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SYNTHESIS OF 2-[(3-SUBSTITUTEDIMINO)-1,2,4-DITHIAZOLO]AMINO-11-(PIPERAZIN-1-YL)DIBENZO [b,f][1,4]OXAZEPINES

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ABSTRACT

*Recently in this laboratory a novel series of 2-[(3-substitutedimino)-1,2,4-dithiazolo]amino-11-(piperazin-1-yl)dibenzo [b,f][1,4]oxazepines **[VIB(a-h)]** was synthesized by the oxidative cyclisation of 2-[substituted-2,4-dithiobiureto]-11-(piperazin-1-yl) dibenzo [b,f] [1,4]oxazepines **[VB(a-h)]** in chloroform medium by making the use of liquid bromine as oxidizing agent. The products were characterized and justified on the basis of elemental analysis, chemical characteristics and spectral studies.*

Key words:- Liquid bromine, 2-[substituted-2,4-dithiobiureto]-11-(piperazin-1-yl) dibenzo [b,f] [1,4]oxazepines and chloroform.

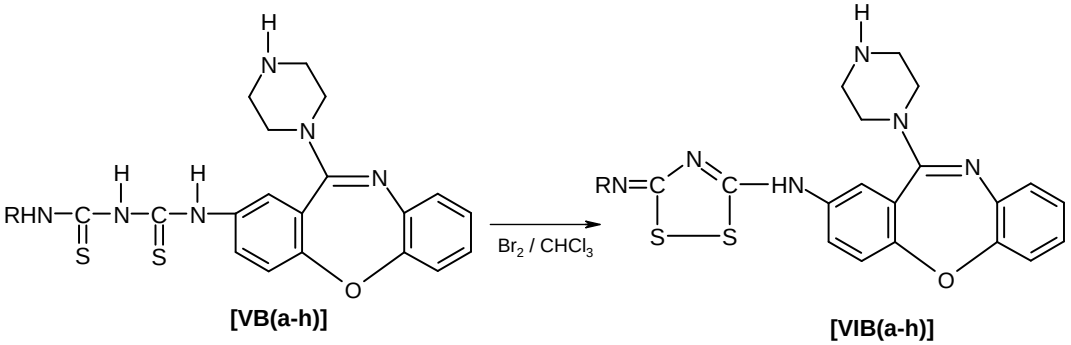
Introduction:

Oxazepine and their derivatives have some important biological pharmacological activities[1] such as enzyme inhibitors[2], analgesic[3], anti-depressant[4] and psychoactive drugs[5]. Oxazepine nucleus is used for treatment of depression, anxiety and agitation[6-7]. Recently new series of 1,2,4-thiadiazoles, 1,3,5-thiadiazines and 1,3,5-dithiazines were synthesized by exploring the synthetic applications of -thiocarbamido, -amino, -halo, -cyano, etc. and their antimicrobial, antifungal, antibacterial, analgesic physiochemical parameters[8-11] were studied. 2-Chloro-11-(piperazin-1-yl)dibenzo [b,f] [1,4] oxazepine.

1,4-oxazepine, 1,2,4-dithiazoles and their derivatives showed agricultural, medicinal, biological, pharmaceutical, industrial significances and applications.

As a part of research work presently undertaken in this laboratory in the synthesis of heteroacycles and heterocycles, it was thought interesting to investigate the cyclisation of 2-[substituted-2,4-dithiabiureto]-11-(piperazin-1-yl)dibenzo[b,f][1,4]oxazepines **[VB(a-h)]** from liquid bromine in chloroform medium to obtain a novel series of 2-[(3-substitutedimino)-1,2,4-dithiazolo]amino-11-(piperazin-1-yl)dibenzo[b,f][1,4]oxazepines **[VIB(a-h)]** which is heither to unknown.

The present work describes a suitable, convenient and one step direct method for this synthesis and depicted in **Scheme-I.**



[VB(a-h)]

2-[Substituted-2,4-dithiobiurato-11-(piperazin-1-yl)dibenzo[b,f][1,4]oxazepines

[VIB(a-h)]

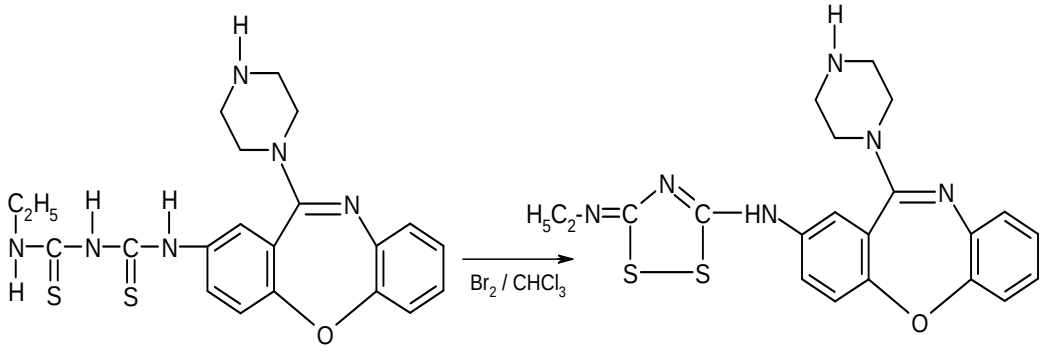
2-[(3-Substitutedimino)-1,2,4-dithiozolo]amino-11-(piperazin-1-yl)dibenzo[b,f][1,4]oxazepines

Where, R= -methyl, -ethyl, -tert-butyl, -phenyl, p-chlorophenyl, -p-tolyl,

Scheme-I

Synthesis of 2-[(3-ethylimino)-1,2,4-dithiazolo]amino-11-(piperazin-1-yl) dibenzo [b,f] [1,4] oxazepine [VIB(b)]

Synthesis of 2-[(3-ethylimino)-1,2,4-dithiazolo]amino-11-(piperazin-1-yl)dibenzo [b,f][1,4]oxazepine **[VIB(b)]** was carried out by the oxidative cyclisation of 2-[phenyl-2,4-dithiabiureto]11-(piperazin-1-yl)dibenzo-[b,f][1,4] oxazepine **[VB(b)]** using liquid bromine in presence of chloroform. In china dish the pest of 2-[phenyl-2,4-dithiabiureto]11-(piperazin-1-yl)dibenzo-[b,f][1,4] oxazepine **[VB(b)]** was taken to it liquid bromine in chloroform was added with constant stirring. Initially the colour of bromine disappeared, the addition was continued till colour of bromine persisted. The reaction mixture was allowed to stand for 4 hours and then on basification with dilute ammonium hydroxide it afforded darkbrown crystals. Recrystalised from aqueous ethanol. Yield 91 %, m.p. 218˚C. The formation of **[VIB(b)]** is depicted below**,**



[VB(b)]

2-[Ethyl-2,4-dithiobiurato-11-(piperazin-1-yl)dibenzo[b,f][1,4]oxazepines

[VIB(b)]

2-[(3-Ethylimino)-1,2,4-dithiozolo]amino-11-(piperazin-1-yl)dibenzo[b,f][1,4]oxazepines

[VIB(b)]

Properties of [VIB(b)]

It is dark brown colour crystalline solid having melting point 218^0C. It gave positive test for nitrogen and sulphur. It was soluble in water, ethanol, DMSO-d_6 while insoluble in carbon tetrachloride, chloroform, benzene, petroleum ether.

It formed picrate having melting point 182^0C.

Elemental Analysis: The result of elemental analysis is given in **Table No. 1**

Table No. 1

Sr.No.	Elements	Found	Calculated
1.	Carbon	56.64	57.33
2.	Hydrogen	04.12	05.02
3.	Nitrogen	18.65	19.17
4.	Sulphur	13.24	14.61

1. **IR spectrum**: The IR spectrum of compound **[VIB(b)]** was perform in KBr-pellets and is reproduced on **IR Plate No. PRK-VIBa** The specific absorption is correlated as follows and is depicted in **Table No. 2**

Table No. 2

Sr. No.	Absorption (cm^{-1})	Assignment	Absorption Expected (cm^{-1})
1.	3045.60	N-H Stretching	3450-3300
2.	2890.30	Ar-CH stretching	3150-3000
3.	1789.94	C = NH (imino grouping)	1789-1471
4.	1494.83	C = N stretching (Ring)	1600-1430
5.	1253.73	C-N stretching	1340-1250
	1145.72	C-O-C streching	1300-1100
	1014.56	C-C streching	1120-1100

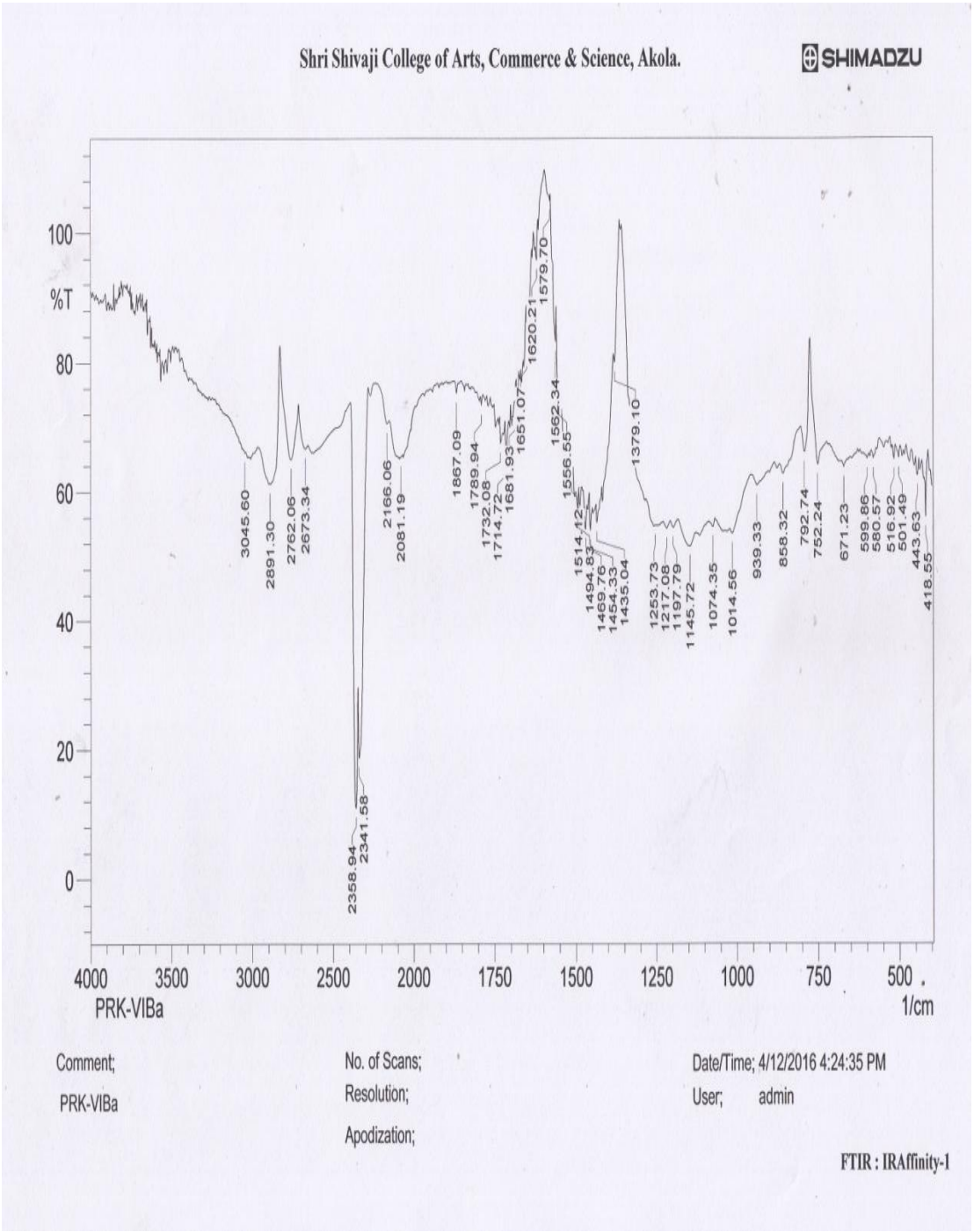
PMR Spectra:- The Ar-H proton signals are shifted[12-17] at δ 8.2104-8.1573 ppm (for 1 Ar-H proton), at δ 8.0235-8.0179 ppm (for 1 Ar-H proton) and at δ 7.9010-7.7246 ppm. The another phenyl ring[12-17] which attached 1,4-oxazepine ring gave four types of δ different signals at δ 7.5844-7.5118 ppm, at δ 7.4910-7.4069ppm, at δ 7.3794-7.2179 ppm, at δ 7.2030-7.1414 ppm. The NH proton flanked[12-17] in between phenyl ring is attached to 1,4-oxazepine ring and also to 1,2,4-dithiazole which is more deshilded at δ 4.7372-4.0159 ppm, another NH proton at δ 3.9601-3.4018 ppm, CH_2 protons at δ 2.5524ppm, CH_3 protons at δ 1.2460.

Similarly, 2-[phenyl-2,4-dithiabiureto]11-(piperazin-1-yl) dibenzo [b,f] [1,4] oxazepine **[VB(b)],** 2-[methyl-2,4-dithiabiureto]11-(piperazin-1-yl)dibenzo[b,f][1,4] oxazepine **[VB(c)],** 2-[t-butyl-2,4-dithiabiureto]11-(piperazin-1-yl) dibenzo [b,f][1,4] oxazepine **[VB(d)],** 2-[p-chlorophenyl-2,4-dithiabiureto]11-(piperazin-1-yl) dibenzo [b,f] [1,4] oxazepine **[VB(e)],** 2-[p-tolyl-2,4-dithiabiureto] 11-(piperazin-1-yl) dibenzo-[b,f][1,4] oxazepine **[VB(f)],** by the oxidative cyclisation bromine in chloroform to obtained 2-[(3-phenylimino)-1,2,4-dithiazolo] amino-11-(piperazin-1-yl)dibenzo[b,f][1,4]oxazepine**[VIB(b)]**, 2-[(3-methylimino)-1,2,4-dithiazolo]amino-11-(piperazin-1-yl)dibenzo[b,f][1,4]oxazepine**[VIB(c)]**, 2-[(3-t-butylimino) -1,2,4-dithiazolo]amino-11-(piperazin-1-yl)dibenzo[b,f][1,4] oxazepine**[VIB(d)],** 2-[(3-p-chloro-phenylimino)-1,2,4-dithiazolo]amino-11-(piperazin-1-yl)dibenzo[b,f][1,4] oxazepine **[VIB(e)],** 2-[(3-p-tolylimino)-1,2,4-dithiazolo]amino-11-(piperazin-1-yl)dibenzo[b,f][1,4] oxazepine **[VIB(f)]** respectively by the above mentioned method and enlisted in **Table No.3**

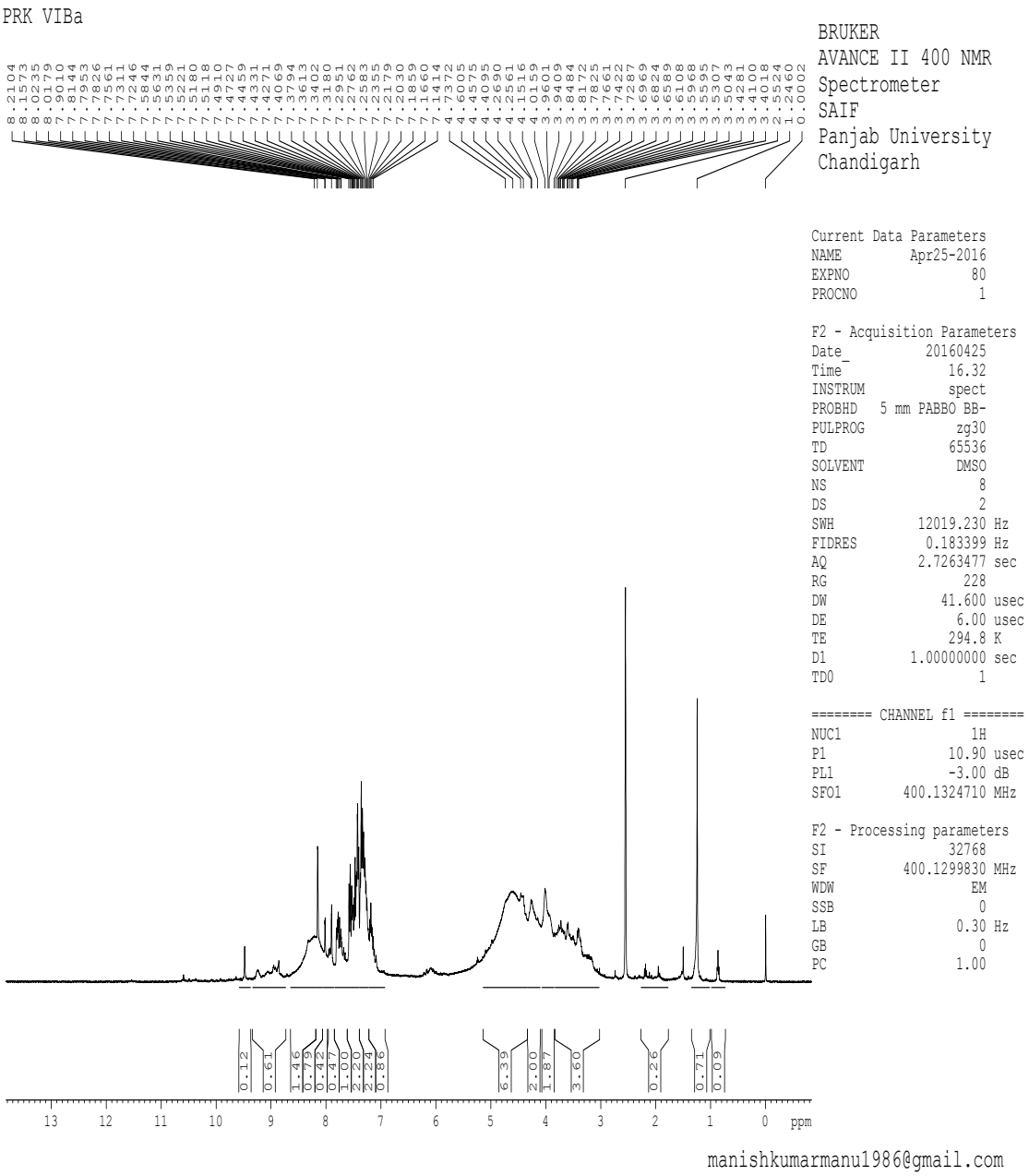
Table No. 3

Sr. No.	**2-[(3-Substituted**imino)-1,2,4-dithiazolo] amino-11-(piperazin-1-yl)dibenzo[b,f][1,4] oxazepine	Yield (%)	M.P. ˚C
1.	**2-[(3-Phenyl----------**oxazepine**[VIB(B)]**	94	237
2.	**2-[(3-Methyl----------** oxazepine**[VIB(c)]**	88	183
3.	**2-[(3-t-Butyl----------** oxazepine**[VIB(d)]**	72	142
4.	**2-[(3-p-Chlorophenyl------**oxazepine**[VIB(e)]**	86	214
5.	**2-[(3-p-Tolyl----------** oxazepine **[VIB(f)]**	89	232

IR Spectra of VIBa



PMR spectra of VIBa



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