

## A novel synthesis of 1,4-Bis[(Substitutedphenyl)-2,4-Dithiobiureto] benzene

M. S. Lunge <sup>1,\*</sup>, Faiza Tasmeeen F Shah <sup>1</sup>, M.B. Shahakar <sup>2</sup> and P.V. Raut <sup>3</sup>

<sup>1</sup> Department of Chemistry, Jagadamba Mahavidyalaya, Achalpur (City), M.S., India.

<sup>2</sup> Department of Chemistry, G. V. I. S. H., Amravati (M.S.), India.

<sup>3</sup> Department of Chemistry, Smt. Rabhabai Sarada Arts, Commerce and Science College, Anjangaon Surji, M.S., India.

International Journal of Science and Research Archive, 2023, 09(01), 328–337

Publication history: Received on 13 April 2023; revised on 25 May 2023; accepted on 27 May 2023

Article DOI: <https://doi.org/10.30574/ijrsra.2023.9.1.0404>

### Abstract

Recently in this laboratory, a direct, suitable and simple method for the synthesis of 1,4-bis[(substituted phenyl)-2,4-dithiobiureto]benzene (III a-d). A novel series of 1,4-Bis[(substituted phenyl)-2,4-dithiobiureto]benzene (III a-d) was synthesized by the interacting 1,4-dithiocarbamidobenzene (I) with substituted phenylisothiocyanates (II a-d) in acetone-ethanol medium on water bath for 4 hours. The structure of the synthesized compounds was justified on the basis of chemical characteristics, elemental and spectral analysis.

**Keywords:** 1,4-dithiocarbamidobenzene; Substituted phenylisothiocyanates; Acetone; Ethanol; Etc.

### 1. Introduction

Thiocarbamido, dithiobiureto and triazino nucleus containing drugs possess an important applications and significances in medicinal, pharmaceutical, industrial, agricultural and biochemical sciences<sup>1-8</sup>. The important reactions of amino compounds have been briefly investigate by Pandey<sup>9</sup>, Pathe<sup>10</sup>, Berad<sup>11</sup>, Aprajit<sup>12</sup>, Tayade<sup>13</sup>, Deohate<sup>14</sup> and Bhagwatkar<sup>15</sup> for the synthesis of several 5, 6 and 7 membered nitrogen, nitrogen and sulphur containing heterocycles with several references to 1,2,4-triazoles, 1,3,5-thiadiazolidines, 1,3,5-dithiazines, 1,3,5-thiadiazines and s-triazines. These molecules possess various medicinal, agricultural, industrial and biochemical applications and importance, hence the present research scheme was designed to describe somewhat suitable and direct method for a synthesis of the novel 1,4-Bis[(substitutedphenyl)-2,4-dithiobiureto]benzene (III a-d).

### 2. Experimental Method

The melting points of all synthesized compounds were recorded using hot paraffin bath. The carbon and Hydrogen analysis was carried out on Carlo-Ebra 1106 analyzer. Nitrogen estimation was carried out n colman-N-analyzer-29. IR spectra were recorded on Shemadzu spectrometer and the range 4000-400 cm<sup>-1</sup> in KBr pellets. PMR spectra were recorded on Bruker AC-300F spectrometer with TMS as internal standard using CDCl<sub>3</sub> and DMSO-d<sub>6</sub> as solvent. The Gel-G plates by TLC with layer thickness of 0.3 mm. All chemical used were of AR grades (India Made).

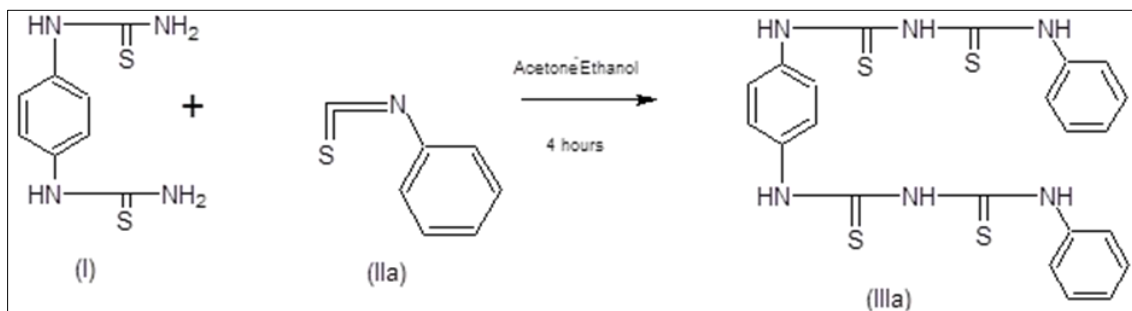
### 3. Result and Discussion

#### 3.1. Synthesis of 1,4-Bis[(S-phenyl)-2,4-dithiobiureto]benzene (IIIa):

1,4-Bis[(S-phenyl)-2,4-dithiobiureto]benzene (IIIa) was synthesized by refluxing the mixture of 1,4-dithiocarbamidobenzene (I) with phenyl isothiocyanate (IIa) in 1:2 molar proportion in acetone-ethanol medium for 4

\*Corresponding author: Mithun Sudhakrrao Lunge

hours on water bath, faint yellow coloured crystals were separated out. They were filtered and dried at room condition. Recrystallised from ethanol, Yield 85%.



**Scheme-1**

### 3.2. Properties of (IIIa)

It was faint yellow crystalline solid having m. p. 180°C. It gave positive test for nitrogen and sulphur elements. It was desulphurized by alkaline plumbite solution. It was soluble in ethanol, acetone while insoluble in benzene. It formed picrate having m. p. 167°C. From the analytical data the molecular formula was found to be C<sub>22</sub>H<sub>20</sub>N<sub>6</sub>S<sub>4</sub>.

#### 3.2.1. IR Spectrum<sup>16-17</sup>

IR spectrum of compound (IIIa) was carried out in KBr-pellets and is reproduced on Plate No. IR FTS-2. The important absorptions are correlated as follows and are depicted in Table No. 1

**Table 1** The important absorptions

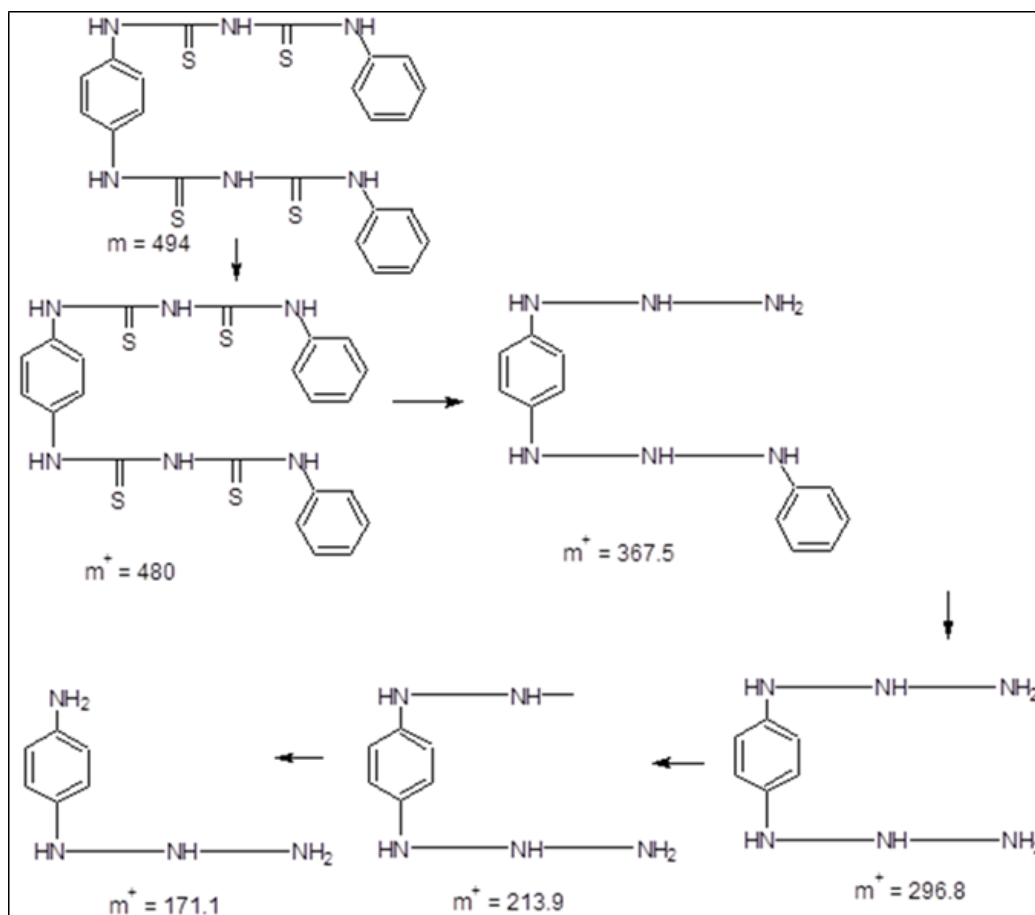
Sr. No.	Absorption observed(cm-1)	Assignment	Absorption expected (cm-1)
1	3395.83	C-H (Ar) (S)	3500-3000
2	1608.70	C = NH (imino group)	1989-1471
3	1092.72	C=S stretching	1200-1050
4	1665.00	N-H stretching	1789-1471
6	1047.39	C-N stretching (ali)	1000-1250

#### 3.2.2PMR Spectrum

PMR Spectrum<sup>18-19</sup> of a compound (3a) was carried out in DMSO-d<sub>6</sub>-CDCl<sub>3</sub> and reproduced on Plate No. PMR FTS-2. This spectrum distinctly displayed the signals due to Ar-H/ pyridino protons at δ 7.2599 ppm, -NH (Ar) protons δ 4.7212-4.6786 ppm and -NH (C-NH-C) protons at δ 1.5596-1.2324 ppm.

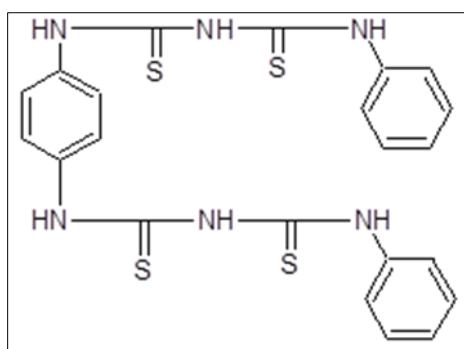
#### 3.2.3Mass spectrum<sup>19-20</sup>

The Mass analysis of the compound was carried out and reproduced on Mass Plate No. FTS-2. The fragmentation occurs during the analysis is given in Mass Scheme-I.



**Figure 1** Mass Scheme (IIIa)

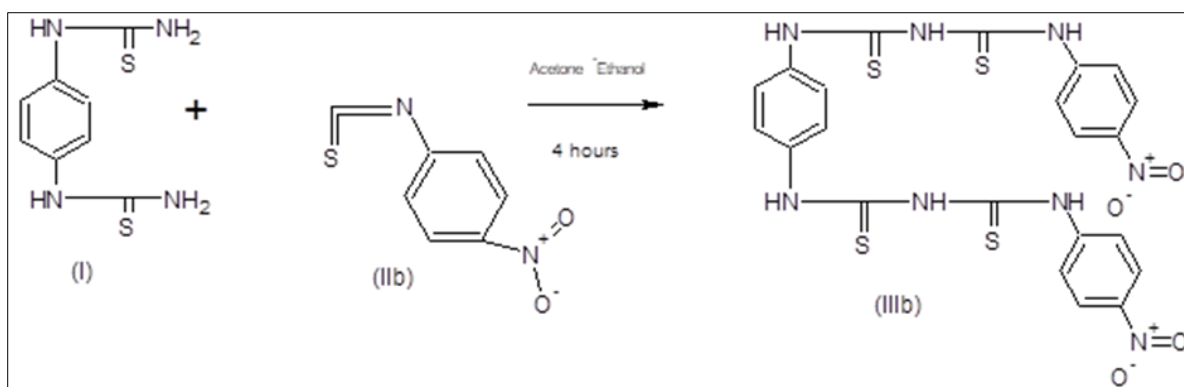
From the above chemical characteristics and analysis, the compound (IIIa) was assigned the structures as 1,4-bis[(S-phenyl)-2,4-dithiobiureto]benzene (IIIa).



**Figure 2** Structure of (IIIa)

### 3.3. Synthesis of 1,4-Bis[(4-nitrophenyl)-2,4-dithiobiureto]benzene(IIIb):

1,4-Bis[(S-phenyl)-2,4-dithiobiureto]benzene (IIIb) was synthesized by refluxing the mixture of 1,4-dithiocarbamidobenzene (I) with 4-nitrophenyl isothiocyanate (IIb) in 1:2 molar proportion in acetone-ethanol medium for 4 hours on water bath, brown coloured crystals were separated out. They were filtered and dried at room condition. Recrystallized from ethanol, Yield 80%.



Scheme-2

### 3.4. Properties of (IIIb)

It was brown crystalline solid having m. p. 165<sup>o</sup>C. It gave positive test for nitrogen and sulphur elements. It was desulphurized by alkaline plumbite solution. It was soluble in ethanol while insoluble in benzene. It formed picrate having m. p. 150<sup>o</sup> C. From the analytical data the molecular formula was found to be C<sub>22</sub>H<sub>18</sub>N<sub>8</sub>S<sub>4</sub>.

#### 3.4.1. IR Spectrum<sup>16-17</sup>

IR spectrum of compound (3b) was carried out in KBr-pellets and is reproduced on Plate No. IR FTS-3. The important absorptions are correlated as follows and are depicted in Table No. 2

Table No. 2

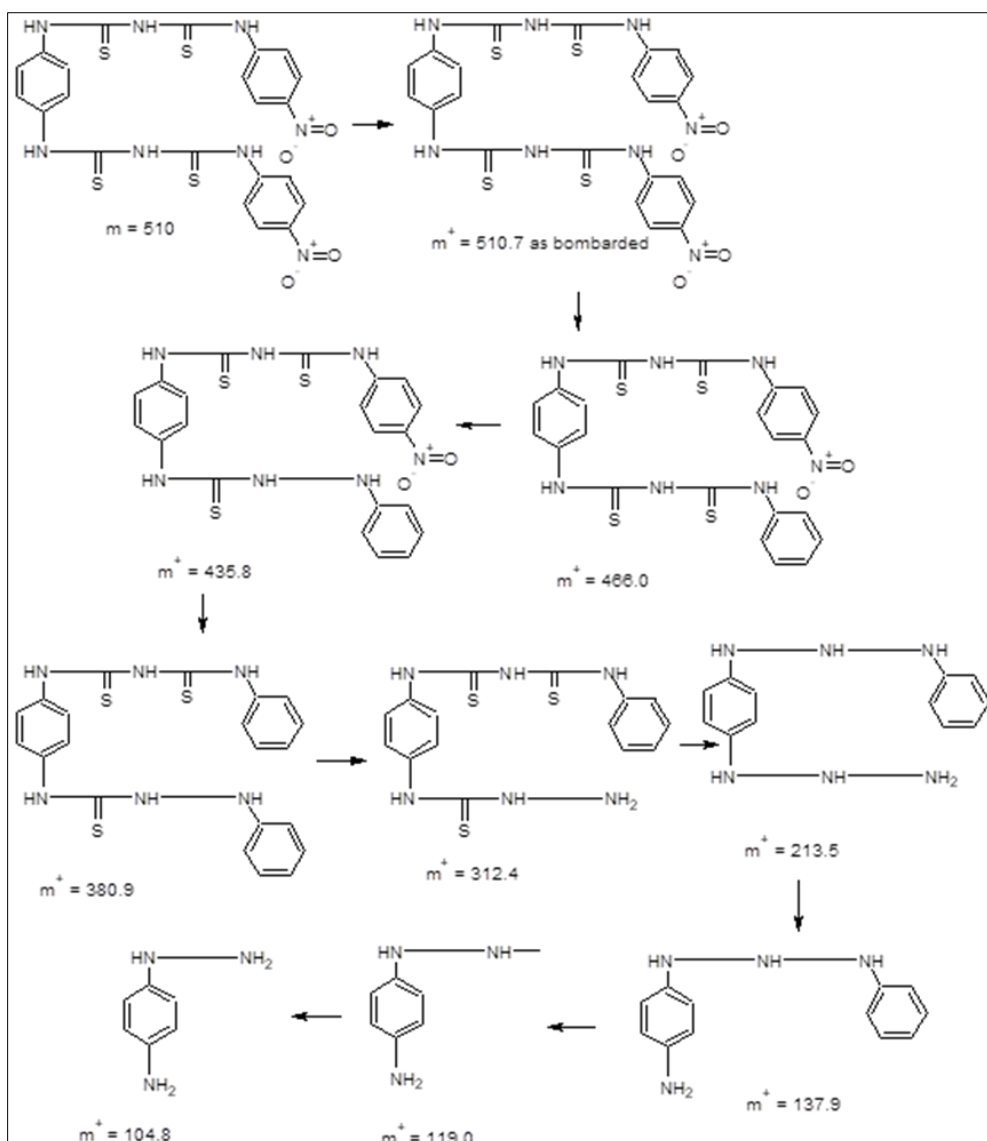
Sr. No.	Absorption observed (cm <sup>-1</sup> )	Assignment	Absorption expected (cm <sup>-1</sup> )
1	3405.47	C -H (Ar) (S)	3500-3000
2	1474.64	C - NH (imino group)	1989-1471
3	1080.49	C=S stretching	1200-1050
4	1642.46	N-H stretching	1789-1471
6	1099.47	C-N stretching (ali)	1000-1250

### 3.5. PMR Spectrum

PMR Spectrum<sup>18-19</sup> of a compound (3a) was carried out in DMSO-d<sub>6</sub>-CDCl<sub>3</sub> and reproduced on Plate No. PMR GVS-2. This spectrum distinctly displayed the signals due to Ar-H protons at δ 7.5106-8.5066 ppm, -NH (Ar) protons δ 3.2890-4.9644 ppm and -NH (C-NH-C) protons at δ 1.2323-2.3642 ppm.

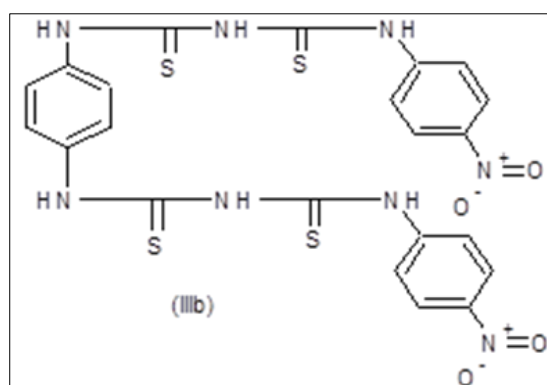
#### 3.5.1. Mass spectrum<sup>19-20</sup>

The Mass analysis of the compound was carried out and reproduced on Mass Plate No. FTS-3. The fragmentation occurs during the analysis is given in Mass Scheme-II.



**Figure 3** Mass Scheme (IIIb)

From the above chemical characteristics and analysis, the compound **(IIIb)** was assigned the structures as 1,4-bis[(4-nitrophenyl)-2,4-dithiobiureto]benzene **(IIIb)**.



**Figure 4** Structure of IIIb



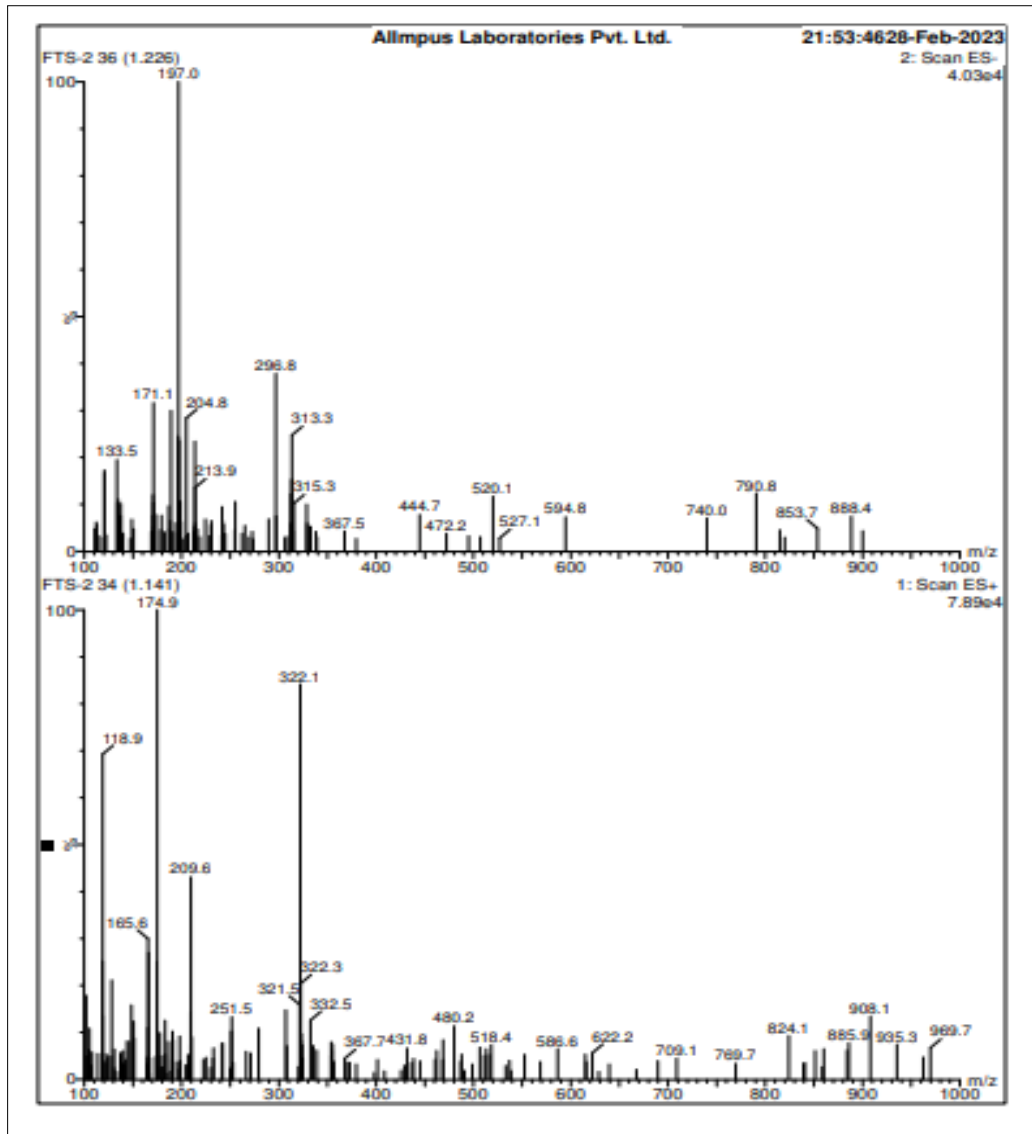


Figure 7 Mass Spectra IIIa

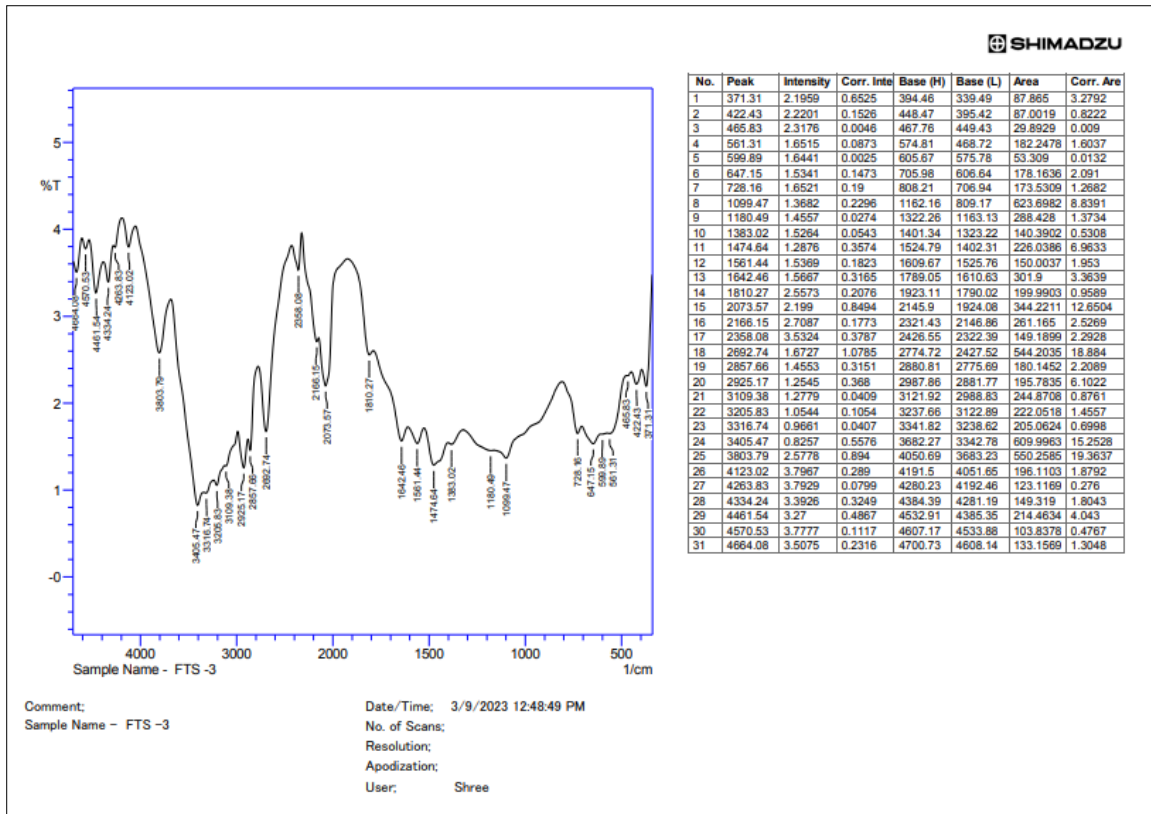


Figure 8 IR Spectra IIIb

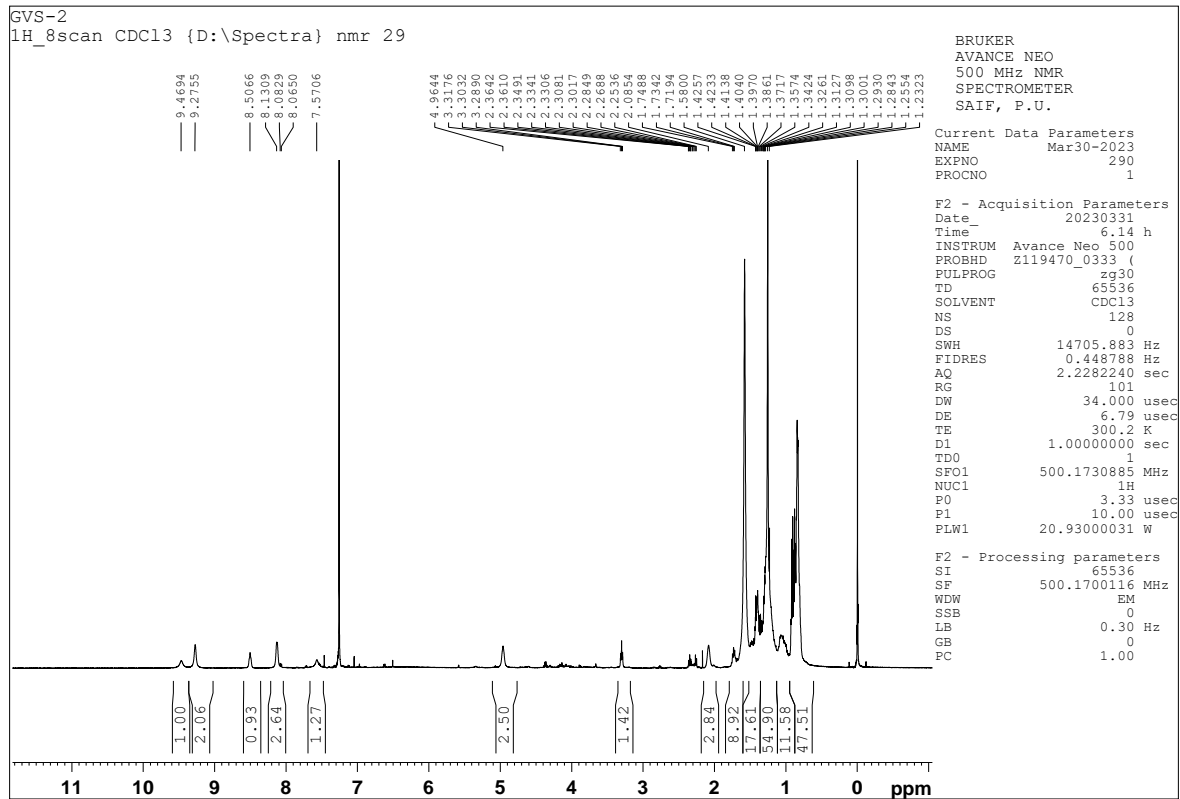


Figure 9 NMR Spectra IIIb



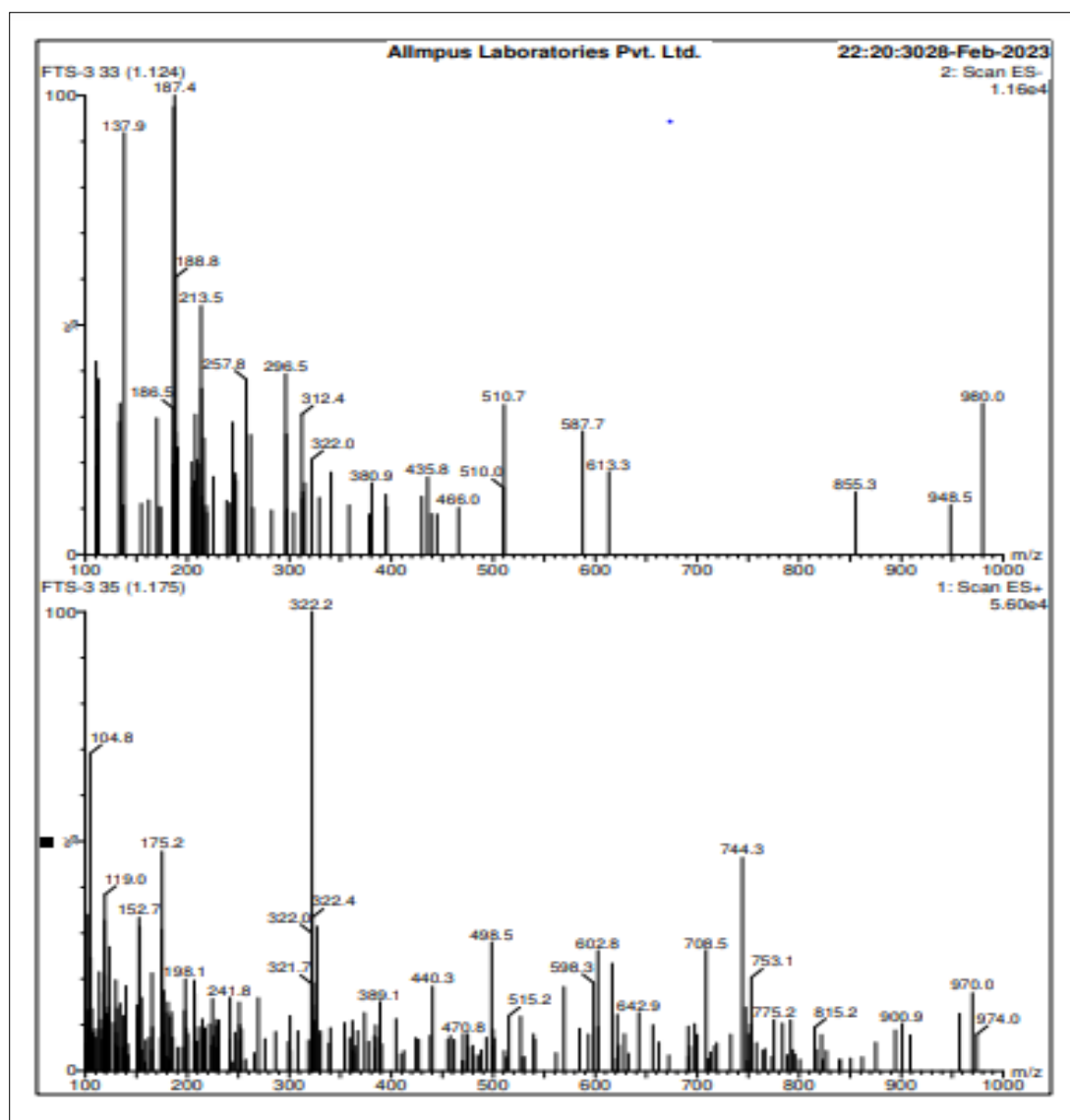


Figure 10 Mass Spectra IIIb

Similarly, 1,4-bis[(2-nitrophenyl)-2,4-dithiobiureto] benzene (IIIc) and 1,4-bis[(4-methylphenyl)-2,4-dithiobiureto] benzene (IIId) were successfully synthesized by refluxing 1,4-dithiocarbamidobenzene (I) with 2-nitrophenyl isothiocyanate (IIc) and 4-methylphenyl isothiocyanate (IIId) in 1:2 proportion in acetone-ethanol medium for 4 hours respectively.

#### 4. Conclusion

1,4-Bis[(substitutedphenyl)2,4-dithiobiureto]benzene (IIIa-d) were successfully synthesized through the three-step procedure that involved the synthesis of 2,4-dithiobiuret, followed by the reaction of 1,4-chlorobenzene with thiourea, and finally substitution of isothiocyanates yields the resulting compound. The purity of the product was confirmed by recrystallization and characterization using various analytical techniques such as chemical characteristics, melting point, IR spectrum, NMR spectrum and Mass spectrum. The synthesis provides a feasible method for the preparation of this important compound with potential applications in materials science and biotechnology.

---

## Compliance with ethical standards

### *Acknowledgments*

The authors thank to the Principal, JMV, Achalpur (City) for granting permission for research facility and also express their gratitude to the Head of the department of chemistry, JMV, Achalpur (city) for kind cooperation.

### *Disclosure of conflict of interest*

The authors declare that they have no known financial or personal conflicts that would have appeared to have an impact on the research presented in this study.

---

## References

- [1] Tayade D.T., Pund D.A., Bhagwatkar R.A., Patil S.U., Ind, J. Chem. Sci., 8(3), 2010, 1695-1698.
- [2] Ali M.U, Meshram H.M. and Paranjpe M.G., Jr. Ind. Chem. Soc., 62, 1985, 666.
- [3] Deshmukh S.P., Berad B.N. and Paranjpe M.G., Jr. Ind. Chem. Soc., 63, 1986, 315.
- [4] Deshmukh S.P. and Paranjpe M.G., Annual Convention of Chemistry, Madras, Paper No. ORG (P)-65, 1981.
- [5] Deshmukh S.P., 'Synthesis of N-Glucosylated trimides and related compounds', Ph.D. Thesis, Nagpur University, Nagpur, 1984.
- [6] Tayade D.T. and Chincholkar M.M., Acta Ciencia Indica, XXI (i), 1995, 37-38.
- [7] Shelke M.E., Jr. Ind. Chem. Soc., 83, 2006, 251-254.
- [8] Tayade D.T., Waghmare J.S. and Patil S.U., Jr. Ind. Chem. Soc., 83, 2006, 1-3.
- [9] Pandey S.N., 'Interaction of 2-chlorobenzothiazoleamidine chloride and acetone with thiocarbamide', Ph.D. Thesis, B.H.U., 1964.
- [10] Pathe P.P., Ambekar M.W., Mimdeokar N.M. and Paranjpe M.G., Ind. Jr. Chem., 59, 1982, 670.
- [11] Berad B.N., 'Organic Chemistry of Nitrogen, Sulphur and Oxygen containing compounds: Synthesis of N-glucosylated Nitrogen and Sulphur containing 5 and 6 membered heterocyclic compounds', Ph.D. Thesis, Nagpur University, 1985.
- [12] Aparajit V.A., Ph.D. Thesis, Nagpur University, Nagpur, 1993.
- [13] Tayade D.T., 'A contribution to the chemistry of Nitrogen, nitrogen and sulphur containing heterocyclic and heterocyclic compounds', Ph.D. Thesis, Amravati University, Amravati, 1996.
- [14] Deohate P.P., 'Application of N-phenylisocyanodichloride, N-phenyl-S-chloroisothiocarbonyl chloride and iodine in the synthesis of heterocyclic system', Ph.D. Thesis, SGB, Amravati University, Amravati, 2004.
- [15] Bhagwatkar A.K., 'Synthesis and antimicrobial analysis of substituted-1,3,5-triazin-6-yl-substitutedamidinothiocarbamides and their cyclisation into 1,3,5-thiadiazines and 1,3,5-triazines', Ph.D. Thesis, SGBAU, Amravati, 2013.
- [16] Margareta Acaram and Maleesov C.H., Infrared Spectroscopy application in organic compounds, 5th Ed, John Wiley and Sons, Inc, NewYork, 1970, 293.
- [17] Vogel A.I., Textbook of practical organic chemistry including qualitative organic analysis, ELBS and Longman Greek and co.ltd, 1954, 615.
- [18] Willams D.H. and Fleming J., Spectroscopic methods of organic chemistry, 4th Tata McGraw Hill, NewDelhi, 55.
- [19] R.M. Sliverstein, G.C. Bassler, T.C. Morill, Spectroscopic identification of organic compounds. 5th Ed, John Wiley and Sons, Inc, NewYork, 1991, 109, 123, 127.
- [20] Steanly G.M., US Pat, 8, 1950, 252479; Chem Abstr., 44, 1958, 59191