



## Intramolecular Proton Transfer Equilibrium in Salicylidene- and Naphthalene-based Tetraimine Schiff Bases

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### Abstract

In this work, two nitro-Schiff bases were synthesized by condensation reaction of 4-nitro-benzaldehyde with p-phenylenediamine and 3-amino-2-naphthol in 2:1 and 1:1 ratios, respectively. Then, the reduction of nitro group to amino group with sodium dithionite and forming the new imine bond by adding aldehyde, as salicylaldehyde, 2-hydroxy-1-naphthaldehyde or terephthaldehyde, asymmetric tetraimine Schiff bases (**L-1**, **L-2**, **L-3**) were prepared. Tetraimines have been characterized by elemental analysis, FT-IR, <sup>1</sup>H/<sup>13</sup>C NMR, UV-Vis, and mass spectroscopy techniques in order to study the structure effect on the phenol-keto tautomerism. Solvent, acid and base effects on the tautomeric equilibrium have been also investigated by using UV-Vis spectra.

## 1. INTRODUCTION

Symmetrical bis-Schiff bases of the type R-N=CH-Ar-CH=N-R or R-CH=N-Ar-N=CH-R are usually synthesized from the condensation reaction of primary amines with active carbonyl groups of dialdehydes in 2:1 molar ratio and the reaction of diamines with aldehydes or ketones in 1:2 molar ratio. However, asymmetric bis-Schiff bases of the type R-N=CH-Ar-N=CH-R can be prepared with a new two step method [1], which is based on the conversion of the nitro group into the amino group.

Schiff bases are a kind of attractive reagents due to specific activities of pharmacology and physiology, such as antibacterial [2], antifungal [3], anti-inflammatory [4], anticonvulsant [5], antiproliferative [6], antitubercular [7], antiviral [8], anthelmintic [9], antitumor [10], antioxidant [11], DNA-binding [12] and enzyme inhibition activities [13]. They are also used as pigments and dyes [14], catalysts [15], polymer stabilisers [16], model molecules for biological oxygen carrier systems [17] and chemosensors [18]. Moreover, they have been of major interest for a long time because of their linear and non-linear optical (NLO) [19], photochromic [20], thermochromic and solvatochromic properties [21] resulting from the intramolecular hydrogen transfer ability. Due to their physicochemical properties, they can serve as the specific type of organic electronic device in optical recording technology, molecular electronics, and computing [22].

Generally for Schiff bases obtained from 2-hydroxy-aldehydes exhibit tautomeric rearrangements because of intramolecular proton transfer between the oxygen and nitrogen atoms [23]. The type of the dominant form strongly depends on the kind of aldehyde used for the preparation of corresponding Schiff bases. For most salicylaldimines and naphthaldimines, the phenol-imine form is usually more stable than the keto-amine form in the gas phase and in solutions at room temperature [24]. It is also known that the position of the proton transfer equilibrium is influenced by the interactions with the solvent molecules [25] as well as on temperature and light. This prototypic equilibrium has been studied by FT-IR [26], UV-Vis [27], mass [28], X-ray diffraction [29], NMR in the liquid and in solid state [30] and density functional theory (DFT) calculation [31].

The aim of this work is to synthesis and characterization of new polydentate asymmetric Schiff bases and investigation of the structure effect on the intramolecular hydrogen bonding and related tautomeric

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equilibrium by spectroscopic methods. Moreover, solvent, acid and base effects on the tautomerism are reported and discussed by using UV-Vis spectra.

## 2. EXPERIMENTAL

### 2.1. Materials and Reagents

3-amino-2-naphthol, p-phenylenediamine, 4-nitro-benzaldehyde, terephthaldehyde, salicylaldehyde, 2-hydroxy-1-naphthaldehyde and sodium dithionite were purchased from Aldrich Chemical Company. All chemicals used were of the analytical reagent grade and of highest purity available. Absolute ethyl alcohol (EtOH) (Sigma-Aldrich), diethylether (Riedel-de-Haen), dimethylsulfoxide (DMSO) (Merck), methanol (MeOH) (Merck) and toluene (Riedel-de-Haen) were used. Organic solvents were spectroscopic pure.

### 2.2. Instrumentation

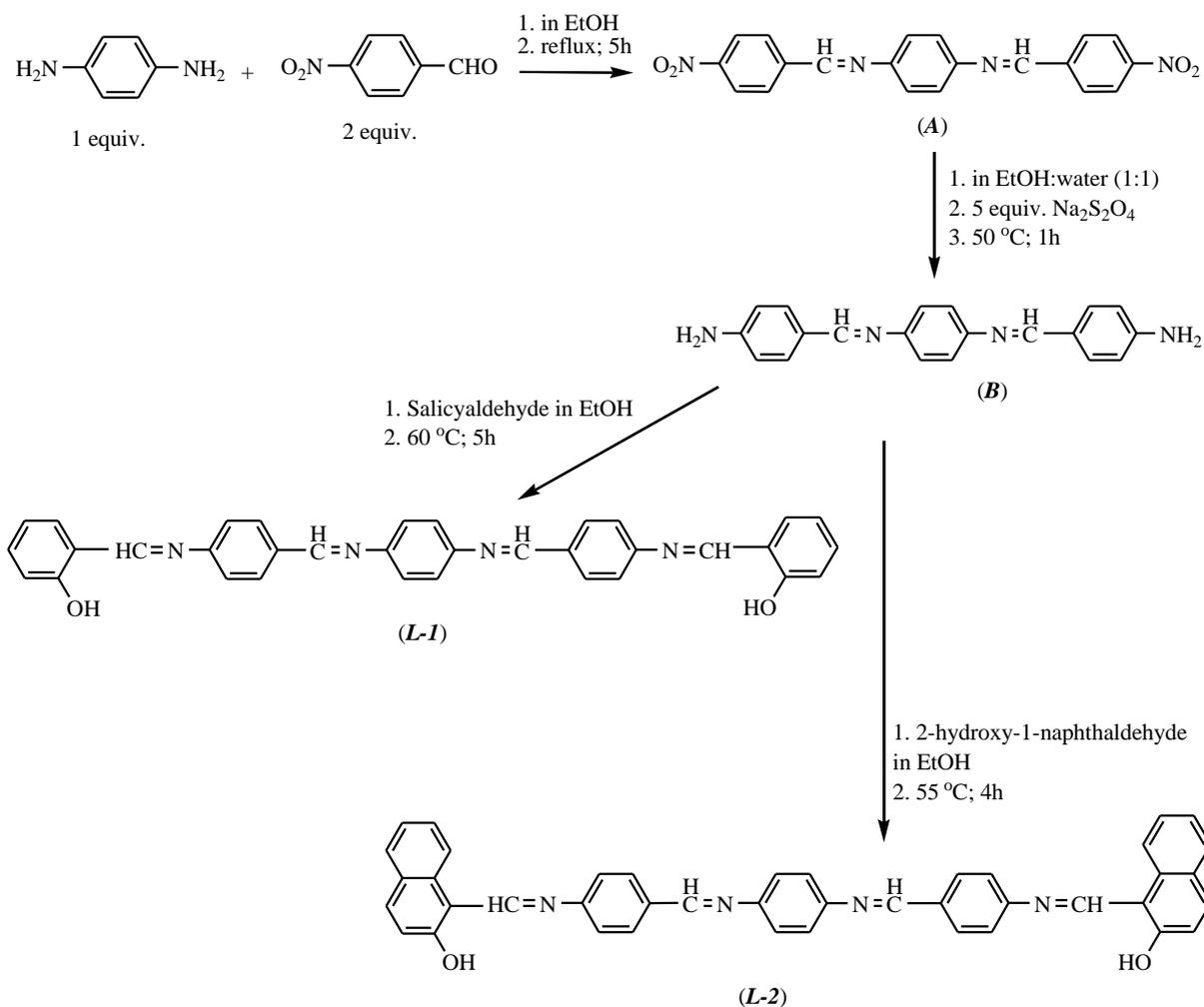
Melting points were recorded on Barnstead Electrothermal BI 9200. Elemental analysis was performed on LECO CHNS-932 analyzer. IR spectra in the 4000-400  $\text{cm}^{-1}$  range were measured using KBr discs on a Mattson 1000 FT-IR spectrophotometer.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were determined with a Bruker Avance DPX FT-NMR ( $^1\text{H}$ : 400 MHz and  $^{13}\text{C}$ : 100 MHz) spectrometer. Chemical shifts are given in  $\delta$  values (ppm) using tetramethylsilane (TMS) as the internal standard, DMSO-*d*<sub>6</sub> as solvent. The mass spectra were recorded using the positive ion electrospray ionization modus (ESI) at 70 eV or 100 eV on an Agilent 1100 MSD mass spectrometer.

### 2.3. Absorption measurements of all Schiff bases

UV-Vis spectra of compounds were measured in pure solvents (DMSO, methanol and toluene) and acidic and basic solutions of these solvents with 0.01 mM concentration. 0.2 mL trifluoroacetic acid and 0.2 mL triethylamine were added to the solvents (5 mL) to provide the acidic and basic media, respectively. The spectra were obtained using Shimadzu UV-1800 UV-Vis spectrophotometer over the wavelength range 270–600 nm at room temperature.

### 2.4. Synthesis of tetraimine-Schiff bases (L-1, L-2)

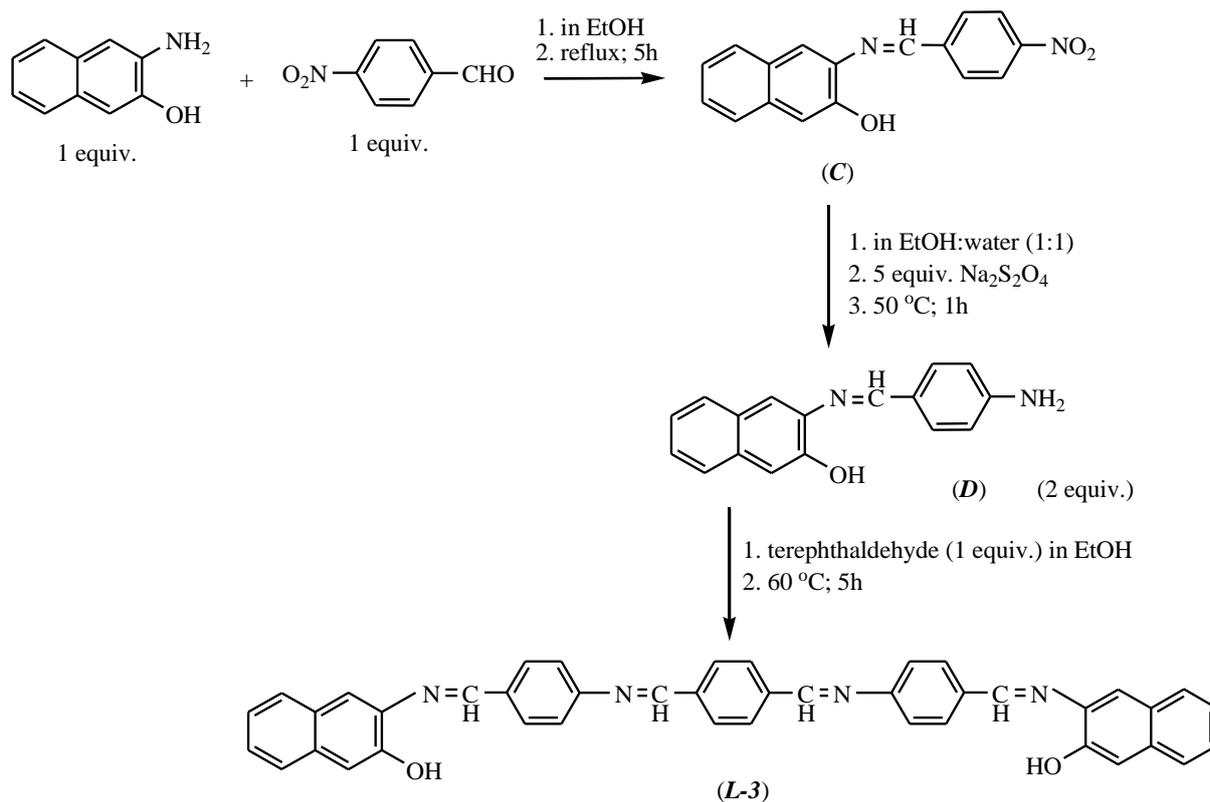
At first, the nitro Schiff base N',N'-bis(4-nitrobenzylidene)benzene-1,4-diamine (Scheme 1A), was synthesized by reacting 4-nitro-benzaldehyde with p-phenylenediamine in EtOH, as reported in the literature [32]. 1 mmol (0.374 g) of (A) was dissolved in ethanol-water mixture (80 mL:80 mL) at 60 °C. 5 mmol (0.871 g) of solid sodium dithionite was slowly added to the solution as small solid pieces over one hour and stirred for one hour at 50 °C for finishing the reducing process. Thus, (B) was obtained in the solution. 1 mmol (0.122 mL) of salicylaldehyde or 1 mmol (0.172 g) of 2-hydroxy-1-naphthaldehyde in 15 mL ethanol was added dropwise during the period of an hour with stirring to the solution (B). The mixture was stirred at 55-60 °C for 4-5 h. The resulting solution was evaporated at room temperature for approximately a week, until a precipitate was formed. The crude product (L-1 or L-2) was treated with warm water (2x25 mL) and EtOH (2x25 mL) and filtered twice; and recrystallized from EtOH.



**Scheme 1.** The preparation of tetraimine Schiff bases (**L-1** and **L-2**).

### 2.5. Synthesis of tetraimine-Schiff base (**L-3**)

At first, the nitro Schiff base 3-(4-nitrobenzylideneamino)naphthalen-2-ol (Scheme 2C), was synthesized by reacting 4-nitro-benzaldehyde with 3-amino-2-naphthol in EtOH, as reported in the literature.<sup>1</sup> 2 mmol (0.5840g) of (**C**) was dissolved in ethanol-water mixture (30 mL:30 mL) at 60 °C. 5 mmol (0.871 g) of solid sodium dithionite was slowly added to the solution as small solid pieces over one hour and stirred for one hour at 50 °C for finishing the reducing process. Thus, (**D**) was obtained in the solution. 1 mmol (0.134 g) of terephthalaldehyde in 15 mL ethanol was added dropwise during the period of an hour with stirring to the solution (**D**). The mixture was stirred at 60 °C for 5 h. The resulting solution was evaporated at room temperature for approximately 4 days, until a precipitate was formed. The crude product (**L-3**) was treated with warm water (2x25 mL) and EtOH (2x25 mL) and filtered twice; and recrystallized from ethanol.



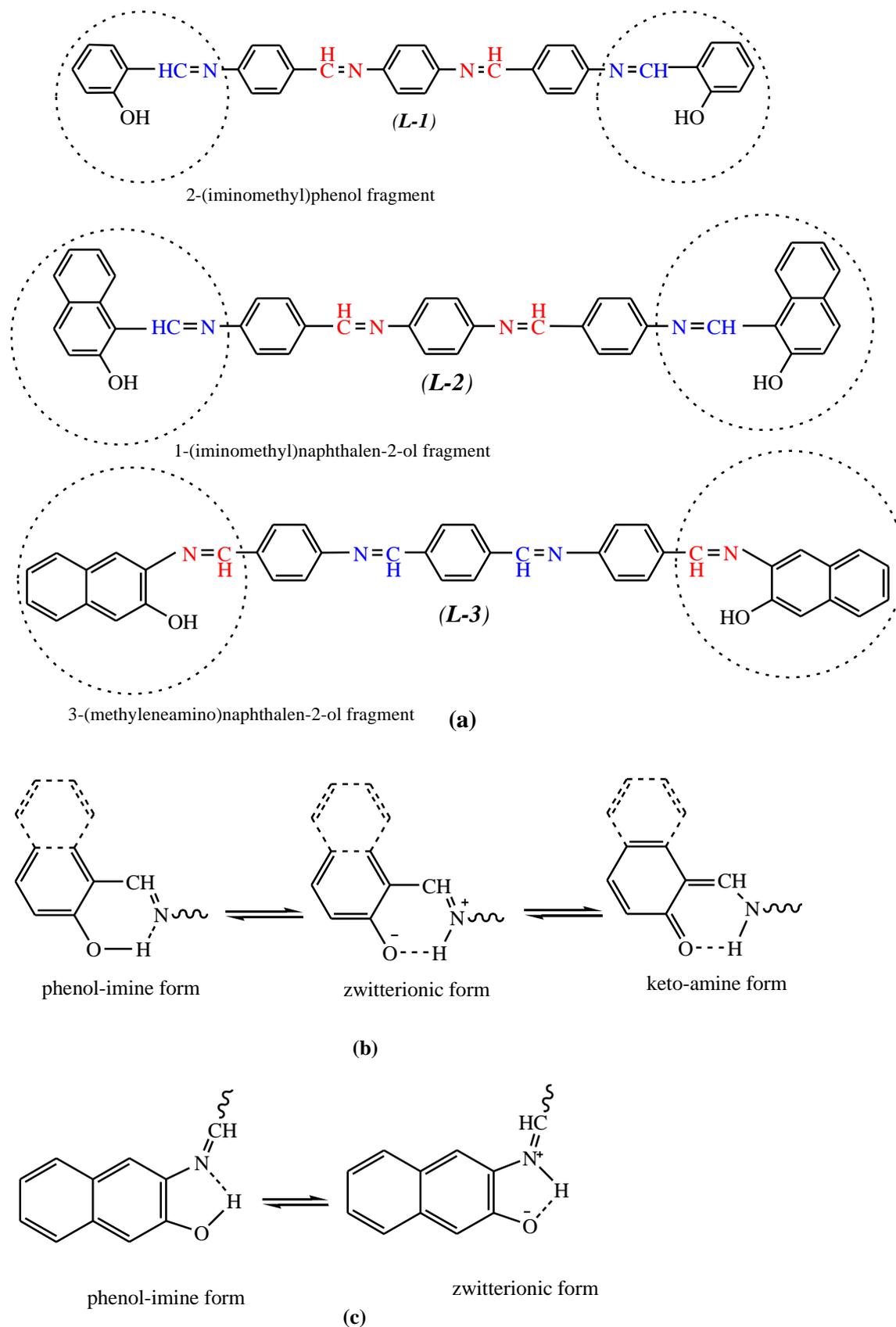
**Scheme 2.** The preparation of tetraimine Schiff base (**L-3**).

### 3. RESULTS AND DISCUSSIONS

As can be seen in Scheme 3a, the prepared tetraimine Schiff bases have different azomethine moieties of the bridging bond  $-\text{CH}=\text{N}-\text{Ar}-\text{CH}=\text{N}-$  or  $-\text{N}=\text{CH}-\text{Ar}-\text{N}=\text{CH}-$  spacers in the solid. These asymmetrical Schiff bases can be divided into three series. The first (**L-1**), and second model (**L-2**) compounds contain 2-(iminomethyl)phenol and 1-(iminomethyl)naphthalen-2-ol

fragments respectively, they are named N-salicylidine-aniline and 1-naphthylidene-aniline Schiff bases, respectively. The third model compound (**L-3**) contains 3-(methyleneamino)naphthalen-2-ol fragments and it may be a part of a series of 3-naphthylazomethine Schiff bases. Consequently, this difference opens the possibility to explore the effect of structure on formation of intramolecular hydrogen bonding.

Two types of intramolecular hydrogen bond (either  $\text{O}-\text{H} \cdots \text{N}$  or  $\text{O} \cdots \text{H}-\text{N}$ ) between the hydroxyl proton and the nitrogen atom of the azomethine group can occur in these Schiff bases. In the presence of **L-1** and **L-2**, the hydrogen bond mentioned above forms a six-membered chelate ring in 2-(iminomethyl)phenol and 1-(iminomethyl)naphthalen-2-ol fragments (Scheme 3b). This ring is planar and it is called a pseudoaromatic chelate ring [33]. In **L-1**, the proton transfer from oxygen to the nitrogen atom is accompanied by loss of the benzene-ring aromaticity. So, this transfer is disfavored and the phenol-imine form is the most stable form for **L-1**. In **L-2**, the proton transfer does not affect  $D_{2h}$  symmetry of the naphthalene ring, and it may lead to the phenol-imine and keto-amine tautomeric forms. Although **L-3** has two naphthyl groups, intramolecular hydrogen bond forms five-membered chelate ring (Scheme 3c). Because of this, it may exist in phenol-imine or zwitterionic forms.



**Scheme 3.** The chemical structures of asymmetrical tetraimine Schiff bases (a); the intramolecular hydrogen bonding in **L-1** and **L-2** (b), and **L-3** (c).

The influence of structure on the tautomeric equilibria has been studied by experimental methods. The experimental investigations have been performed in the solid state by using IR spectra, in DMSO solution by using NMR spectra and in different solvents, acidic and basic solutions by using UV–Vis spectra.

### 3.1. IR Spectra

From the IR spectra, it is possible to assign the imine (C=N) vibration which is accountable partially for the existence phenol-imine form and the carbonyl (C=O) vibration of the keto-amine form. The band at the region (1614-1623  $\text{cm}^{-1}$ ) may be due to the vibration of C=N [34]. It is also possible to assign other absorptions which are either specific to the enol or the keto forms. A characteristic band of intermediate intensity at 1100-1300  $\text{cm}^{-1}$  may be related to a stabilization of phenolic C–O bond and suggests a high percentage of phenol-imino tautomer [35].

The analytical data and the characteristic infrared spectral data are listed in Table 1. The exemplary spectra are given in Fig. 1. IR spectra of tetramines (**L-1** and **L-2**), distinct bands due to imine groups within the range of 1612–1626  $\text{cm}^{-1}$  are routinely noticed [36]. Broad bands, centered at about 2793-2762  $\text{cm}^{-1}$ , are attributed to the intramolecular hydrogen bonded OH stretching vibrations for **L-1** and **L-2** respectively. A weak band at 3404  $\text{cm}^{-1}$  is also observed for **L-2**. As well, the absorption bands at 3051-3057 and 1542-1580 and 2858–2999  $\text{cm}^{-1}$  are assigned to  $\nu(\text{Ar-H})$ ,  $\nu(\text{C=C})$  and  $\nu(\text{C-H})$  of imine group, respectively. The band found at 1138-1189  $\text{cm}^{-1}$  may be due to the phenolic C–O bond.

In IR spectra of the tetraimine (**L-3**),  $\nu(\text{C=N})$  vibration corresponding to the different azomethine moieties appear at 1600-1632  $\text{cm}^{-1}$  [37]. Free  $\nu(\text{OH})$  groups are generally observed at 3450  $\text{cm}^{-1}$  as a broad band. The bands due to  $\nu(\text{Ar-H})$ ,  $\nu(\text{C=C})$  and  $\nu(\text{C-H})$  vibration of imine bond appear at 3057, 1560, and 2922-2967  $\text{cm}^{-1}$ , respectively. A strong band at 1205  $\text{cm}^{-1}$  is assigned as phenolic (C–O) vibration.

**Table 1.** Analytical, physical and significant infrared spectral data of tetraimine Schiff bases.

Comp.	Empirical formula (Molecular weight)	Color Yield (%)	M.p. (°C)	Found (Calcd.) %			IR spectra				
				C	H	N	OH	C-H arom.	CH=N	C=C	C-O
							C-H alip.				
<b>L-1</b>	C <sub>34</sub> H <sub>26</sub> N <sub>4</sub> O <sub>2</sub> (522 g/mol)	Orange 46	212-213	77.75(78.16)	5.06(4.98)	10.04(10.73)	2793 (center)	3057(w) 2999(w)/2865(w)	1612(s)	1574(s) 1554(w)	1189(m)
<b>L-2</b>	C <sub>42</sub> H <sub>30</sub> N <sub>4</sub> O <sub>2</sub> (622 g/mol)	Red 50	305-307 <sup>a</sup>	80.54(81.03)	5.13(4.82)	8.84(9.00)	3404(w) 2762 (center)	3051(w) 2960(w)/2858(w)	1626(s)	1580(m) 1542(m)	1138(m)
<b>L-3</b>	C <sub>42</sub> H <sub>30</sub> N <sub>4</sub> O <sub>2</sub> (622 g/mol)	Brown 48	226-229	81.29(81.03)	5.76(4.82)	8.69(9.00)	3450(s)	3057(w) 2967(w)/2922(w)	1632(m) 1600(m)	1560(m)	1205(s)

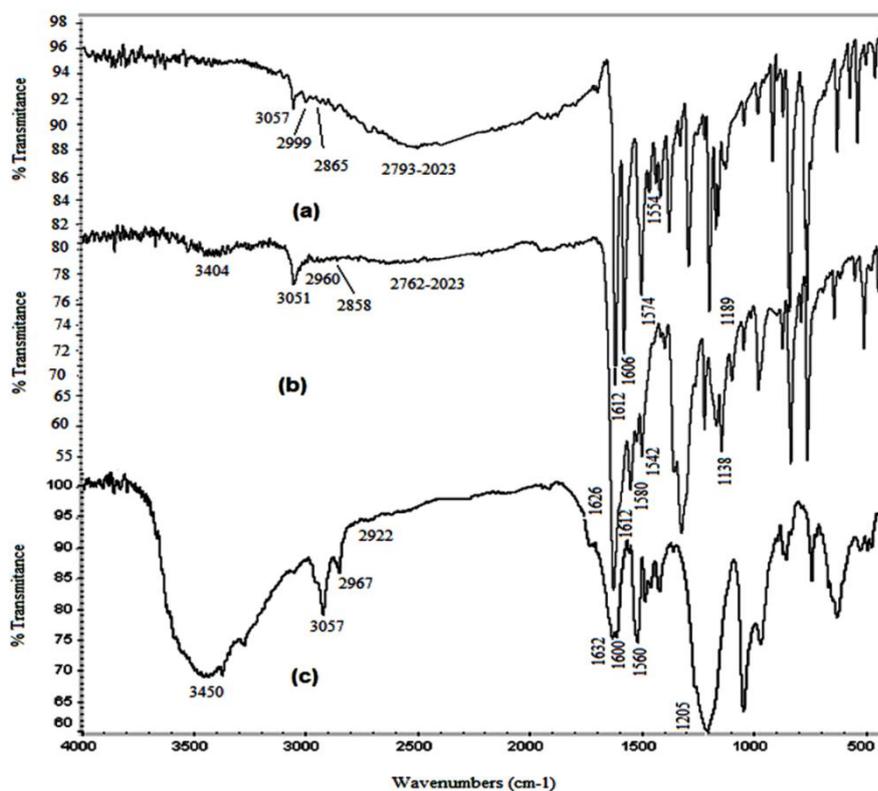


Figure 1. IR spectra of L-1 (a), L-2 (b), and L-3 (c).

### 3.2. $^1\text{H}$ NMR Spectra

The  $^1\text{H}$  NMR data can support the existence of intramolecular proton transfer process which is responsible for the phenol-keto tautomerism in Schiff bases. The broad signal observed in the range 13.1–13.5 ppm indicates the chemical shift of the phenolic OH proton involved a medium strong  $\text{OH}\cdots\text{N}$  intramolecular hydrogen bond [38]. The signal of NH proton at higher ppm is assigned to the proton from the  $\text{O}\cdots\text{H}-\text{N}$  intramolecular hydrogen bond. The coupling constant  $^3J_{(\text{NH},\text{H})}$  on imine proton confirms the splitting of the imine proton signal and the existence of the keto-amine form in equilibrium [39].

$^1\text{H}$  NMR spectra of tetraimines were carried out in  $\text{DMSO}-d_6$  solvent at room temperature, using tetramethylsilane (TMS) as internal standard. The chemical shifts of the different types of protons are summarized in Table 2.  $^1\text{H}$  NMR results for L-1 exhibit that the phenol-imine form is obtained exclusively in DMSO without presence of keto tautomer. The phenolic OH protons involved in the  $\text{O}-\text{H}\cdots\text{N}$  type intramolecular hydrogen bond are observed at 13.07 ppm (Fig. 2a). The imine ( $-\text{CH}=\text{N}$ ) protons are found at 9.04 ppm, as singlet [40]. The aromatic protons appear from 6.97 to 7.69 ppm.

In contrast,  $^1\text{H}$  NMR data for L-2 prove that tautomeric equilibria is present in DMSO. Keto-amine tautomer is favored in the 1-(iminomethyl)naphthalen-2-ol fragment of the molecule. The NH signal of the  $\text{O}\cdots\text{H}-\text{N}$  proton of keto-amine tautomer appear at 15.86 ppm [41]. The OH signal of the  $\text{O}-\text{H}\cdots\text{N}$  proton of phenol-imine tautomer is detected as a broad singlet in the offset region at 10.82 ppm (Fig. 2b). The peaks appearing as two different singlets at 9.54 ppm and 9.74 ppm are attributed to the imine protons. The signal at 8.54–8.56 ppm, as doublet ( $J = 8.48$ ), corresponds to the enamine ( $=\text{CH}-\text{N}$ ) proton of keto-amine tautomer. The aromatic region is a set of multiplets in the range 6.99–7.96 ppm.

$^1\text{H}$  NMR spectrum of L-3 shows that phenol-imine tautomer is dominant for all of the molecule in DMSO. Upon examination, the phenolic OH protons are observed at 10.22 ppm [40]. The resonance due to imine protons appear at 9.93 ppm, as singlet (Fig. 2c). The chemical shifts of the aromatic protons are obtained within the 6.87–7.73 ppm region of spectrum.

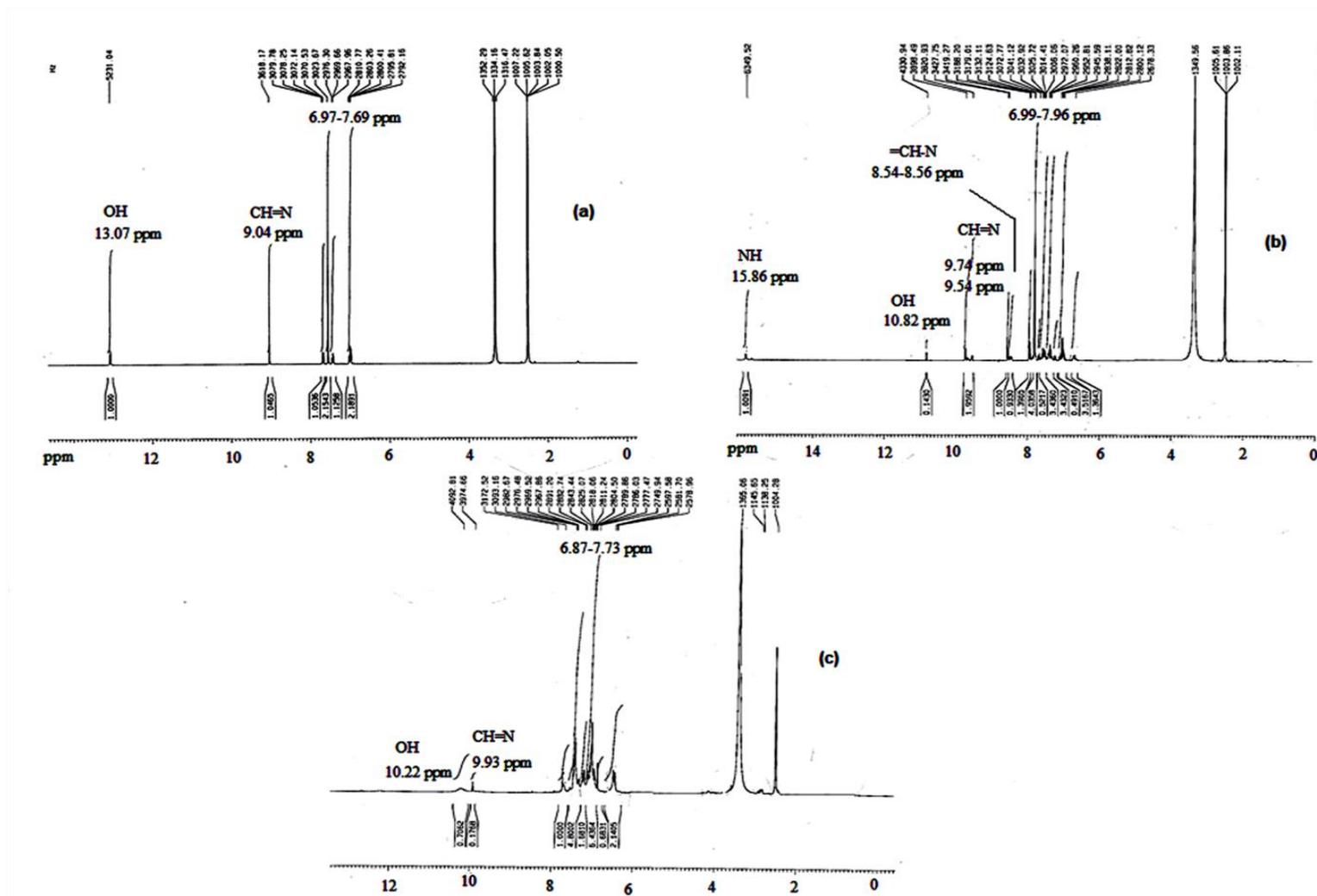


Figure 2.  $^1\text{H-NMR}$  spectra of **L-1** (a), **L-2** (b), and **L-3** (c) in  $\text{DMSO-d}_6$ .

### 3.3. $^{13}\text{C}$ NMR Spectra

$^{13}\text{C}$  NMR studies of Schiff bases in solution show that the phenolic (C-OH) carbon atom is the most sensitive atom for proton transfer equilibrium. This signal is close to 150 ppm for the phenol-imine form. When the proton transfer process occurs from oxygen atom to nitrogen atom, it is downfield shifted to about 170 ppm [42].

The proton de-coupled  $^{13}\text{C}$  NMR spectra of tetraimines were carried out in DMSO-*d*<sub>6</sub> solvent at room temperature.  $^{13}\text{C}$  NMR spectral data are consistent with  $^1\text{H}$  NMR spectral data. In  $^{13}\text{C}$  NMR spectrum of **L-1**, the imine (-CH=N) carbons appear at 163.62 ppm [43]. The peak at 160.76 ppm is attributed to phenolic (C-OH) carbons (Fig. 3a). The resonance at 117.09-147.14 ppm is assigned to phenyl carbons.

$^{13}\text{C}$  NMR spectrum of **L-2** exhibits the carbonyl carbon signal at 170.89 ppm [44]. It implies the presence of the keto-amine tautomer in the 1-(iminomethyl)naphthalen-2-ol fragment of the molecule. The imine carbon peaks are observed at 158.20 ppm. The signals belong to phenolic (C-OH) carbons appear at 155.65 ppm (Fig. 3b). A new signal at 143.0 ppm indicates the presence of the enamine (=CH-N) carbon of keto-amine tautomer. The aromatic carbon atoms are recorded in the region 102.0-137.0 ppm.

$^{13}\text{C}$  NMR spectrum of **L-3** shows iminic carbons resonance as functional groups signals at 168.0 ppm. The upfield peak at 161.0 ppm is assigned to phenolic (C-OH) carbons (Fig. 3c). The chemical shifts for the aromatic carbon atoms are recorded in the region 104.22–146.51 ppm

**Table 2.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data of tetraimine Schiff bases

Comp.	$^1\text{H}$ NMR signals (ppm)				
	-NH	Ar-OH	-CH=N	=CH-N	Aromatic protons
<b>L-1</b>	-	13.07 (s)	9.04 (s)	-	6.97-7.02 (m, J = 7.45 Hz) 7.41-7.43 (t, J = 8.33 Hz) 7.55 (s) 7.67-7.69 (d-d, J = 7.64)
<b>L-2</b>	15.86 (s)	10.82 (s)	9.54 (s) 9.74 (s)	8.54-8.56 (d, J = 8.48)	6.99-7.11 (m, J = 11.60 Hz) 7.23-7.26 (d, J = 9.02 Hz) 7.36-7.42 (m, J = 8.82) 7.51-7.60 (m, J = 8.76) 7.67-7.70 (d, J = 8.49) 7.80-7.82 (d, J = 7.48) 7.93-7.96 (t, J = 7.27)
<b>L-3</b>	-	10.22 (s)	9.93 (s)	-	6.87 (s) 7.0-7.12 (m, J = 7.58 Hz) 7.20-7.25 (t, J = 9.92) 7.42-7.47 (m, J = 6.90) 7.69-7.73 (m, J = 6.89)

<sup>13</sup> C NMR signals (ppm)					
	-C=O	-C-OH	-CH=N	=CH-N	Aromatic carbons
<b>L-1</b>	-	160.75	163.61	-	117.09, 119.69, 119.83, 123.03, 133.04, 133.84, 147.14
<b>L-2</b>	170.89	155.65	158.20	143.0	102.0, 109.0, 113.50, 115.0, 119.0, 120.98, 122.24, 122.58, 124.03, 127.18, 128.59, 129.50, 131.0, 134.0, 137.0
<b>L-3</b>	-	161.0	168.0	-	104.22, 107.18, 108.48, 115.88, 121.66, 123.16, 125.00, 125.87, 127.85, 128.48, 129.83, 130.01, 137.71, 137.87, 138.94, 143.10, 146.11, 146.51

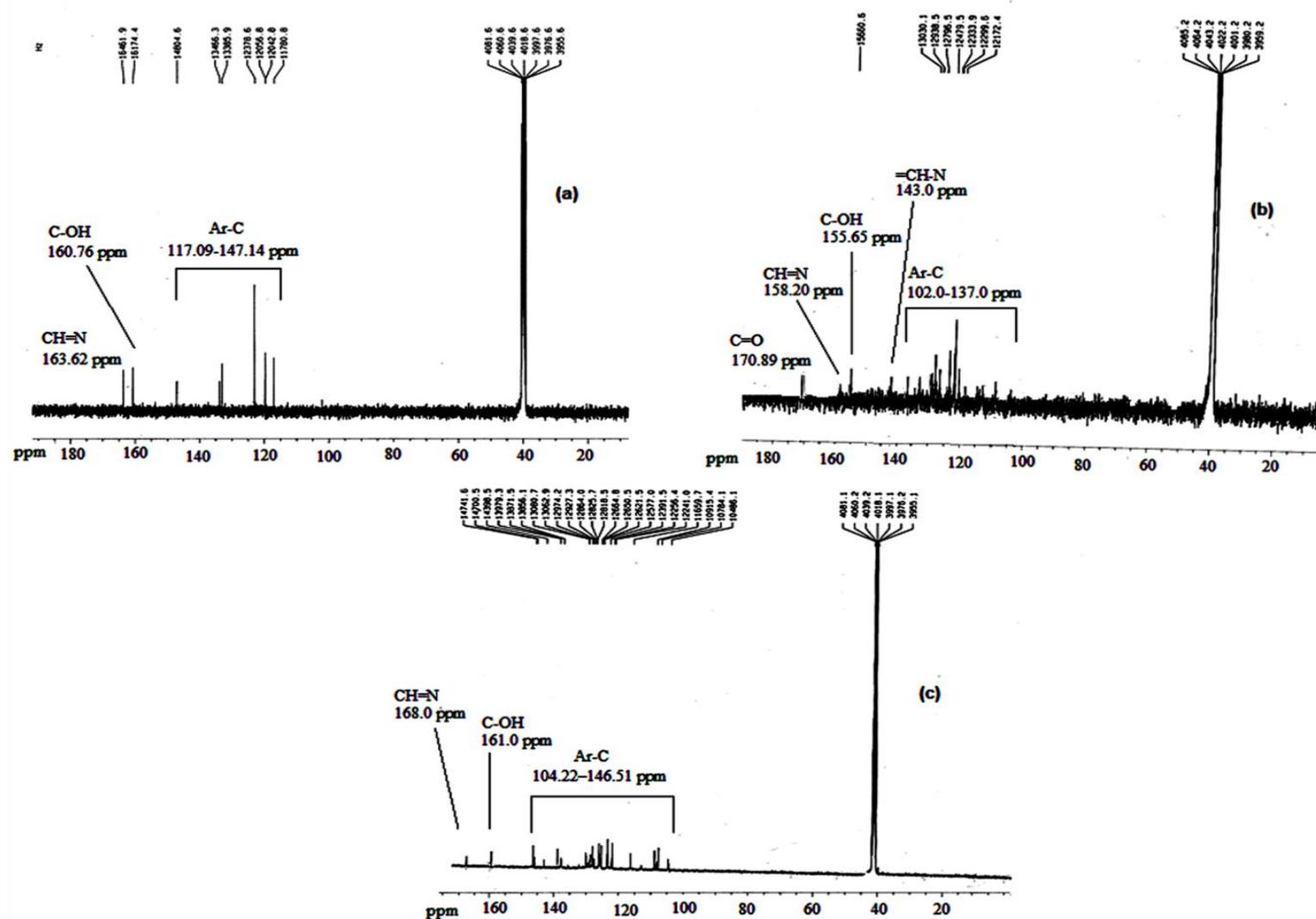


Figure 3.  $^{13}\text{C}$ -NMR spectra of L-1 (a), L-2 (b), and L-3 (c) in DMSO- $d_6$ .

### 3.4. Mass spectra

Mass spectrums of tetraimines were obtained using the chemical ionization technique (API-ES/positive) (70 eV or 100 eV) (Fig. 4). The fragmentation patterns are taken as a general scheme showing the main fragmentation paths involved (Scheme 4).

The mass spectrum of **L-1** shows the fragment ions at  $m/z = 525.3$  (1.4%), 521.3 (1.4%), 505.3 (19.0%), 489.2 (3.3), 475.3 (23.1%), 447.3 (22.7%), 336.2 (0.6), 325.2 (100%), 314.3 (18.2%), 286.3 (13.6%), 273.1 (18.5%), 233.1 (19.3%), 215.1 (3.9%). The peak at  $m/z$  521 corresponds to the loss of a hydrogen radical of molecule. The loss of (OH) group gives the characteristic peak at  $m/z$  505. It is followed by loss of the other (OH) group, two benzal rings ( $C_6H_4$ ), (CH) group and ( $C_6H_6N$ ) group; giving the peaks at  $m/z$  489, 336, 325 and 233, respectively (Scheme 4a).

The mass spectrum of **L-2** shows the fragment ions at  $m/z = 625$  (4.3%), 616.2 (16.1%), 602.2 (32.7%), 525.2 (4.7%), 462.1 (2.7%), 385.1 (6.1%), 314.4 (54.3%), 286.3 (28.9%), 177.1 (21.0%), 109.2 (60.5%), 79.2 (100%). The loss of naphthol ring ( $C_{10}H_7O$ ), (OH) group, naphthalene ring ( $C_{10}H_6$ ), ( $C_7H_5N$ ) group and two neutral molecules of (HCN) give the peaks at  $m/z$  479 (0.3%), 462 (2.7%), 336 (1.2%), 233 (1.9%) and 179 (12.3), respectively (Scheme 4b).

As can be seen in Scheme 4c, the mass spectrum of **L-3** exhibits the fragment ions at  $m/z = 622.3$  (0.8%), 621.3 (2.5%), 602.2 (8.2%), 505.2 (4.8%), 447.3 (4.7%), 389.2 (6.6%), 325.3 (100%), 271.2 (7.1%), 160.1 (11.6%), 101.2 (44.0%). The ion at  $m/z$  621 and important fragments at 447, 325, 233(2.6%) and 103(2.2%) are obtained by loss a hydrogen radical, ( $C_{10}H_7NO + OH$ ) group, naphthalene ring ( $C_{10}H_6$ ), ( $C_7H_5$ ) group and ( $C_8H_6N_2$ ) group, respectively.

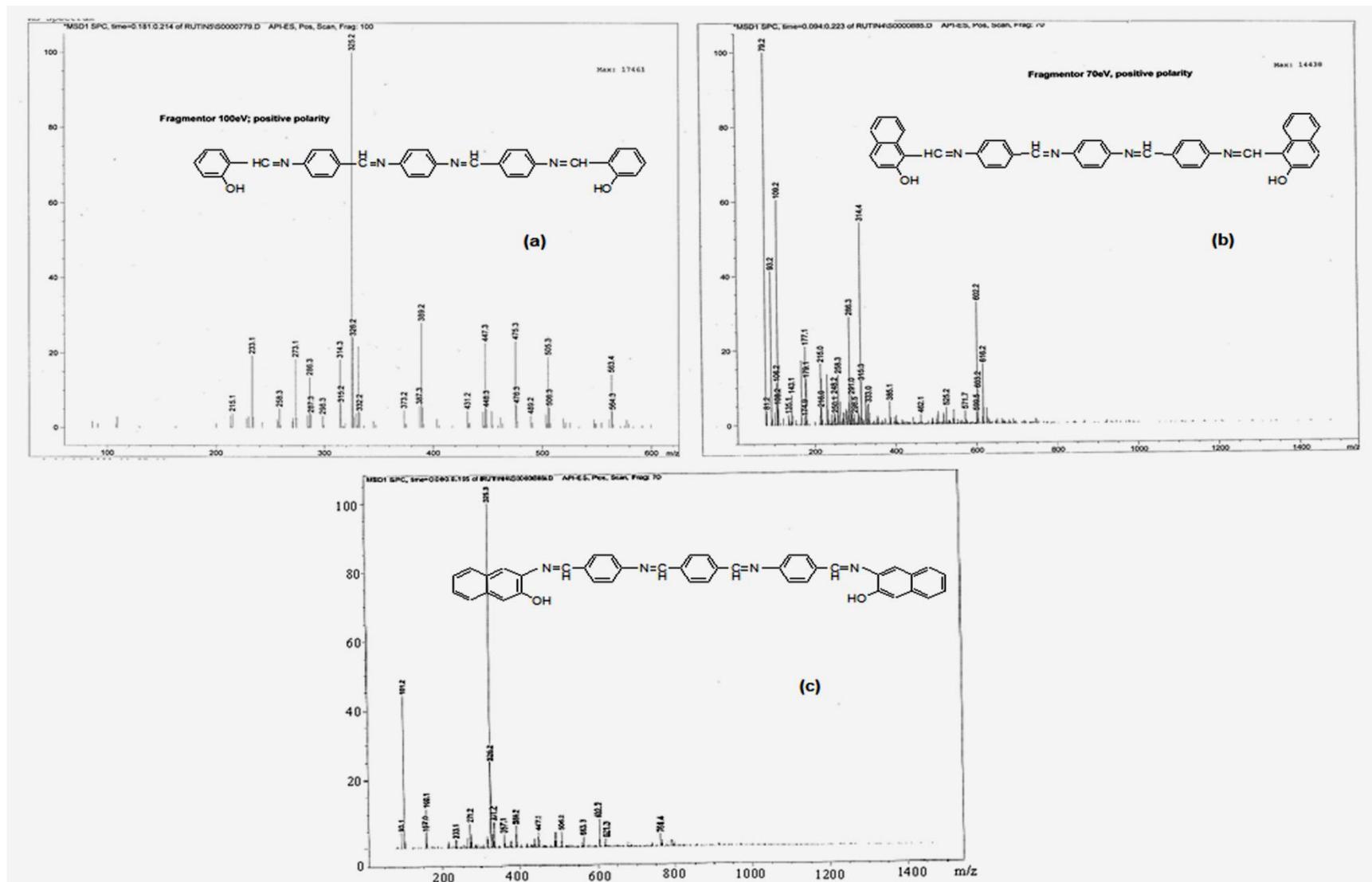
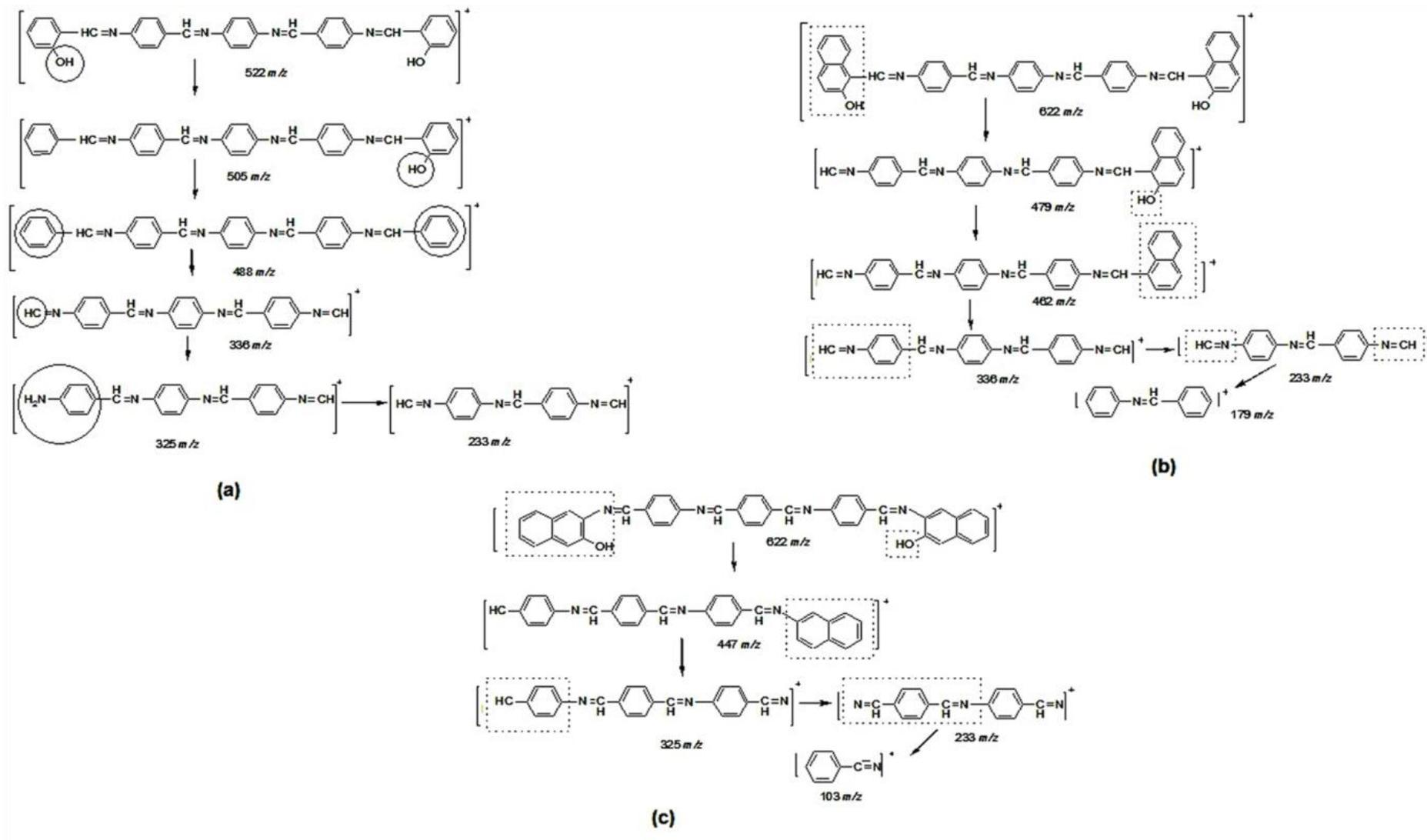


Figure 4. Mass spectra of L-1 (a), L-2 (b), and L-3 (c).



Scheme 4. Fragmentation patterns of L-1 (a), L-2 (b), and L-3 (c).

### **3.5. UV–Vis spectra**

UV–Vis spectroscopy is known to be a very sensitive method for studying tautomeric equilibrium in Schiff bases. The Schiff bases show absorption in the range greater than 400 nm in polar and nonpolar solvents. It is point out that the new band belongs to the keto-amine form of the Schiff bases [1, 45].

The absorption spectra of tetraimines were studied in polar (DMSO and MeOH) and nonpolar (toluene) solvents and both acidic and basic solutions. The spectral data are given in Table 3.

**Table 3.** UV-Vis data of tetraimine Schiff bases in various solvents, acidic and basic solutions.

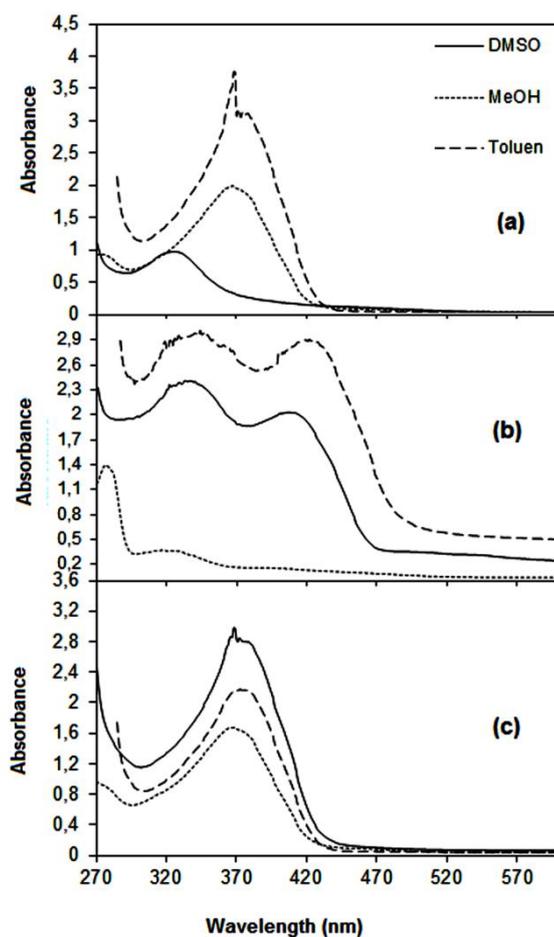
		$\lambda_{\max}$ (log $\epsilon$ )									
		<b>L-1</b>			<b>L-2</b>			<b>L-3</b>			
		Pure	Acidic	Basic	Pure	Acidic	Basic	Pure	Acidic	Basic	
Solvent	Tautomer										
DMSO	Phenol-imine	328(4.98)	328(5.38)	368(5.47)	325(5.14)	320(5.06)	320(5.11)	281(5.10)	277(5.08)	281(5.10)	
					337(5.13)				291(5.12)	288(4.95)	291(5.12)
									341(5.17)	318 (4.80)	341(5.16)
	Keto-amine	-	406(5.31)	-	409(5.25)	462(5.13)	463(5.17)	-	-	-	
					494(5.11)	491(5.15)					
MeOH	Phenol-imine	367(5.30)	323(4.56)	369(5.23)	318(4.89)	318(4.91)	320(4.90)	276(5.00)	274(4.98)	277(4.99)	
						355(4.80)		286(5.00)	285 (4.85)	287 (4.99)	
								332(4.98)	303(4.67)	332(5.00)	
	Keto-amine	-	-	-	465(5.16)	453(5.10)	465(5.12)	-	-	-	
								329(4.79)			
Toluene	Phenol-imine	369(5.58)	347(5.48)	372(5.34)	324(4.71)	300(2.94)	324(4.62)	286(5.09)	288(4.68)	290(5.02)	
		379(5.49)				371(2.83)		299(5.06)	314(4.78)	302(4.99)	
								338(5.16)	328(4.85)	340(5.26)	
	Keto-amine	-	426(5.46)	-	415(3.20)	496(3.67)	415(4.11)	-	-	-	

### 3.6. Solvent effects on the tautomeric equilibria

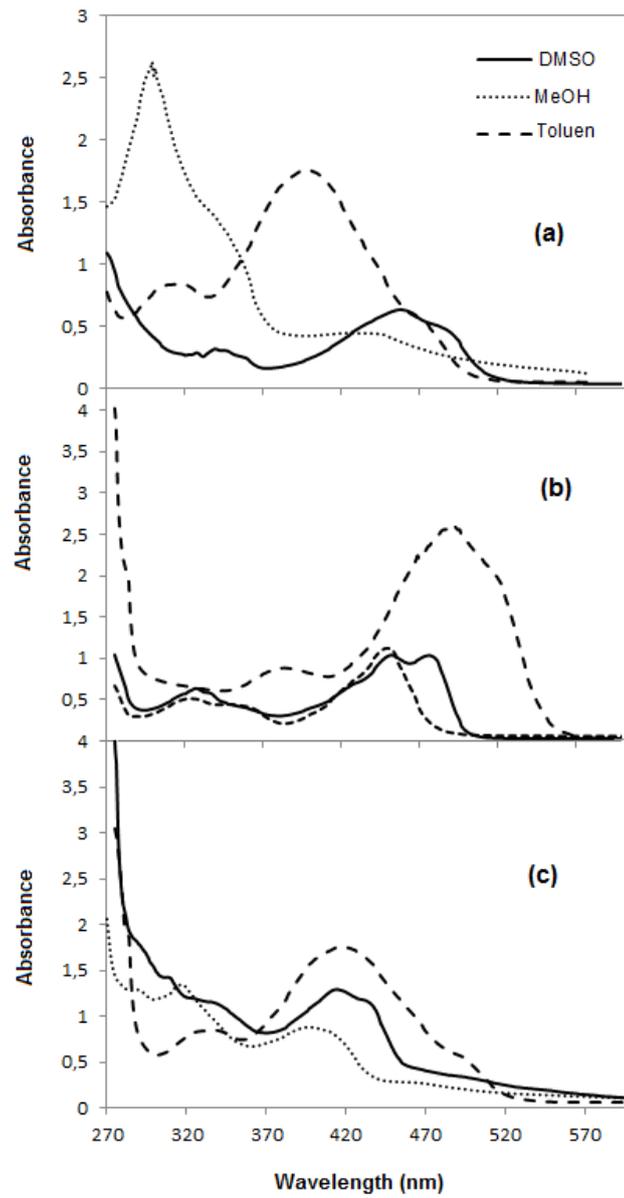
**L-1** shows one absorption maximum at 328 nm in DMSO, 367 nm in MeOH, and two maxima at 369 and 379 nm in toluene (Fig. 5a). It proves that phenol-imine form fully prevails in the solvents used, no equilibrium is present, which is in agreement with NMR results. The bands are assigned to the  $\pi-\pi^*$  or  $n-\pi^*$  transition of imine chromophores. It also indicates that  $\lambda_{\text{max}}$  values of **L-1** are shifted bathochromically relative to the solvent polarity.

On the other hand, the electronic absorption spectra of **L-2** in all solutions differs significantly from those in the other compounds. **L-2** exhibits absorption maxima at 325, 337 and 409 nm in DMSO, 318 and 465 nm in MeOH, 324 and 415 nm in toluene (Fig. 6a). These results suggest that **L-2** may exist as a mixture of phenol-imine and keto-amine forms in solution. The absorbance bands in region 318-337 nm indicate phenol-imine form and they correspond to the  $\pi-\pi^*$  transition of imine chromophores. The bands in region 409-465 nm indicate keto-amine form and they are due to the  $n-\pi^*$  transition of carbonyl chromophore. Furthermore, the absorption maxima of **L-2** do not significantly change with the polarity of solvents.

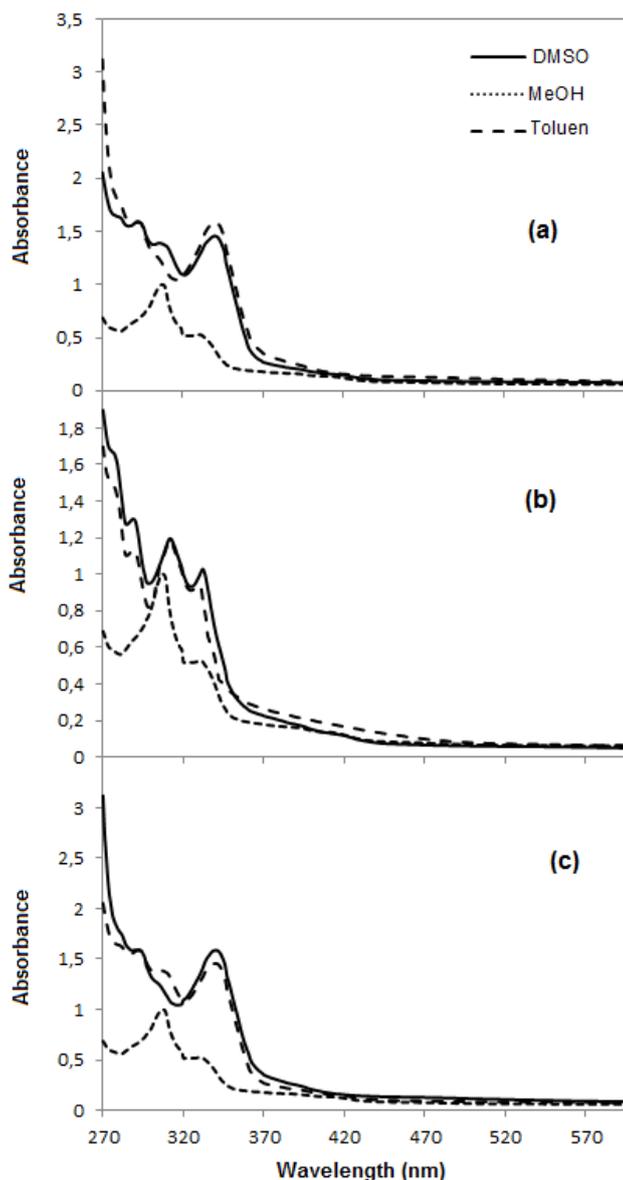
The spectrum of **L-3** shows three absorption maxima in all solutions (Fig. 7a). The bands in region 276-299 nm and 332-341 nm are attributed to the  $\pi-\pi^*$  transition of aromatic ring and the  $\pi-\pi^*$  transition of imine chromophores of the phenol-imine form, respectively [46]. These results show that **L-3** is in favour of the predominantly single tautomeric form in the solvents used.



**Figure 5.** UV-Vis spectra of **L-1**; in various solvents (a), in acidic solutions (b), and in basic solutions (c).



**Figure 6.** UV-Vis spectra of **L-2**; in various solvents (a), in acidic solutions (b), and in basic solutions (c).



**Figure 7.** UV-Vis spectra of **L-3**; in various solvents (a), in acidic solutions (b), and in basic solutions (c).

### 3.7. Acid effects on the tautomeric equilibria in various solvents

When acid (trifluoroacetic acid) is added to solution of **L-1** in DMSO, a second maximum is observed at 406 nm. In MeOH solution,  $\lambda_{\text{max}}$  value shows a high hypsochromic shift ( $\Delta\lambda_{\text{max}} = 44$  nm). In contrast,  $\lambda_{\text{max}}$  value shows small hypsochromic shift ( $\Delta\lambda_{\text{max}} = 22$  nm), and also a second maximum at longest wavelength (426 nm) appears when a small amount of acid is added to its toluene solution (Figure 5(b)).

**L-2** is very sensitive to acid. **L-2** shows absorption maxima at 320, 462 and 494 nm in DMSO, 318, 355 and 453 nm in MeOH, 300, 371 and 496 nm in toluene with the addition of acid to its solutions (Figure 6(b)). So  $\lambda_{\text{max}}$  values of  $\sim 300$  nm shift hypsochromically (5 nm in DMSO, 4 nm in toluene) and  $\lambda_{\text{max}}$  values of  $\sim 400$  nm shift bathochromically (53 nm in DMSO, 81 nm in toluene) due to the solvent polarity. Also a new maximum at 494, 355 and 371 nm is observed in DMSO, MeOH and toluene, respectively.

In addition, there is a hypsochromic shift in acidic solutions of **L-3** (e.g.  $\Delta\lambda_{\text{max}}$  values are 10 nm in DMSO, 3 nm in MeOH and 10 nm in toluene). Also a new maximum at 318, 303 and 314 nm is observed in DMSO, MeOH and toluene, respectively (Figure 7(b)).

These indicate that **L-1** and **L-3** exist in phenol-imine form in all acidic solutions, except DMSO and toluene for **L-1**. In contrast, the equilibrium between the tautomeric forms (phenol-imine and keto-amine) is observed in all solutions for **L-2**.

### 3.8. Base effects on the tautomeric equilibria in various solvents

$\lambda_{\text{max}}$  values of **L-1** show small bathochromic shifts with the addition of triethylamine to its solutions ( $\Delta\lambda_{\text{max}}$  values are 40 nm in DMSO, 2 nm in MeOH and 3 nm in toluene) (Fig. 5c). In the case of **L-2**, there is no significant change in MeOH and toluene (Figure 6(c)). In DMSO,  $\lambda_{\text{max}}$  value of ~400 nm shift bathochromically (53 nm) and a new maximum appeared at 491 nm. On the other hand,  $\lambda_{\text{max}}$  values do not significantly change for **L-3** in all solutions (Figure 7(c)).

It suggests that although **L-1** and **L-3** exist in phenol-imine form, the tautomeric equilibrium is detected in the case of **L-2**, in basic media.

## 4. CONCLUSION

In the present work, a new method has been established for the synthesis of tetraimine Schiff bases bearing N-salicylidene-aniline and N-naphthylidene-aniline parts. For this, two nitro-Schiff bases have been synthesized firstly. Nitro group in these Schiff bases has been reduced to the amino group by using sodium dithionite and these amino derivatives have been reacted with various aldehydes (terephthalaldehyde, salicylaldehyde or 2-hydroxy-1-naphthaldehyde). Then, it gave the respective tetraimine Schiff bases (**L-1**, **L-2**, **L-3**). The structure of the newly synthesized compounds has been elucidated on the basis of elemental analysis and spectral data (IR, NMR, MS, and UV-Vis spectra).

It is known that 2-hydroxy-Schiff bases derived from salicylaldehyde or naphthaldehyde show phenol-imine and keto-amine tautomerism. IR spectra of the structurally closely related the investigated tetraimines indicate that they are in the phenol-imine form in the solid state. Because, there is no evidence in IR spectra for the presence of the keto-amine form. NMR methods confirm that **L-2** exists primarily in the keto-amine form, whereas in **L-1** and **L-3**, keto form coexist. The absorption spectra provide clear evidence that they exhibit a different behaviour in the solution. The existence of the phenol-imine form is suggested in DMSO, MeOH and toluene for **L-1** and **L-3**. The absorption maxima of this form are in the range 328–379 nm. **L-2** presents the characteristics of the Schiff bases of 2-hydroxynaphthaldehyde that absorbs strongly in the 409–465 nm range in these solvents. The influences of the acidity and basicity on the absorption spectra are also investigated. The results show that **L-1** exists as the enol-form in all solutions, except acidic DMSO and toluene. **L-2** is found to be the tautomeric mixture in both acidic and basic media and exhibits solvatochromism in acidic media, **L-3** is present primarily as the enol-form and are not solvatochromic.

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## CONFLICT OF INTEREST

No conflict of interest was declared by the authors

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