SYNTHESIS AND STRUCTURAL STUDIES OF 2-THIOPHENE-4-AMINOPHENYL BENZIMIDAZOLE

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Abstract
Synthesis of 2-Thiophene-4-aminophenyl benzimidazole, from 4-aminophenyl benzimidazole and 2thiophenaldehyde under green synthetic approach. The obtained product was analyzed by IR, Electronic and ^{1}H-NMR spectroscopic methods to evaluate the structure of the compound.

Key words: 4-aminophenyl Benzimidazole, 2-Thiophenaldehyde, 2-Thiophene-4-aminophenyl Benzimidazole

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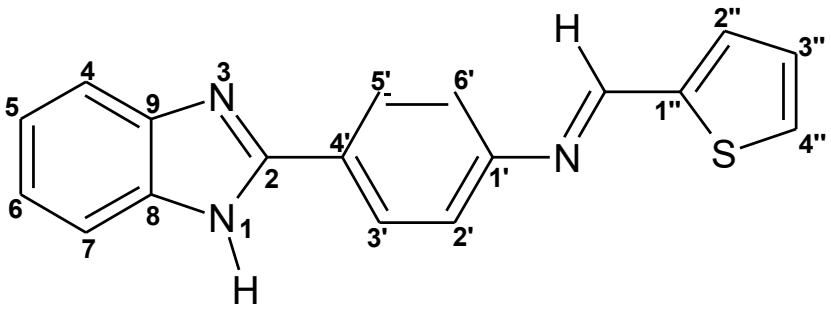
1. Introduction

Benzimidazolemoiety is a well-known molecule found in natural products such as vitamin-B_{12}. Benzimidazole derivatives are extensively studied due to their antidiabetic, antiviral, antioxidant, antihypertensive, antihelminthic, antimicrobial, anti-inflammatory, antitumor and antifungal activities[1]. Schiff bases derived from benzimidazoles are also known to exhibit similaractivities[2-5]. Present study is focused on synthesis of new schiff base 2-Thiophene-4-aminophenyl benzimidazole (Figure -1), and evaluation of its structure via different spectroscopic techniques[17-21].



Structure - 1: 2-Thiophene-4-aminophenyl benzimidazole.

2. Experimental

All chemicals used for the synthesis were of LR grade, the solvents were distilled prior to their use.

Instrumentation:

The IR spectrum of the compound was recorded on a Shimadzu IR Affinity spectro meter in the range 4000 - 400 cm^{-1}in KBr pellet method.The electronic spectrum was recorded in DMSO in the range 200-1100 nm on Elico- UV-visible spectrophotometer. The ^{1}H-NMR spectrum was recorded on a Bruker 400 MHz NMR spectrometer in DMSO-d_6(using TMS as a internal reference).

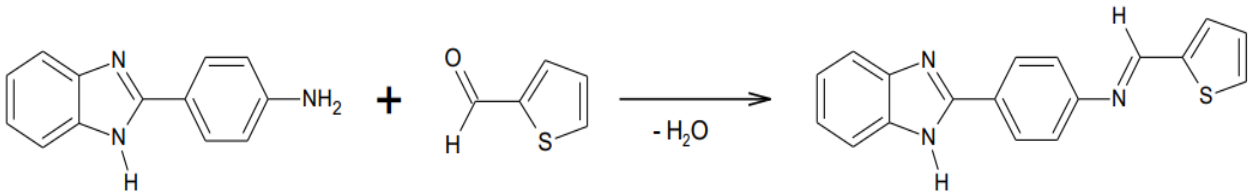
2.1. Preparation of heterocycle

2.1.1. Preparation of 4-aminophenyl benzimidazole(4-APbzlH).

The ligand 4-APbzlH was prepared according to the reported literature method[6].

2.1.2. Preparation of 2-Thiophene-4-aminophenyl benzimidazole

The heterocycle (Schiff Base),2-Thiophene-4-aminophenyl benzimidazole was obtained as a Solid by refluxing a mixture of4-APbzlH(5.0 g) and 2-Thiophenaldehyde(3.05ml)in ethanol forabout 6hrs followed by evaporation of the solvent to a small volume,the solid was washed with ether and recrystallized from ethanol and dried in vacuum. Yield = 5.95 g.



Scheme -1: Preparation of 2-Thiophene-4-aminophenyl benzimidazole

3. Results and Discussion:

3.1. IR Spectrum

The physical properties and analytical data of the prepared compounds are shown in **Table-1**. IR spectrum of 4-APbzlH shown in **Table-2**, the bands at 3439,3362cm^{-1} are assigned to $\gamma_{NH2}$and γ_{NH}respectively[7].The bands at 1620,1600cm^{-1} are assigned to $\gamma_{C=C}$ and $\gamma_{C=N}$ .The appearance of a peak at 1514 cm^{-1} is due to the bending mode of NH_2[8].

The IR spectrum (Fig-1) of 2-Thiophene-4-aminophenyl benzimidazole showed a band in the range 3400-2600 cm^{-1} assigned to $\gamma_{NH\&\ CH}$. Two more bands observed at 1600 and 1618cm^{-1} are assigned to the $\gamma_{N=CH}$ of methyl group and $\gamma_{C=C}$ of the C_6H_4 rings respectively. A peak at 1591 cm^{-1} is assigned to the $\gamma_{N=C}$ of the imidazole ring[9] and a band at 709cm^{-1} is attributed to γ_{C-S} of the thiophene moiety[10].

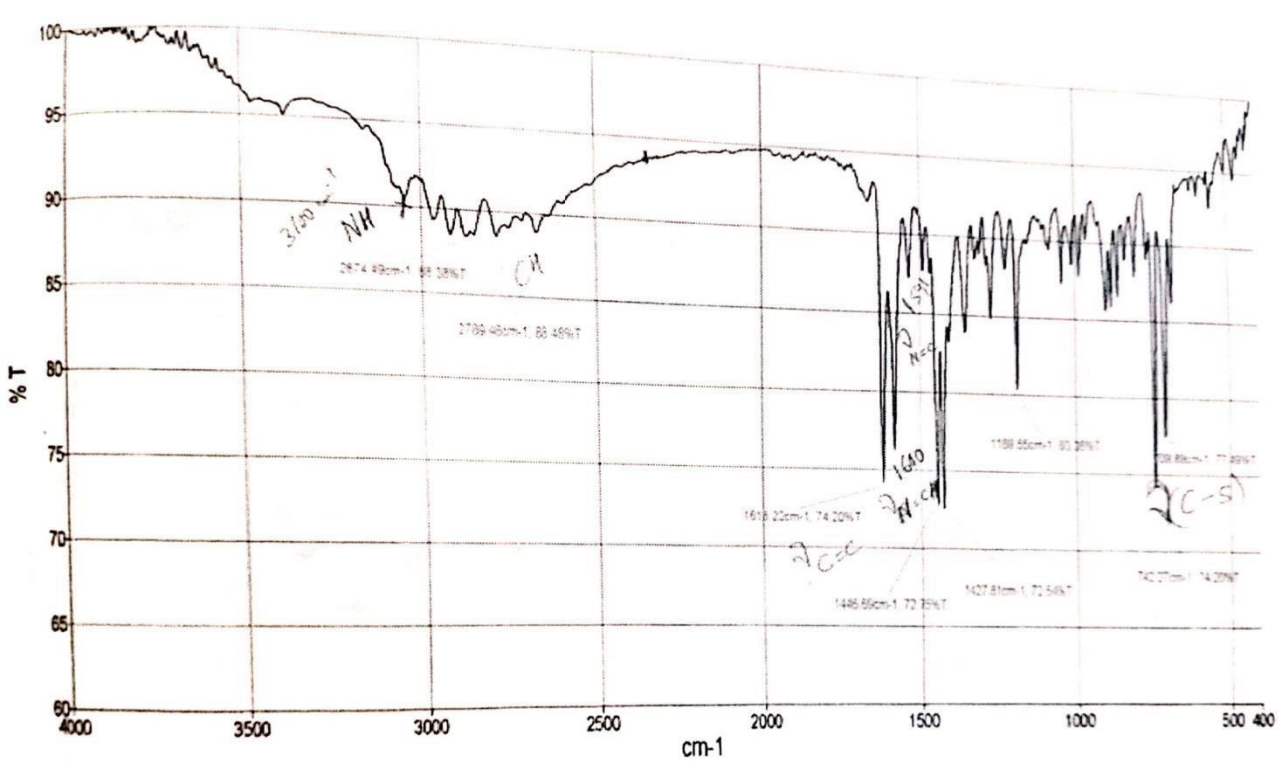


Fig-1: IR spectrum of 2-Thiophene-4-aminophenyl benzimidazole

Table-1: Physical and analytical data of 4-aminophenyl-benzimidazole and 2-Thiophene-4aminophenylbenzimidazole.

Compound	Yield(%)/M.P(^{0}C)	% C	% H	%N
4-aminophenyl benzimidazole	90 / >250	73.65 (74.64)	5.15 (5.26)	20.12 (20.09)
2-Thiophene-4aminophenyl benzimidazole	82 / 218	70.65 (71.28)	4.13 (4.29)	13.05 (13.86)

***Calculated values are in Parenthesis**

Table-2: IR spectral data of 4-aminophenyl-benzimidazole and 2-Thiophene-4-aminophenyl Benzimidazole

Compound	γNH2 (cm^{-1})	γNH (cm^{-1})	γN=C (cm^{-1})	γN=CH (cm^{-1})	γC=C (cm^{-1})	γNH2 (cm^{-1}) Bending	γC-S (cm^{-1})
4-aminophenyl benzimidazole	3439	3362	1600	--	1620	1541	--
2-Thiophene-4aminophenyl benzimidazole	--	γNH , CH 3400-2600	1591	1600	1618	--	709

3.2. Electronic Spectrum

The electronic spectrum(Fig-2) of 2-Thiophene-4-aminophenyl benzimidazole (**Table -3)** recorded in DMSO exhibits broad bands at 283, 316-379 nm .These bands are assigned to n → π* & π → π* transitions[11].

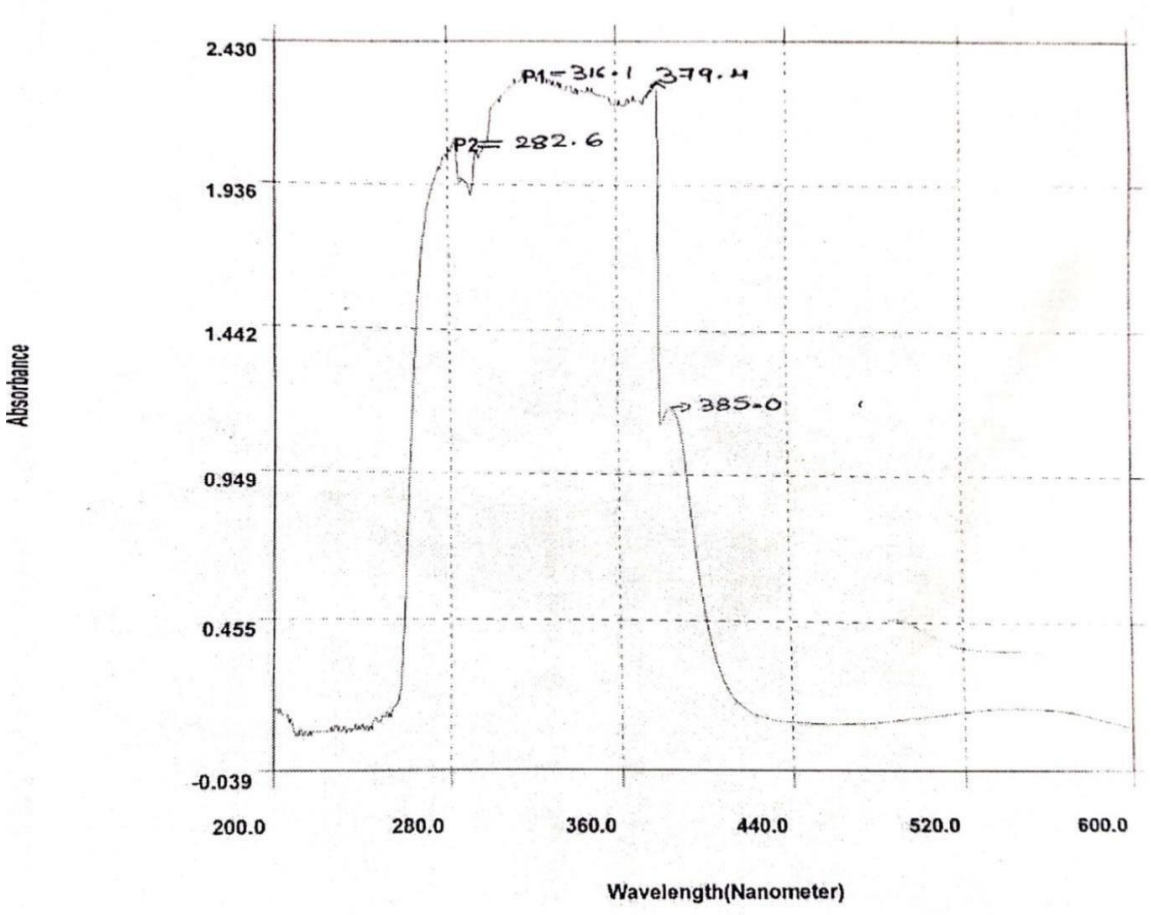


Fig-2: Electronic spectrum of 2-Thiophene-4-aminophenyl benzimidazole

Table-3: Electronic spectral data of 4-aminophenyl-benzimidazole and 2-Thiophene-4- aminophenyl benzimidazole.

Compound	**λ,nm (cm-1)**	**Transition**
4-aminophenyl benzimidazole	280 (35,715) 301 (33,222) 380 (26,315) 412 (24,271)	n → π* & π → π*
2-Thiophene-4aminophenyl benzimidazole	283(35,335) 316(31,645) 379(26,385)	n → π* & π → π*

3.3. Mass Spectrum

Mass spectrum(Fig-3) of4-APbzlH and 2-Thiophene-4-aminophenyl benzimidazole showed molecular ion peaks at m/z 210, 304 corresponding to M+1 species respectively[12].

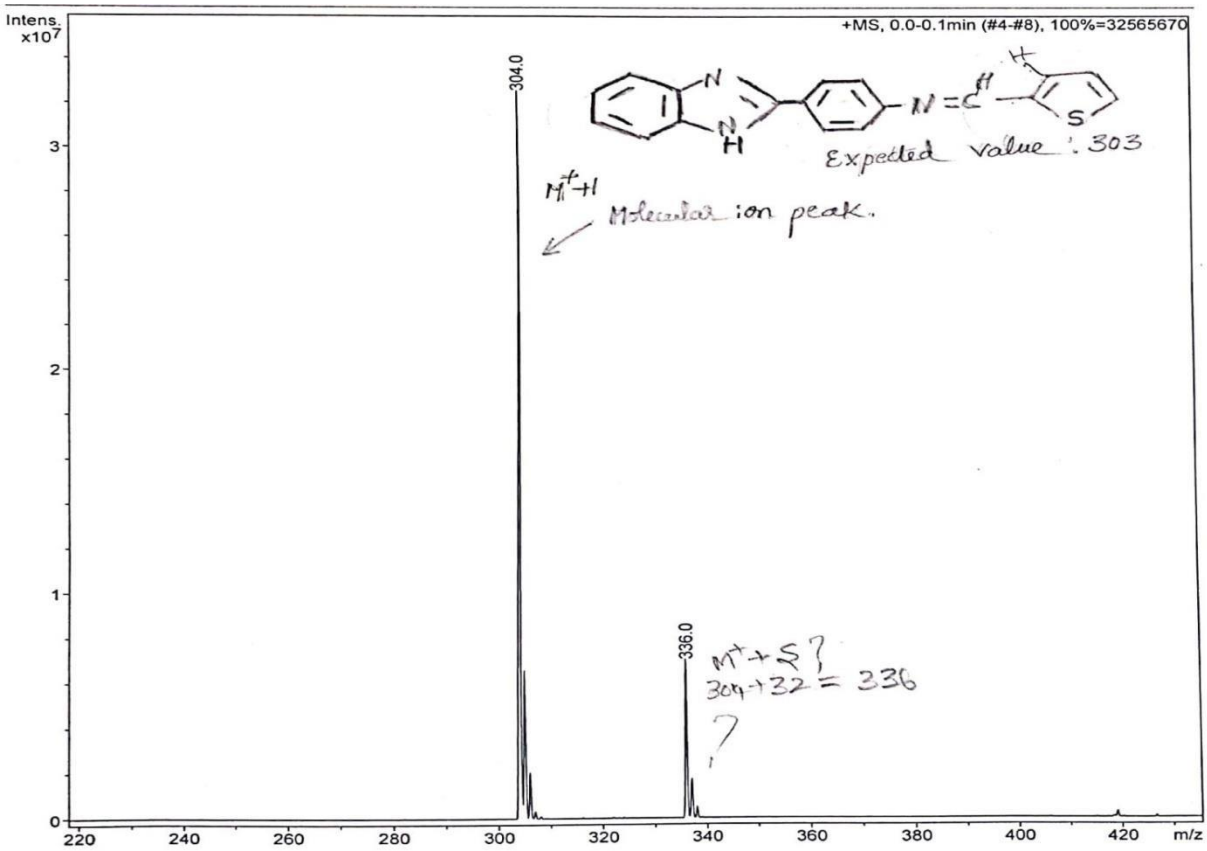


Fig-3: Mass spectrum of 2-Thiophene-4-aminophenyl benzimidazole

3.4. ^{1}H-NMR Spectrum

The proton NMR spectrum of 2-Thiophene-4-aminophenyl benzimidazole (Figs:4-7) described in **Table-4** displayed signals at δ,12.88 and 8.88ppm and these are assigned to the protons of NH and N=CH respectively. Two triplets, two doublets observed at δ 7.86, 7.73 ppm are assigned to 2'' and 4'' respectively. Two triplets at δ 8.20ppm is assigned to protons 3' and 5'. Two doublets observed at δ 7.65, 7.52 ppm are assigned to 7 and 4 respectively. A multiplet observed at δ 7.20, 7.25 ppm are assigned to 5,6 and 3'' respectively. A triplet observed at δ 7.43 is assigned to 2' and 6'[13-16].

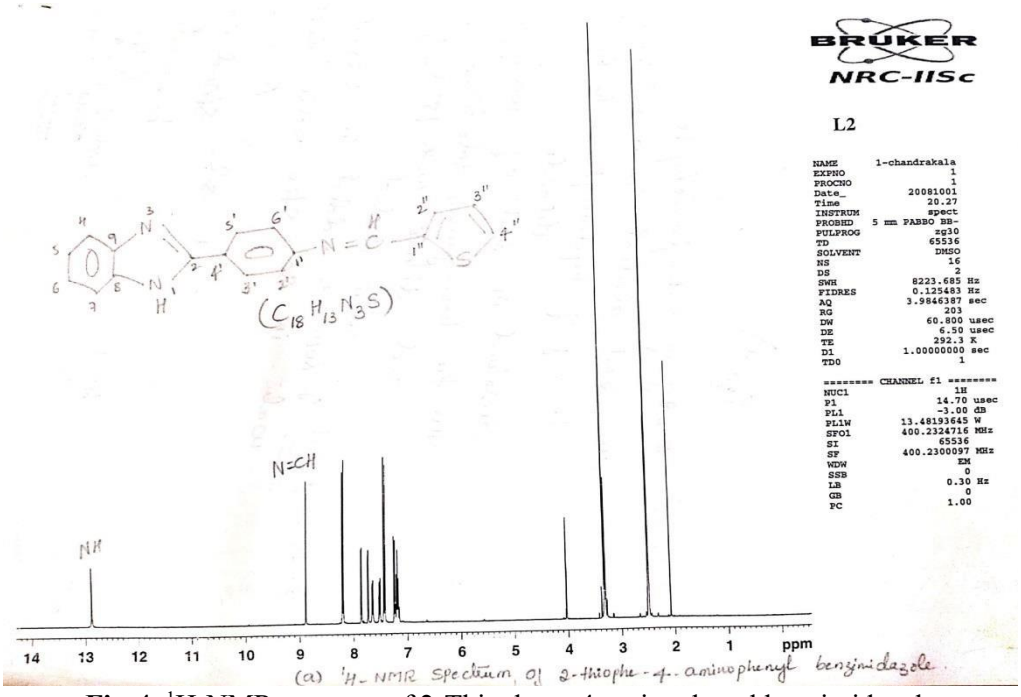


Fig-4: ^{1}H-NMR spectrumof 2-Thiophene-4-aminophenyl benzimidazole

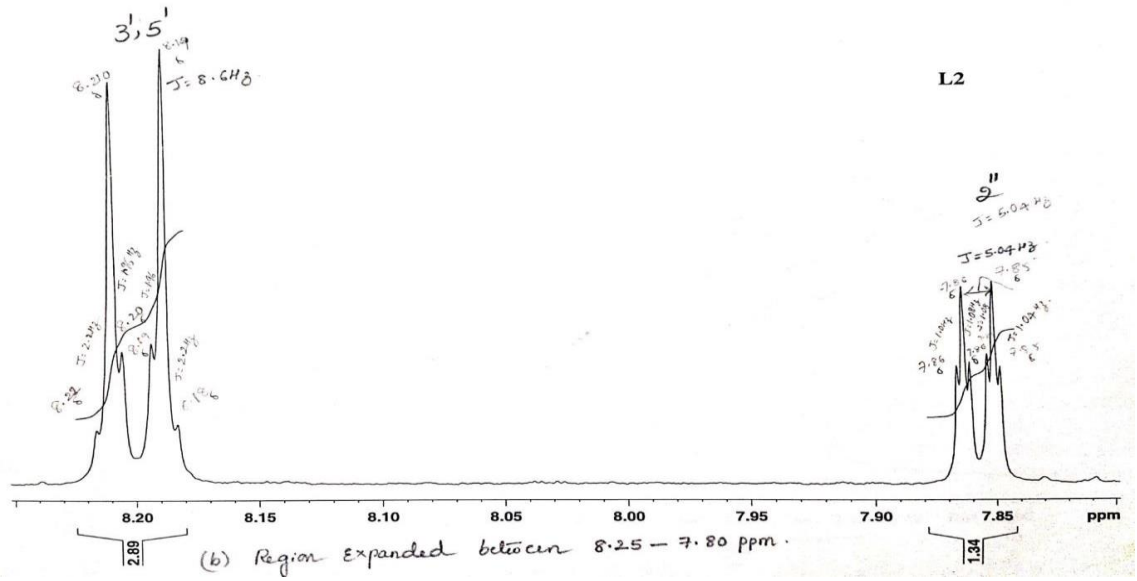


Fig-5: [1]H-NMR spectrumof 2-Thiophene-4-aminophenyl benzimidazole

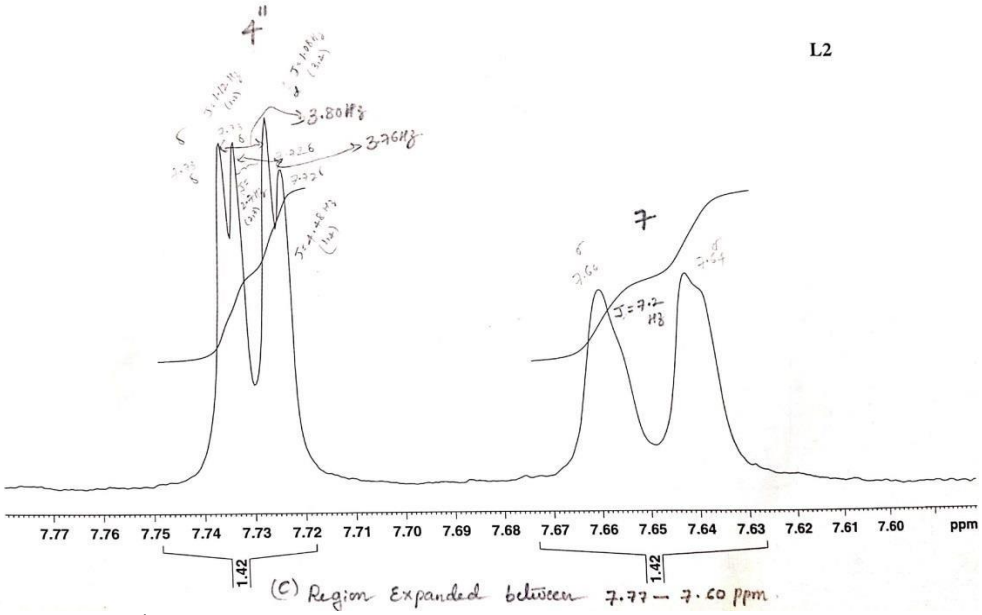


Fig-6: [1]H-NMRspectrum of 2-Thiophene-4-aminophenyl benzimidazole

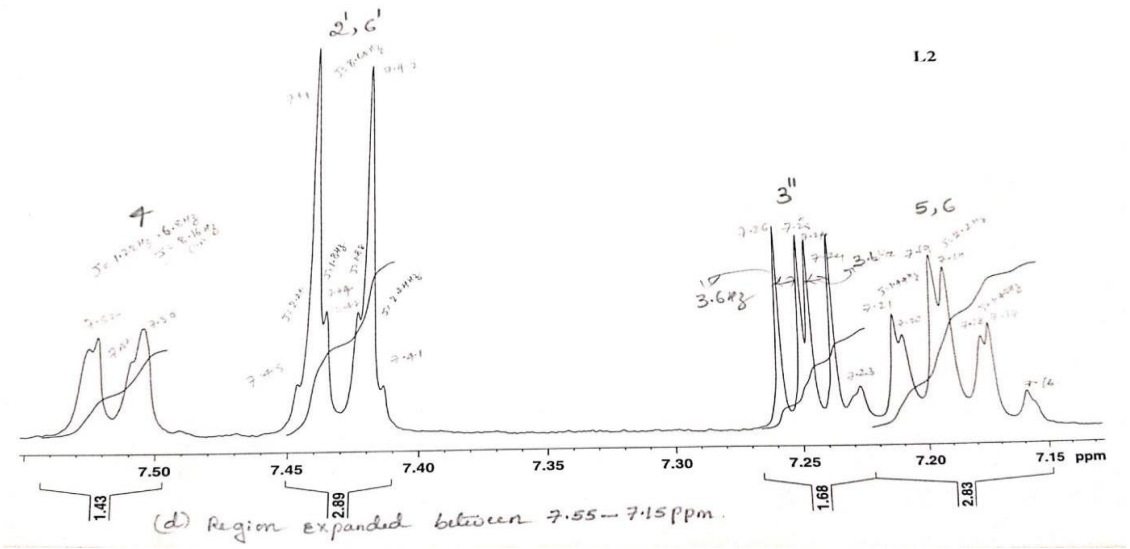


Fig-7: [1]H-NMR spectrum of 2-Thiophene-4-aminophenyl benzimidazole

Table-4: ^{1}H-NMR spectraldata of 4-aminophenyl-benzimidazole and 2-Thiophene-4- aminophenyl benzimidazole.

Compound	Benzimidazole ring				Aminophenyl ring				Thiophene ring			
	NH	H_4	H_7	H5,6	H2',6'	H3'5'	NH_2	N=CH	H1"	H2"	H3"	H4"
4aminopheny l benzimidazole	12.40 s	7.48 (7.90)	7.46s (7.90)	7.11 m	6.70 d (8.60)	7.84 d (8.60)	5.60 s	---	---	---	---	---
2-Thiophene-4aminophenyl benzimidazole	12.88 s	7.52 (8.16)	7.65 (7.20)	7.20 m	7.43 (8.64)	8.20 (8.40)	--	8.88s	---	7.86 (5.04)	7.2 5 m	7.73 (3.80)

*Spectra have been recorded in DMSO-d6 ,δ in ppm & coupling in Hz are given in parenthesis

4.Conclusion

IR , Electronic and ^{1}H-NMR spectral studies of 2-Thiophene-4-aminophenyl benzimidazole, it is evident that,**Structure-1**has been proposed for the compound.

Acknowledgements

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