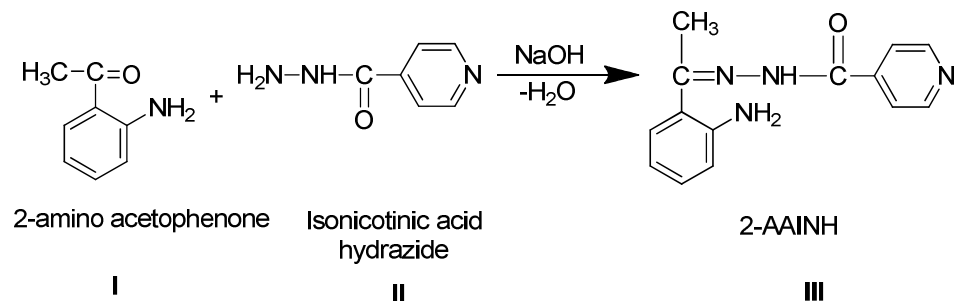

Chapter – 2

SOLUTIONS & INSTRUMENTS

Section i: Synthesis and Characterization of 2-amino acetophenone isonicotinoyl hydrazone (2-AAINH)

2-AAINH is prepared by condensing purified samples of isonicotinic acid hydrazide and 2-amino-acetophenone by gentle heating in aqueous methanol in presence of sodium hydroxide using the general procedure¹. The yellow product is recrystallised from ethanol in the presence of norit. The melting point of the product is 183–185°C.



The structure of the product obtained is ascertained from IR and NMR spectral studies.

IR spectral studies^{2,3}

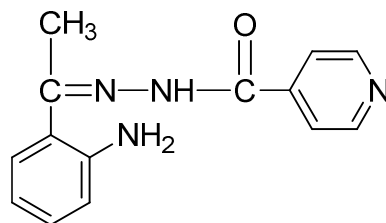
The infrared (IR) spectrum of the compound is recorded in KBr pellet and presented in Fig. 2.i.1. The peaks observed at 3406 cm⁻¹ and 3286 cm⁻¹ may be due to symmetric and asymmetric -N-H stretching frequency of primary amino group. The peak noticed at 1664 cm⁻¹ may be

assigned to C=O stretching frequency of the amide (amide I band). The peaks at 1545 cm^{-1} and 1245 cm^{-1} are assigned to amide II band due to interaction between -N-H bending and -C-N stretching of C-N-H group. The peaks observed between $1604\text{-}1432\text{ cm}^{-1}$ are assigned to C=C of benzene ring and C=N ring stretching frequency of pyridine ring. The peaks at 748 cm^{-1} and 701 cm^{-1} are due to -C-H out of plane bending of pyridine ring.

NMR spectral studies^{2,3}

The NMR spectrum of the compound is shown in Fig. 2.i.2. The peak observed at δ value 11.2 (singlet) is characteristic of enolic -OH group. The peaks found at δ values 8.8 and 7.8 (doublets) are due to the pyridine ring protons. The peaks noticed at δ values 7.4, 7.0, 6.75, 6.45 (two doublets and two triplets) are due to four aromatic protons. The broad peak observed at δ value 3.8 is due to -NH amide linkage. The peak observed at δ value 2.3 is due to -CH₃ group. The peak shows at δ value 2.5 may be assigned to -NH₂ protons.

Thus the IR and NMR spectral studies indicate that the position of the spectral peaks clearly suggest the following structure for the compound, 2-amino acetophenone isonicotinoyl hydrazone (2-AAINH).



Section ii: Preparation of Experimental reagent of 2-AAINH solution and salt solutions employed in the present investigations

All the chemicals used were of analytical grade unless otherwise specified.

a. Stock solution of 2-AAINH

2-AAINH solution (1×10^{-2} M) is prepared in dimethylformamide (DMF). 0.0635 g of the reagent (2-AAINH) is transferred into a 25 ml volumetric flask and made up to the mark with DMF. The stock solution is suitably diluted to get the required concentration wherever necessary. Fresh reagent solution is prepared every day before use.

b. Manganese (II) solution

A stock solution of Mn (II) (1×10^{-2} M) is prepared by dissolving 0.1979 g of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (Mol. wt. 197.91) in doubly distilled water in 100 ml volumetric flask and the solution is standardized⁴ complexometrically. Working solution is prepared by diluting the stock solution.

c. Ni (II) solution

0.2808 g of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ is dissolved in doubly distilled water containing few drops of conc. H_2SO_4 in 100 ml standard flask to get 1×10^{-2} M solution, which is then standardized⁵ gravimetrically using DMG.

d. Molybdenum (VI) solution

Stock solution of Mo (VI) (1×10^{-2} M) is prepared from $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (Mol. wt. 241.95) with doubly distilled water in a 100 ml volumetric flask and standardised gravimetrically⁶. The stock solution is suitably diluted with distilled water to get required concentration.

e. iron (III) solution

0.01M solution of Fe (III) solution was prepared by dissolving 0.4822 g of $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (E. Merck) in distilled water containing few drops of concentrated sulphuric acid and diluting to 100 ml with distilled water. The stock solution was standardized⁷ and diluted suitably with distilled water to get the working solutions.

f. Vanadium (V) solution

A 1×10^{-2} M stock solution of ammonium metavanadate is prepared in hot distilled water and standardized titrimetrically⁸.

g. Cobalt (II) solution

Stock solution of Co(II) (1×10^{-2} M) is prepared by dissolving required amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (mol. wt. 291.04) in doubly distilled water containing a few drops of Conc. HNO_3 in a 100 ml volumetric flask and standardized gravimetrically⁹.

h. Preparation of other inorganic salt solutions

The inorganic salt solutions are prepared by dissolving the suitable salt in requisite quantity in doubly distilled water. A few drops of suitable acid are added to avoid hydrolysis before dilution wherever necessary. Solutions thus prepared are standardised if needed by standard procedures. The solvents employed are distilled and purified by standard procedures. The formulae, quality, molecular weight or specific gravity and the quantity of chemicals used are presented in the Table 2.ii.1.

TABLE 2.ii.1: Salt solutions used with qualitative and quantitative studies

Ion	Formula	Quality	Sp. Gr./ Mol. wt.	Weight/ Volume	Molarity of the stock solution
Na ⁺	NaNO ₃	AR BDH	84.99	0.8499	0.01
Ag ⁺	AgNO ₃	AR BDH	169.87	0.1699	0.01
Mg ⁺²	MgSO ₄ .7H ₂ O	AR BDH	246.50	0.2465	0.01
Mn ⁺²	MnSO ₄ .4H ₂ O	GR SM	223.06	0.2231	0.01
Fe ⁺²	(NH ₄) ₂ SO ₄ FeSO ₄ .6H ₂ O	AR BDH	392.14	0.3921	0.01
Co ⁺²	Co(NO ₃) ₂ .6H ₂ O	AR BDH	291.04	0.2910	0.01
Ni ⁺²	NiSO ₄ .7H ₂ O	AR BDH	280.80	0.2808	0.01
Cu ⁺²	CuSO ₄ .5H ₂ O	AR BDH	249.68	0.2497	0.01
Hg ²⁺	HgCl ₂	AR BDH	271.50	0.2715	0.01
Zn ²⁺	ZnSO ₄ .7H ₂ O	GR E.Merck	287.54	0.2875	0.01

Ion	Formula	Quality	Sp. Gr./ Mol. wt.	Weight/ Volume	Molarity of the stock solution
Pb ²⁺	Pb(NO ₃) ₂	AR BDH	331.20	0.3312	0.01
Al ³⁺	Al ₂ (SO ₄) ₃ (NH ₂)SO ₄ ·24H ₂ O	AR BDH	453.33	0.4533	0.01
Cr ³⁺	CrCl ₃ ·3H ₂ O	E.Merck	266.36	0.2664	0.01
Fe ³⁺	NH ₄ Fe(SO ₄) ₂ ·12H ₂ O	AR BDH	482.19	0.4822	0.01
Ti ⁴⁺	K ₂ TiO(C ₂ O ₄) ₂ ·2H ₂ O	AR BDH	354.17	0.3542	0.01
Mo ⁺⁶	Na ₂ ·MoO ₄ ·2H ₂ O	E.Merck	241.95	0.2419	0.01
Ce ⁴⁺	(NH ₄) ₂ [Ce(NO ₃) ₆]	AR BDH	548.23	0.5482	0.01
Th ⁴⁺	Th(NO ₃) ₄ ·6H ₂ O	AR BDH	588.05	0.5881	0.01
V ⁵⁺	NH ₄ VO ₃	AR Riedel	116.98	0.1170	0.01
Cr ⁶⁺	K ₂ Cr ₂ O ₇	AR BDH	294.19	0.2942	0.01
W ⁶⁺	Na ₂ WO ₄ ·2H ₂ O	AR BDH	329.86	0.3298	0.01
Zr ⁴⁺	ZrOCl ₂ ·8H ₂ O	AR BDH	322.12	0.3221	0.01
CH ₃ COO ⁻	CH ₃ COONa·3H ₂ O	AR BDH	136.09	1.3609	0.1
F ⁻	NaF	Becker and Adams, USA	42.00	0.4200	0.1
Cl ⁻	KCl	AR BDH	74.56	0.7465	0.1
Br ⁻	NaBr	AR BDH	102.91	1.0291	0.1
I ⁻	KI	AR BDH	166.00	1.660	0.1
ClO ₄ ⁻	NaClO ₄ ·H ₂ O	Riedel	140.04	1.4004	0.1
CO ₃ ²⁻	Na ₂ CO ₃	AR BDH	106.00	1.0600	0.1

Ion	Formula	Quality	Sp. Gr./ Mol. wt.	Weight/ Volume	Molarity of the stock solution
SO ₄ ²⁻	K ₂ SO ₄	AR BDH	174.25	1.7425	0.1
PO ₄ ³⁻	Na ₂ HPO ₄ .2H ₂ O	Renel, Hungery	177.99	1.7799	0.1
Persulphate	K ₂ S ₂ O ₈	E.Merck	270.33	2.7033	0.1
Thiourea	NH ₂ CSNH ₂	GR E.Merck	76.120	0.7612	0.1
Thio- sulphate	Na ₂ S ₂ O ₃ .5H ₂ O	E.Merck	248.18	2.4818	0.1
Citrate	(NH ₄) ₃ C ₆ H ₅ O ₇	GR E.Merck	243.22	2.4322	0.1
Tartrate	KNaC ₄ H ₄ O ₆ .2H ₂ O	GR E.Merck	246.19	2.4619	0.1
Oxalate	K ₂ C ₂ O ₄ .2H ₂ O	AR BDH	184.24	1.8424	0.1
EDTA	Na ₂ C ₁₀ H ₁₄ N ₂ O ₈ . 2H ₂ O	AR BDH	372.24	3.7224	0.1
Ascorbic acid	C ₆ H ₈ O ₆	GR SM	176.13	1.7613	0.1
DMF	HCoN(CH ₃) ₂	GR E.Merck	73.09	-	-
Acetic acid	CH ₃ COOH	AR BDH	60.05	-	-

i. Buffer solutions

Buffer solutions of different pH values were prepared by mixing the corresponding salts, acids and bases in suitable proportions as shown below. The pH of the resultant solutions was measured and adjusted to the required value using a pH meter.

pH	Constituents
1.0-3.0	1 M sodium acetate + 1 M hydrochloric acid
3.2-6.0	0.2 M sodium acetate + 0.2 M acetic acid
7.0	1.0 M sodium acetate + 0.2 M acetic acid
8.0 - 12.0	2.0 M ammonia + 2.0 M ammonium chloride.

Section iii: Instruments employed in the present investigations

a. UV-visible Spectrophotometer

UV- Visible (Perkin Elmer-Lambda 25) double beam spectrophotometer was used to carry out absorption measurements. It was developed by Perkin Elmer Singapore private limited, Singapore. Its main features are

1. Wavelength scanning system by CPU control without using sine bar to realize high speed wavelength scanning.
2. All in one type of spectrophotometer with CRT and printer controlled.
3. Back up parameters are available so as to enable single action operation.
4. Easy data processing, since the obtained spectrum is available by the conversion with CRO.

Specifications of UV Spectrophotometer

Measuring wavelength	:	200 – 1100 nm
Spectral band width	:	1 nm
Wavelength readability	:	0.1 nm increment
Wavelength Scanning speed	:	Monochromator setting speed is nearly 3600nm/min. Medium-nearly 1500nm/min. slow - nearly 480nm/min.

Wavelength accuracy	:	0.5nm with automatic wavelength correction
Light source Switching	:	Automatic switching according to wavelength can be selected between 295nm and 364nm
Photometric System	:	Double beam system
Recording mode	:	Print out measured data and calculated results
Recording mode	:	Mixed samples up to eight components can be determined. Mixed samples can be used as standards. Standard sample data can be stored in the back up memory (up to 16 standards)
Light source	:	50W long life Halogen lamp (2000hrs) and socket type Deuterium lamp (500hrs) with automatic control of maximum sensitivity, monochromatic.
Monochromator	:	Aberration corrected concave holographic grating with $f = 4.2$
Detector	:	A method pair of Silicon photodiode
Recorder	:	Computer controlled thermal graphic printer

CTR	:	9-inch with graphic function 240-320 dots
Sample compartment	:	Inner size 1100 nm wide
Distance between the sample and reference beam	:	100 nm
Power requirements	:	100 to 250V AC, 50/60 Hz, 259V

b. pH meter

Model LI-120 Elico digital pH meter, manufactured by M/S Elico private limited, Hyderabad, was used for measuring the pH of different buffer solutions used in the present study. The pH meter has temperature compensate arrangement. The reproducibility of the measurements is with in $\pm 0.01\text{pH}$.

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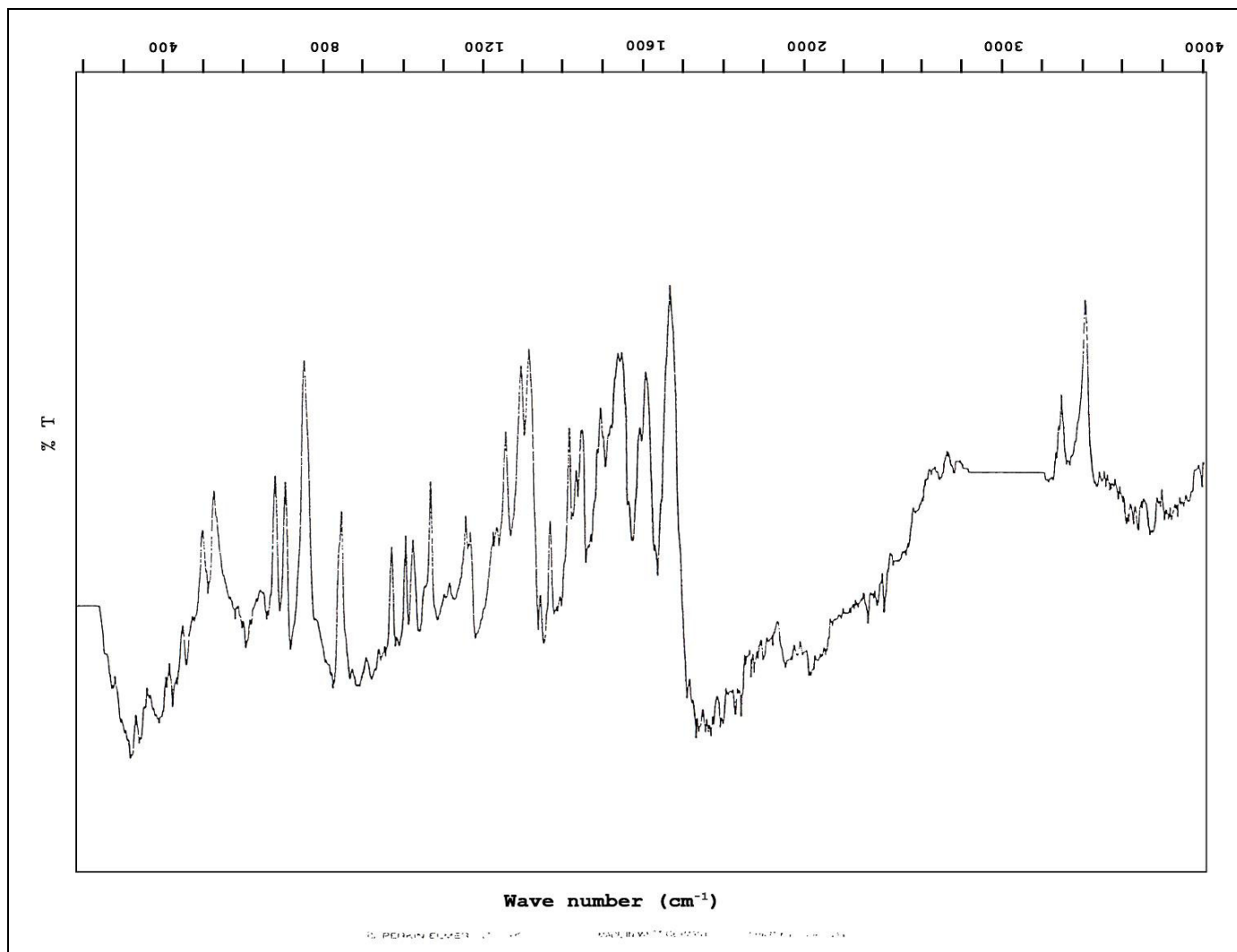


Fig. 2.i.1 : IR Spectrum of 2-Amno-acetophenone isonicotinoyl hydrazone (2-AAINH)

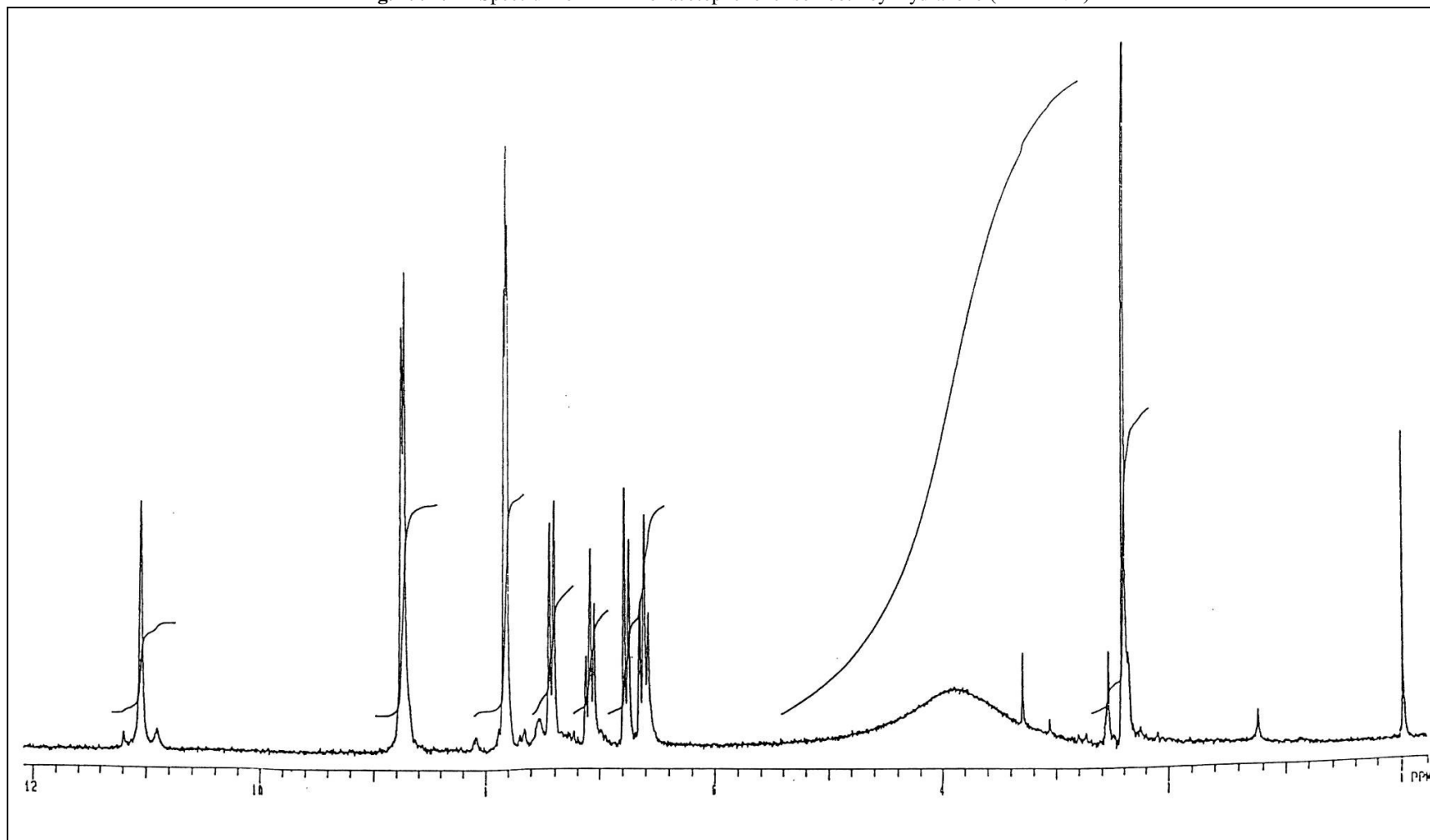


Fig. 2.i.2 : NMR Spectrum of 2-Amino-acetophenone isonicotinoyl hydrazone (2-AAINH)