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Synthesis and Characterization of Schiff Bases Derived from 1-Naphthylamine Hydrochloride, Syria: Homs

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Abstract
The three Schiff bases namely NPNA (L^1): N-[(E)-Pheny lmethylene]Naphthalene-1-Amine, newly NNNA (L^2): N-[(E)-1-Naphthylmethylene]Naphthalene-1-Amine and NFNA (L^3): N-[(E)-2-Furylmethylene] Naphthalene-1-Amine have been synthesized in equimolar reaction of 1-Naphthylamine hydrochloride with or naphthalene-1-carbaldehyde or 2-furfuraldehyde in the presence of acetic acid glacial. The characterization of Schiff bases was done by^{1}HNMR, UV–VIS, IR, spectral studies and analytical data.
Keywords: Schiff bases, aromatic aldehyde, spectroscopic studies.
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1. Introduction

Schiff bases are named in the owner of Hugo Schiff (1834-1915) [1-2]. Their formula is {HR-C=N-R} R=aryl group and Hugo Schiff prove it in (1864) [1].They are formed by condensation of aldehyde compounds with primary amine compounds in alcoholic medium in the presence of acetic acid as catalyst to make PH ranges between(4.5-5) [3]. Schiff base is called imine, azomethine, aldimine and anil. Schiff base derived from aromatic aldehyde and aromatic amine is more stable because the having effective conjugation and readily synthesized. Schiff bases used as antibacterial [4], antifungi [5], anti-inflammatory [6], analgesic [6], anticancer [7] and corrosion Inhibition [8]. In industry section they are used as antioxidant agents [9], and as primary compound to synthesis new compounds [10]. The goal of the study presented here is to synthesize from condensation of 1-Naphthyl amine hydrochloride with benzaldehyde or naphthalene-1-carbaldehyde or 2-furfuraldehyde.

2. Experimental

2.1. Materials and instrumentation

1-Naphthyl amine hydrochloride was supplied from Titan Biotech LTD. Benzaldehyde was supplied from Uni-Chem. naphthalene-1-carbaldehyde, acetonitrile, TLC aluminium sheets was supplied from Merck. 2-Furfural was supplied from Fluka. EtOH, $CHCl_3$, $(C_2H_5)_2O$, $CH_3COOC_2H_5$, DMF, n-Hexan were supplied from Sigma-Aldrich. CH_2Cl_2 Were supplied from Surechem Products LTD. Acetic acid glacial, cyclohexan, were supplied from BDH. IR measurements (KBr pellets) were carried out on Jasco 4100 FT- Samples were dissolved in $(CD_3)_2CO$ with TMS as internal reference IR spectrometer. NMR measurements were performed on a Bruker 400 MHz spectrometer.

Ultraviolet-Visible spectra were recorded using a Optizen UV 3220 Spectro- photometer in the range of 200–800 nm and DMF is used as a solvent. Elemental analyses (C, N,H) were analyzed on FEI Quanta 200 Scanning Electron Microscopes. Decomposing point of the compounds were recorded using Electro Thermal Melting Point Apparatus (10-370 °C). Differential Thermal Analyzer (DTA) were recorded for only NFNA using Shimadzu.

2.2. General procedure for the synthesis of the ligands NPNA , NNNA and NFNA

solution of (3mmol, 0.03gr) of Benzaldehyde or (3mmol, 0.47gr) of naphthalene-1-carbaldehyde or (3mmol, 0.29gr) of 2-furfuraldehyde in (6ml) absolute ethanol added dropwise to a solution of (3mmol,0.55gr) of 1-Naphthylamine hydrochloride in (6ml) absolute ethanol in round bottom flask (50ml), then(1ml) of acetic acid glacial was added to this solution. The mixture was refluxed 23h for NPNA and 21h for NNNA in an oil bath at (77–79°C).The reaction was monitored through TLC. After completion of the reaction (TLC analysis) the flask was cooled on crush ice to afford a solid product. The precipitates obtained were filtered, washed with acetonitrile and ethanol. Then they recrystallization from (CH_2Cl_2:EtOH) in ratio (1:2). Then they driedunder vacuum.

Through TLC we mointred the reaction of Schiff bases by using mix of solvents: (cyclohexan: diethylether) in ratio (3:2) for NPNA, (cyclohexan: chloroform) in ratio (3:1) for NNNA, (n-hexan: Ethyl acetate) in ratio (2:1) for NFNA. The TLC is listed in Table 1.

I. N-[(E)-Phenylmethylene]Naphthalene-1-Amine **NPNA (L^1):** Yield: 90.82(%). Color (yellow). DP.

183°C. IR (KBr, cm^{-1}): 1636(HC=N). ^{1}HNMR (CD_3COCD_3, δ, ppm) 7.14-7.16 (2,d,Ar), 7.3-7.4 (3,d,Ar), 7.4-7.44 (2,t,Ar), 7.46-7.52 (4,tet,Ar) 7.92-7.98 (2,m, H-C=N, Ar). UV (DMF, nm) 301 (π→π*, CH=N). Anal. Calc. For $C_{17}H_{13}N$ (231.29): C: 88.28; H: 5.67; N: 6.06; found: C: 88.18; H: 5.87; N: 5.95.

II. N-[(E)-1-Naphthylmethylene]Naphthalene-1-Amine **NNNA (L^2):** Yield: 84.76(%). Color (yellow). DP. 310°C. IR (KBr, cm^{-1}): 1633(HC=N). ^{1}HNMR (CD_3COCD_3, δ, ppm) 7.02-7.03 (2,t,Ar), 7.24-7.33 (2,tet,Ar), 7.48-7.54 (2,t,Ar), 7.59-7.64 (2,t,Ar) 7.79-7.81 (2,d,Ar), 7.92-7.94 (2,d,Ar), 8.01-8.05 (1,d,Ar), 8.12-8.14 (2,m, H-C=N, Ar). UV (DMF, nm) 308 (π→π*, CH=N). Anal. Calc. For $C_{21}H_{15}N$ (281.35): C: 89.65; H: 5.37; N: 4.98; found: C: 89.61; H: 5.58; N: 4.81.

III. N-[(E)-2-Furylmethylene]Naphthalene-1-Amine NFNA (L^3): Yield: 79.59(%). Color (red). DP. 118°C. IR (KBr, cm^{-1}): 1637(HC=N). ^{1}HNMR (CD_3COCD_3, δ, ppm) 7.4-7.42 (2,m,Ar), 7.5-7.52 (5,m,Ar), 7.84-7.92 (4,m, H-C=N, Ar). UV (DMF, nm) 330 (π→π*, CH=N). Anal. Calc. For $C_{21}H_{15}N$ (281.35): C: 81.43; H: 5.01; N: 6.33; O: 7.23; found: C: 81.40; H: 5.04; N: 6.18; O: 7.18.

3. Results and discussion

The Schiff base NPNA (scheme1) was prepared by condensation in ethanol of 1-Naphthyl amine hydrochloride and benzaldehyde. The same method was used for the preparation of the ligand NNNA and NFNA. (scheme1) The structure of Schiff bases thus formed was established by IR, ^{1}HNMR, UV and CHN analysis. The synthesized Schiff bases were soluble in DMF, DMSO. The composition of the ligands was consistent with their NMR, IR, and CHN data. The results of the elemental analyses of the ligands, which are recorded in Table 1, are in good agreement with those required by the proposed formulae.

3.1. IR spectra

The characteristic bands of IR spectra of ligands L^1, L^2 and $L^3$are reported in Table 2. Peak corresponding to ν(C=O) stretching vibrations was absent in IR spectra of L^1 and, instead, a new band assigned to azomethine ν(HC=N) linkage appeared at 1636 cm^{-1} confirming the formation of Schiff base [3]. Similarly, the peak at 1633 cm^{-1}in L^2 corresponds to ν(HC=N) linkage [3], and similarly, the peak at 1637 cm^{-1}in L^3 corresponds to ν(HC=N) linkage [3]. A medium intensity band due to ν(C-O-C) stretching vibration of furan appeared at 1200 cm^{-1} in the ligands L^3 [3].

Table 1

Physical measurements and analytical data of the ligands L^1, L^2, L^3 .

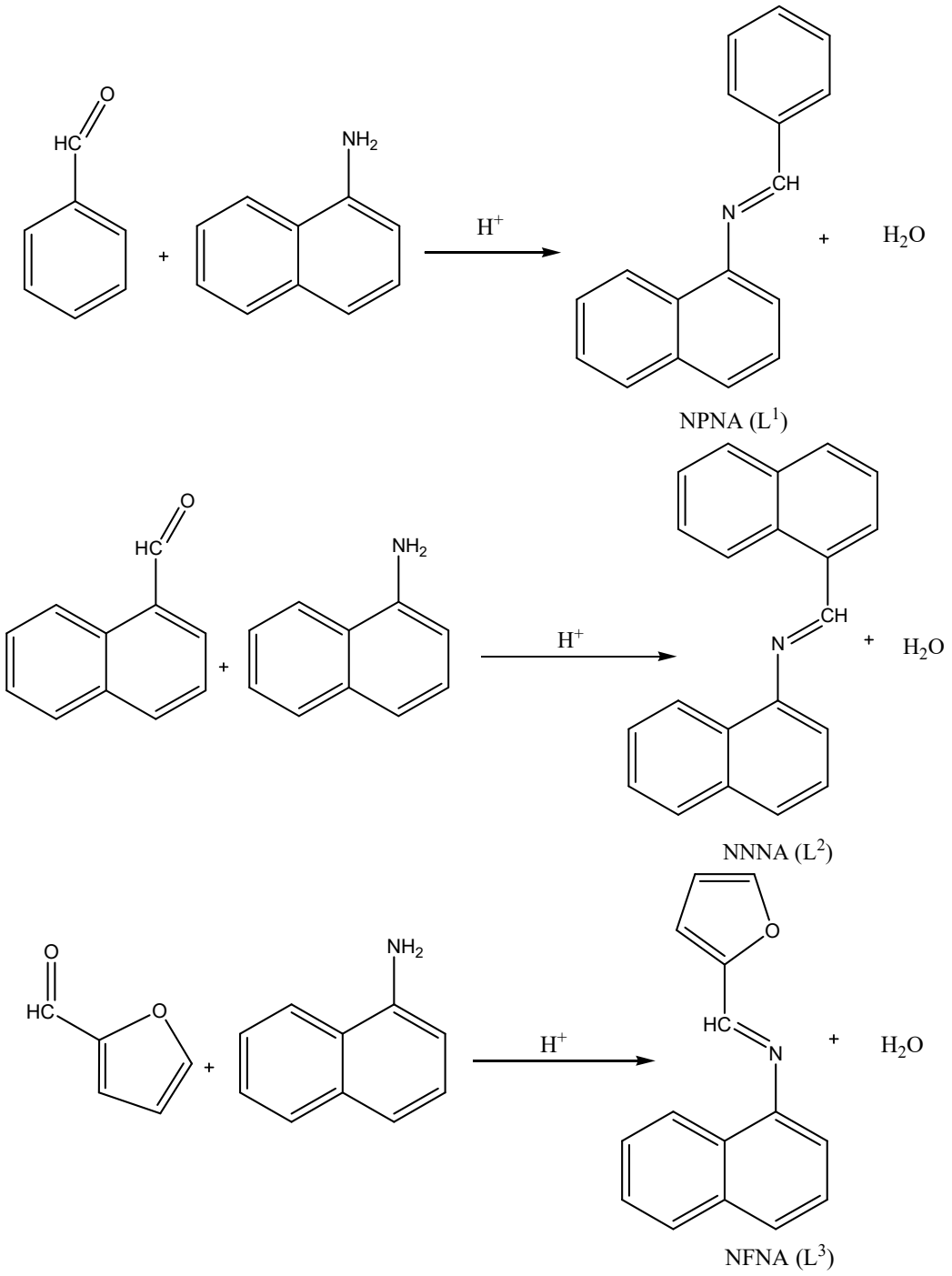
No	molecular formula	DP (°C)	TLC	Yield (%)	Elemental analysis (%) calculate (found)			
					C	N	H	O
L^1	NPNA (L^1) [$C_{17}H_{13}N$]	183	0.91*	90.82	88.28 (88.18)	6.06 (5.95)	5.67 (5.87)	---
L^2	NNNA (L^2) [$C_{21}H_{15}N$]	310	0.83**	84.76	89.65 (89.61)	4.98 (4.81)	5.37 (5.58)	---
L^3	NFNA (L^3) [$C_{15}H_{11}NO$]	125	0.85***	82.34	81.43 (81.40)	6.33 (6.17)	5.01 (5.04)	7.23 (7.18)

*- (cyclohexan: diethylether) in ratio (3:2), **- (cyclohexan: chloroform) in ratio (3:1)
***- (n-hexan: Ethyl acetate) in ratio (2:1),

Table 2

IR, UV–Vis data of the ligands L^1, L^2, L^3 .

No	Color	IR (cm^{-1})	UV (nm)		
		ν(CH=N)	π→π*(Ar)	π→π*(CH=N)	n→π*(CH=N)
L^1	Yellow	1636	281	301	400
L^2	Yellow	1633	277	308	403
L^3	Red	1637	287	330	395



Scheme 1. Preparation of Schiff bases

3.2. ^{1}HNMR spectra

The 1H NMR spectra have been recorded for ligand L^1, L^2 and L^3. The spectra of ligand L^1 (Fig. 1) displayed azomethine (H-C=N) proton as a multiply at 7.92-7.98 ppm [3]. In the spectra of the ligand L^2 (Fig. 2) the azomethine (H-C=N) proton appeared as doublet at 8.12-8.14 ppm [3].

Similarly In the spectra of the ligand L^3 (Fig. 3) the azomethine (H-C=N) proton appeared as multiply at 7.84-7.92 ppm [3].

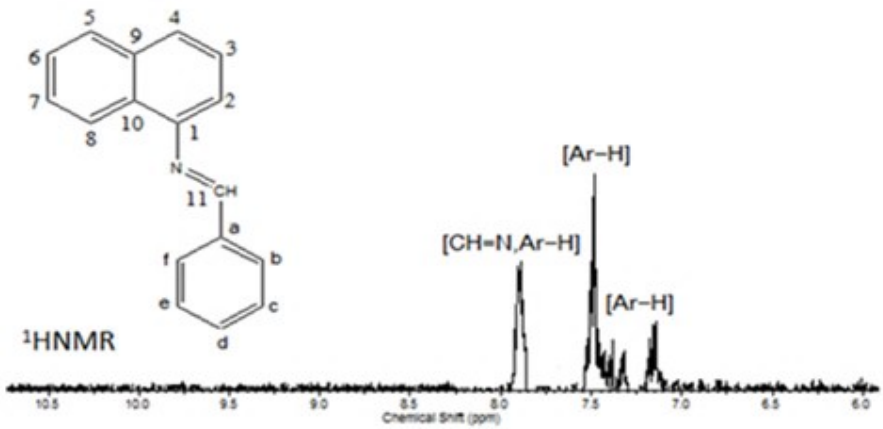


Fig.1. ^{1}HNMR spectrum of L^{1} ligand

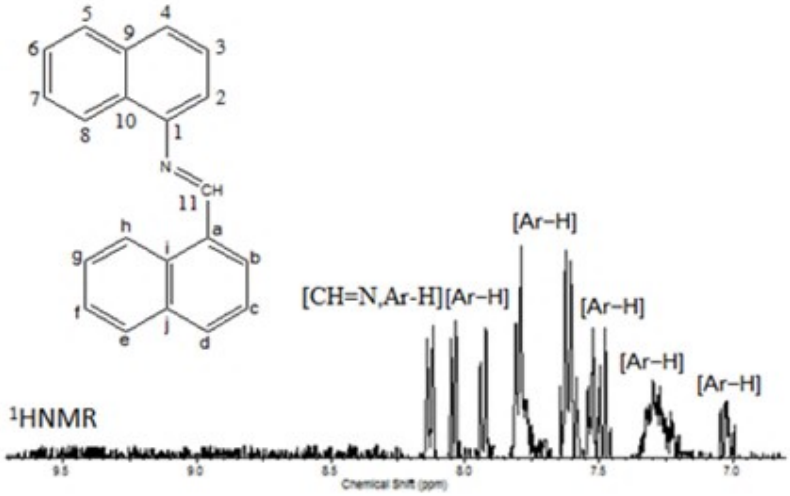


Fig.2. ^{1}HNMR spectrum of L^{2} ligand

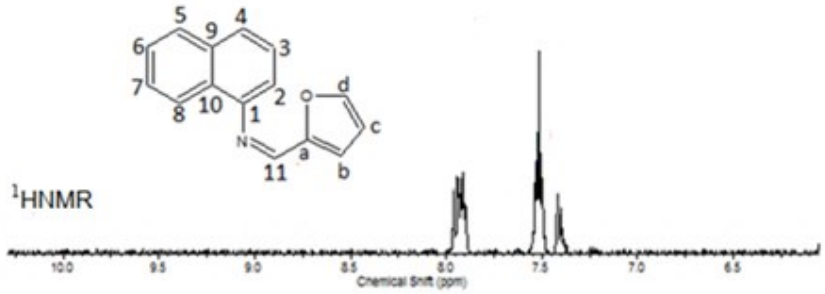


Fig.3. ^{1}HNMR spectrum of L^{3} ligand

3.3. Electronic spectra

The electronic spectra of the ligands and their complexes were recorded in DMF medium at room temperature. All the spectra of the ligands show band in range (301,308, 330nm) are attributable to the transition ($\pi \rightarrow \pi^*$) of the azomethine corresponding of the ligands (L^{1},L^{2},L^{3}) respectively [12,11,5].

3.4. Thermal analysis

The DTA curve of the ligand L^3 (Fig 4) shows an endothermic band at 84.87°C which represent the loss of lattice water [13].

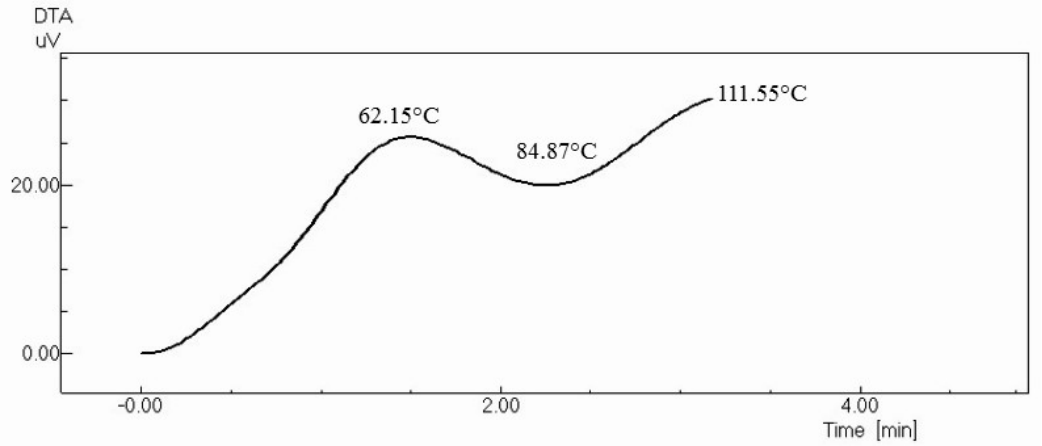
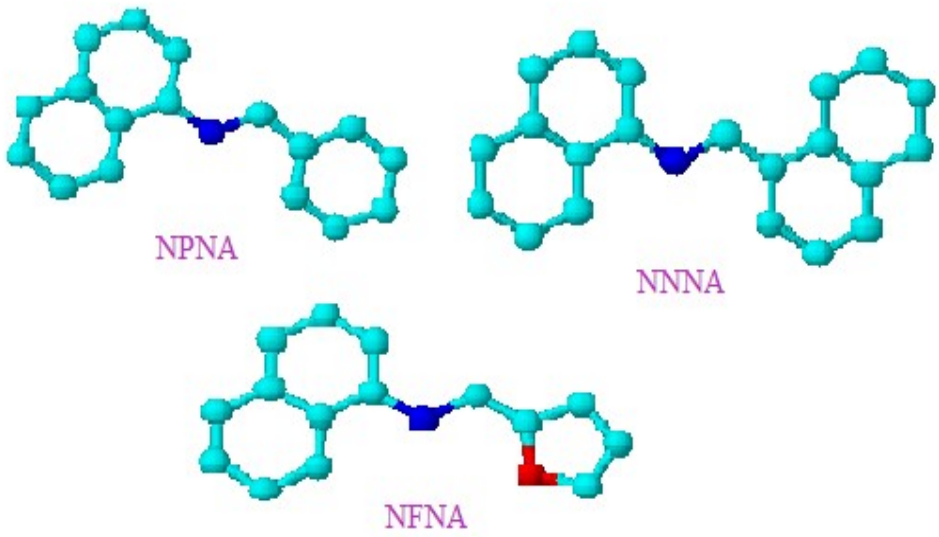


Fig.4. DTA curve of L^3 ligand



Scheme 1. structure of Schiff bases

4. Conclusion

Three Schiff bases mono dentate NPNA, NNNA and di dentate NFNA were synthesized from 1-Naphthyl amine hydrochloride with benzaldehyde or naphthalene-1-carbaldehyde or 2-furfuraldehyde. The ligands were confirmed from ^{1}HNMR,UV–VIS, IR, spectral studies and analytical data.

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