlorophenylamino-1,2-dihydro-s-triazine [19b(i)]:

2-p-Chlorophenylamino-4-(1-p-chlorophenylthiocarbamido-3-yl)-6-phenylimino-1,3,5-thiadiazine [12b(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [19b(i)], yield 73%, m.p. 197°C.

Experiment No. 119:

Synthesis of 1-p-chlorophenyl-2-thio-(1H)-4-(1-p-chlorophenylthiocarbamido-3-yl)-6-p-chlorophenylamino-1,2-dihydro-s-triazine [19b(ii)]:

2-p-Chlorophenylamino-4-(1-p-chlorophenylthiocarbamido-3-yl)-6-p-chlorophenylimino-1,3,5-thiadiazine [12b(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [19b(ii)], yield 69%, m.p. 212°C.
Experiment No. 120:

Synthesis of 1-ethyl-2-thio-(1H)-4-(1-p-chlorophenylthiocarbamido-3-yl)-6-p-chlorophenylamino-1,2-dihydro-s-triazine [19b(iii)]:

2-p-Chlorophenylamino-4-(1-p-chlorophenylthiocarbamido-3-yl)-6-ethylimino-1,3,5-thiadiazine [12b(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [19b(iii)], yield 72%, m.p. 205°C.

Experiment No. 121:

Synthesis of 1-phenyl-2-thio-(1H)-4-(1-p-tolylthiocarbamido-3-yl)-6-p-tolylamino-1,2-dihydro-s-triazine [19c(i)]:

2-p-Tolylamino-4-(1-p-tolylthiocarbamido-3-yl)-6-phenylimino-1,3,5-thiadiazine [12c(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [19c(i)], yield 64%, m.p. 213°C.

Experiment No. 122:

Synthesis of 1-p-chlorophenyl-2-thio-(1H)-4-(1-p-tolylthiocarbamido-3-yl)-6-p-tolylamino-1,2-dihydro-s-triazine [19c(ii)]:

2-p-Tolylamino-4-(1-p-tolylthiocarbamido-3-yl)-6-p-chlorophenylimino-1,3,5-thiadiazine [12c(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [19c(ii)], yield 69%, m.p. 221°C.

Experiment No. 123:

Synthesis of 1-ethyl-2-thio-(1H)-4-(1-p-tolylthiocarbamido-3-yl)-6-p-tolylamino-1,2-dihydro-s-triazine [19c(iii)]:

2-p-Tolylamino-4-(1-p-tolylthiocarbamido-3-yl)-6-ethylimino-1,3,5-thiadiazine [12c(iii)] (0.05 M) was suspended in 5% aqueous ethanolic
sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [19c(iii)], yield 58%, m.p. 191°C.

**Experiment No. 124:**

Synthesis of 1-phenyl-2-thio-(1H)-4-(1-ethylthiocarbamido-3-yl)-6-ethylamino-1,2-dihydro-s-triazine [19d(i)] :

2-Ethylamino-4-(1-ethylthiocarbamido-3-yl)-6-phenylimino-1,3,5-thiadiazine [12d(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [19d(i)], yield 64%, m.p. 187°C.

**Experiment No. 125:**

Synthesis of 1-/?-chlorophenyl-2-thio-(1H)-4-(1-ethylthiocarbamido-3-yl)-6-ethylamino-1,2-dihydro-s-triazine [19d(ii)] :

2-Ethylamino-4-(1-ethylthiocarbamido-3-yl)-6-/?-chlorophenylimino-1,3,5-thiadiazine [12d(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [19d(ii)], yield 71%, m.p. 182°C.

**Experiment No. 126:**

Synthesis of 1-ethyl-2-thio-(1H)-4-(1-ethylthiocarbamido-3-yl)-6-ethylamino-1,2-dihydro-s-triazine [19d(iii)] :

2-Ethylamino-4-(1-ethylthiocarbamido-3-yl)-6-ethylimino-1,3,5-thiadiazine [12d(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [19d(iii)], yield 69%, m.p. 179°C.
Experiment No. 127 :

Synthesis of 1-phenyl-2-thio-(1H)-4-(1-methylthiocarbamido-3-yI)-6-methylamino-1,2-dihydro-s-triazine [19e(i)] :

2-Methylamino-4-(1-methylthiocarbamido-3-yI)-6-phenylimino-1,3,5-thiadiazine [12e(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [19e(i)], yield 72%, m.p. 167°C.

Experiment No. 128 :

Synthesis of 1-p-chlorophenyl-2-thio-(1H)-4-(1-methylthiocarbamido-3-yI)-6-methylamino-1,2-dihydro-s-triazine [19e(ii)] :

2-Methylamino-4-(1-methylthiocarbamido-3-yI)-6-p-chlorophenylimino-1,3,5-thiadiazine [12e(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [19e(ii)], yield 76%, m.p. 171°C.

Experiment No. 129 :

Synthesis of 1-ethyl-2-thio-(1H)-4-(1-methylthiocarbamido-3-yI)-6-methylamino-1,2-dihydro-s-triazine [19e(iii)] :

2-Methylamino-4-(1-methylthiocarbamido-3-yI)-6-ethylimino-1,3,5-thiadiazine [12e(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [19e(iii)], yield 68%, m.p. 168°C.
Experiment No. 130:

Synthesis of 1-phenyl-2-thio-(1H)-4-(1-t-butyIthiocarbamido-3-yl)-6-t-butyIamino-1,2-dihydro-s-triazine [19f(i)]:

2-t-Butylamino-4-(1-t-butyIthiocarbamido-3-yl)-6-phenylimino-1,3,5-thiadiazine [12f(i)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [19f(i)], yield 79%, m.p. 193°C.

Experiment No. 131:

Synthesis of 1-p-chlorophenyl-2-thio-(1H)-4-(1-t-butyIthiocarbamido-3-yl)-6-t-butyIamino-1,2-dihydro-s-triazine [19f(ii)]:

2-t-Butylamino-4-(1-t-butyIthiocarbamido-3-yl)-6-p-chlorophenylimino-1,3,5-thiadiazine [12f(ii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [19f(ii)], yield 74%, m.p. 168°C.

Experiment No. 132:

Synthesis of 1-ethyl-2-thio-(1H)-4-(1-t-butyIthiocarbamido-3-yl)-6-t-butyIamino-1,2-dihydro-s-triazine [19f(iii)]:

2-t-Butylamino-4-(1-t-butyIthiocarbamido-3-yl)-6-ethylimino-1,3,5-thiadiazine [12f(iii)] (0.05 M) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and was refluxed for 2 hr on water bath afforded crystals of [19f(iii)], yield 67%, m.p. 177°C.
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