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Spectroscopic Properties of 4-Halo-2-(4-chlorophenyliminomethyl)phenol and 4-Halo-2-(4-bromophenyliminomethyl)phenol

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4-Halo-2-(4-chlorophenyliminomethyl)phenol and 4-halo-2-(4-bromophenyliminomethyl)phenol have been synthesized and then characterized by elemental analysis, FTIR, ^{1}H NMR and UV-Vis spectroscopy. The spectroscopic data of all the investigated compounds revealed that the tautomeric equilibrium of the studied Schiff bases favour the enol form.

Key Words: Schiff base ligand, Spectroscopic studies, Tautomerism.

INTRODUCTION

2-Hydroxy Schiff base ligands and their complexes derived from the reaction of salicylaldehyde and 2-hydroxy-1-naphthaldehyde with amines have been extensively studied[1–11]. Such ligands are of interest mainly due to existence of (O—H····N and N—H····O) type hydrogen bonds and tautomerism between enol and keto forms. It has been concluded that the tautomerism occurs as a result of hydrogen bonding between the solvent acidic hydrogen and the imine nitrogen of the aniline[12]. Tautomerism in 2-hydroxy Schiff bases has been investigated using different spectroscopic techniques in both solution and solid states[12–26]. In the present study, the synthesis and elemental analysis of the compounds **1–8** have been carried out **(Scheme-I)** and then, the extent of the tautomeric equilibrium of each Schiff base has been established by IR, ^{1}H NMR and UV-Vis spectroscopy. The UV-Vis data support the presence of the enol form for all the compounds investigated. The IR data located at 1395–1108 cm^{-1} indicate the enol form in the solid state. And also, the ^{1}H-NMR data for the compounds **1–8** reveal that the tautomeric equilibrium favours the enol form in $CDCl_3$.

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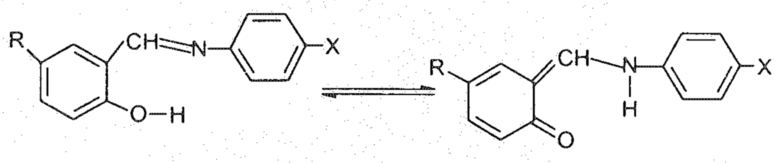

(Enol) (Keto)

Compound	R	X
1	Cl	F
2	Cl	Cl
3	Cl	Br
4	Cl	I
5	Br	F
6	Br	Cl
7	Br	Br
8	Br	I

Scheme-I. Enol and keto tautomerism of the compounds **1–8**.

EXPERIMENTAL

2-Hydroxy-5-chlorosalicylaldehyde, 2-hydroxy-5-bromosalicylaldehyde, 4-fluoroaniline, 4-chloroaniline, 4-bromoaniline, 4-iodoaniline, dimethylsulfoxide (DMSO), chloroform ($CHCl_3$), ethanol, methanol, tetrahydrofuran (THF) and cyclohexane were purchased from Merck (Germany). Melting points were measured on a Gallonkamp apparatus using a capillary tube. The elemental analyses were performed on a Leco CHNS-932 CHN analyzer. Infrared absorption spectra were obtained from a Mattson 1000 FTIR spectrometer in KBr discs. UV-visible spectra were measured using a Perkin- Elmer Lambda 2 series spectrometer. Proton (400 MHz) NMR spectra were recorded with a Bruker DPX FT-NMR spectrometer ($CDCl_3$ as an internal standard).

Synthesis of the compounds

4-Fluoro-2-(4-chlorophenyliminomethyl)phenol **1** was prepared by condensation of 2-hydroxy-5-chlorosalicylaldehyde (5 mmol) and 4-fluoraniline (5 mmol) in 100 mL ethanol. The reaction mixture was stirred for 3 h and then placed into a freezer for 12 h. The yellow precipitate was collected by filtration and then washed with cold ethanol. After recrystallization, yellow crystals were collected and dried *in vacuo*, m.p. 121°C. The compounds **2–8** were also synthesized with the same method.

RESULTS AND DISCUSSION

The analytical and experimental details of all the compounds studied were listed in Table-1.

TABLE-1
ANALYTICAL AND EXPERIMENTAL DETAILS

Compd.	m.f.	Colour	m.p. (°C)	M (g/M)	Elemental analysis: Calcd. (Found) (%)		
					C	H	N
1	$C_{13}H_9NOClF$	Yellow	121–3	249.7	62.54 (62.20)	3.63 (3.98)	5.61 (5.34)
2	$C_{13}H_9NOCl_2$	Yellow	136–7	266.1	58.67 (58.30)	3.41 (3.75)	5.26 (4.98)
3	$C_{13}H_9NOClBr$	Yellow	162–4	310.6	50.32 (50.43)	2.88 (3.08)	4.48 (4.42)
4	$C_{13}H_9NOClI$	Yellow	195–7	357.6	43.67 (43.37)	2.54 (2.87)	3.92 (3.76)
5	$C_{13}H_9NOFBr$	Yellow	146–8	294.1	53.09 (53.46)	3.08 (3.65)	4.76 (4.45)
6	$C_{13}H_9NOClBr$	Yellow	163–5	310.6	50.28 (50.43)	2.92 (3.08)	4.51 (4.42)
7	$C_{13}H_9NOBr_2$	Yellow	174–6	355.1	43.10 (43.93)	2.46 (2.53)	4.08 (3.94)
8	$C_{13}H_9NOBrI$	Brown	204–6	402.0	38.84 (38.42)	2.26 (2.62)	3.48 (3.52)

For compounds **1–8** key vibrational bands obtained by the FT-IR spectra are given in Table-2 and IR spectra of the compounds **3**, **5** and **7** are given in Fig. 1. The IR spectrum of all the studied compounds reveal the weak and broad bands at 3124–3065 cm^{-1} due to ν(O—H). The absorption bands assignable to the stretching of (C=N) and (C=O) bonds are observed at frequency 1624–1557 cm^{-1}. The sharp and strong first band is located at 1624, 1622, 1621, 1620, 1618, 1616, 1615 and 1614 cm^{-1} ν(C=N), and the other with a shoulder and weak

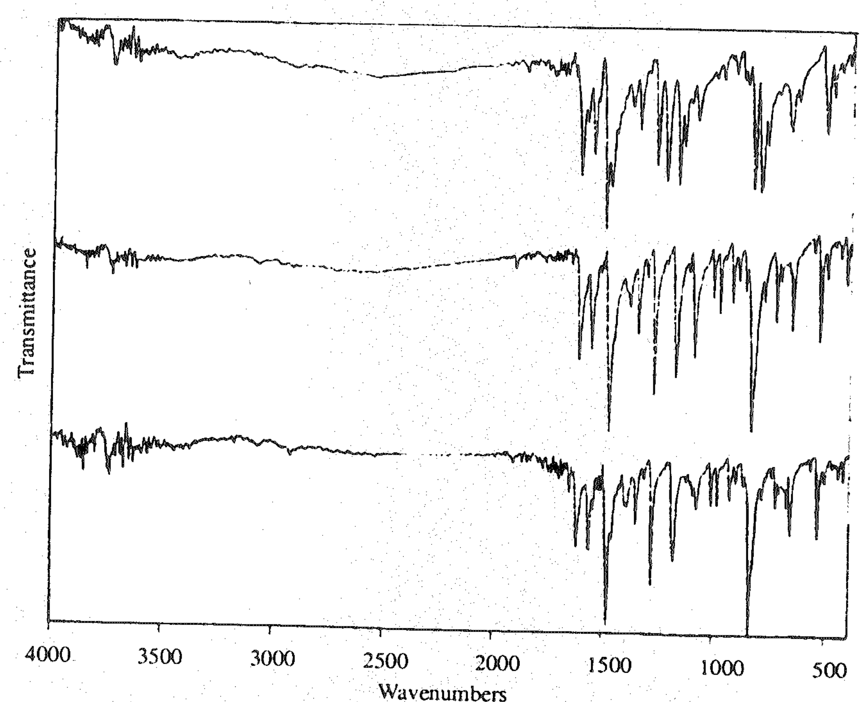

Fig. 1. FTIR spectra of the compounds **3**, **5** and **7**

intensity at 1557 cm^{-1} ν(C=O) is located by the first band. Most probably, these new bands are due to $C=NH^+$ stretching motion of a zwitter ionic structure[26].

TABLE-2
KEY IR (cm^{-1}) VIBRATIONAL ASSIGNMENTS OF COMPOUNDS 1–8

Compd.	ν(C—C) (arom.)	ν(C—O)	ν(C—X)	ν(O—H)	ν(C=N)	ν(C—N)	ν(C=O)
1	1600–1450	1322–1108	1251–1087	3071	1624	1386	1594–1588
2	1590–1440	1334–1108	739–620	3070	1622	1388	1612–1590
3	1600–1443	1341–1108	650–512	3056	1621	1387	1601–1582
4	1608–1455	1338–1110	466–434	3065	1620	1391	1598–1580
5	1620–1440	1354–1176	1276–1092	3124	1618	1385	1595–1561
6	1614–1473	1349–1177	785–637	3069	1616	1384	1614–1557
7	1590–1470	1320–1145	654–514	3080	1615	1385	1610–1586
8	1613–1472	1395–1173	529–501	3072	1614	1395	1578–1560

The absorption bands at 1620–1440 cm^{-1} might be related to the keto structure (C=C external double bond)[26], *i.e.*, these bands could appear only if there is a considerable amount of the keto tautomer. However, the broad bands located at 1395–1108 cm^{-1} which is the phenolic C—OH stretching region, indicates enol form in the solid state. From the FT-IR spectra of all the investigated compounds, it is observed that the IR absorption for the (C=O) and (C=N) groups in both keto and enol forms might be assigned. Moreover, the other absorptions which are specific to both keto and enol forms might also be obtained. The bands observed at 1614–1624 cm^{-1} (Table-2) are assigned to the C=N stretching frequency[6]. The observation of phenolic ν(C—O) at 1395–1108 cm^{-1} for all the compounds is the evidence for the existence of the enol form ((N····H—O) intermolecular hydrogen bonding) only in the solid state[12].

^1H NMR spectra of the ligands have been recorded in $CDCl_3$ and the assignments are given in Table-3.

TABLE-3
^1H NMR DATA (δ ppm)

Compd.	δ_{OH}	$\delta_{CH=N}$	$\delta_{C=C-H}$	Form
1	12.91 s 1H	8.35 s 1H	6.79–7.19 (arom.) m 7 H	Enol
2	12.83 s 1H	8.36 s 1H	6.79–7.24 (arom.) m 7 H	Enol
3	12.81 s 1H	8.34 s 1H	6.80–7.33 (arom.) m 7 H	Enol
4	12.80 s 1H	8.36 s 1H	6.79–7.59 (arom.) m 7 H	Enol
5	12.60 s 1H	8.24 s 1H	6.89–7.64 (arom.) m 7 H	Enol
6	12.56 s 1H	8.26 s 1H	6.89–7.76 (arom.) m 7 H	Enol
7	12.54 s 1H	8.27 s 1H	6.90–7.79 (arom.) m 7 H	Enol
8	12.52 s 1H	8.26 s 1H	6.89–7.88 (arom.) m 7 H	Enol

Very similar spectra were obtained for all the compounds **1–8**. It is important to emphasize that ^{1}H NMR resonance of the (N····H—O) group at 12.52–12.91 ppm is due to existence of the intramolecular hydrogen bonding[22, 23]. The azomethine protons for compounds studied are observed as singlet 8.35, 8.36, 8.34, 8.36, 8.24, 8.26, 8.27 and 8.26 ppm, respectively. The imine protons for all the compounds are located at $\delta = 8.26–8.35$ ppm. In conclusion, ^{1}H NMR data for the compounds **1–8** show that the tautomeric equilibrium favours the enol form in $CDCl_3$.UV-Vis studies

The UV-Vis spectra of the compounds **1–8** have been studied in several solvents DMSO, ethanol, THF, chloroform and cyclohexane. Figs. 2–4 show the UV-visible absorption spectra of the compounds **5**, **6** and **8**, respectively, in all the solvents used. It is seen that the compounds **1–8** have given rather strong absorption bands in the UV region. Table-4 shows the maximum absorption wavelengths (λ) and molar extinction coefficients (ε) obtained from the UV-Vis spectral analysis of the synthesized compounds.

TABLE-4
THE MAXIMUM ABSORPTION WAVELENGTHS AND MOLAR EXTINCTION COEFFICIENTS, RESPECTIVELY, OBTAINED FROM THE UV-VIS SPECTRAL ANALYSIS OF THE COMPOUNDS 1–8 IN SOLVENTS OF DIFFERENT POLARITY

Compd.	Solvent	λ, nm ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1})		
	DMSO	352.0 (1.8)	335.0 (1.5)	306.0 (1.4)
	Ethanol	347.0 (3.1)	321.0 (2.6)	306.0 (2.4)
1	$CHCl_3$	348.0 (2.1)	320.0 (1.9)	308.0 (1.7)
	THF	352.0 (2.4)	323.0 (2.1)	310.0 (1.9)
	Cyclohexane	358.0 (2.0)	318.0 (1.8)	310.0 (1.6)
	DMSO	348.0 (1.9)	326.0 (1.8)	308.0 (1.7)
	Ethanol	351.0 (1.6)	323.0 (1.5)	309.0 (1.4)
2	$CHCl_3$	356.0 (1.8)	327.0 (1.6)	309.0 (1.4)
	THF	353.0 (2.0)	324.0 (1.8)	310.0 (1.6)
	Cyclohexane	347.0 (1.5)	322.0 (1.3)	310.0 (1.2)
	DMSO	349.0 (3.4)	327.0 (3.2)	311.0 (2.9)
	Ethanol	347.0 (2.6)	326.0 (2.4)	310.0 (2.1)
3	$CHCl_3$	360.0 (3.1)	324.0 (3.9)	312.0 (4.1)
	THF	354.0 (1.6)	333.0 (1.4)	313.0 (1.2)
	Cyclohexane	359.0 (4.9)	327.0 (5.0)	313.0 (5.3)
	DMSO	351.0 (3.4)	337.0 (3.2)	311.0 (2.9)
	Ethanol	349.0 (2.6)	329.0 (2.4)	312.0 (2.1)
4	$CHCl_3$	359.0 (2.4)	331.0 (2.2)	313.0 (2.0)
	THF	355.0 (1.7)	324.0 (1.5)	313.0 (1.2)
	Cyclohexane	352.0 (1.9)	318.0 (1.8)	314.0 (1.5)

Compd.	Solvent	λ, nm (ε × 10^{-4}, M^{-1} cm^{-1})		
5	DMSO	348.3 (5.6)	320.0 (4.9)	306.0 (4.7)
	Ethanol	348.3 (1.6)	320.0 (1.5)	306.0 (1.5)
	$CHCl_3$	351.9 (3.3)	322.0 (3.0)	308.0 (2.9)
	THF	349.6 (2.1)	320.0 (1.9)	310.0 (1.7)
	Cyclohexane	355.0 (1.4)	323.3 (1.4)	310.0 (1.9)
6	DMSO	351.6 (1.9)	326.6 (1.8)	309.0 (1.8)
	Ethanol	351.6 (1.4)	326.3 (1.3)	309.0 (1.4)
	$CHCl_3$	355.0 (2.6)	325.8 (2.4)	310.0 (2.4)
	THF	351.6 (2.7)	325.0 (2.5)	309.0 (2.5)
	Cyclohexane	358.0 (2.7)	326.6 (2.4)	310.0 (2.4)
7	DMSO	349.0 (4.9)	336.0 (3.2)	326.0 (2.9)
	Ethanol	348.0 (2.6)	325.0 (2.3)	318.0 (2.1)
	$CHCl_3$	358.0 (4.5)	327.0 (4.3)	312.0 (4.0)
	THF	354.0 (2.9)	324.0 (2.9)	310.0 (2.6)
	Cyclohexane	359.0 (2.3)	328.0 (1.8)	313.0 (1.5)
8	DMSO	354.7 (1.5)	330.0 (1.4)	313.0 (1.3)
	Ethanol	354.6 (2.1)	330.0 (2.1)	311.0 (2.0)
	$CHCl_3$	355.8 (3.2)	330.0 (3.2)	314.0 (3.1)
	THF	355.0 (1.9)	329.6 (1.8)	313.0 (1.7)
	Cyclohexane	358.3 (1.0)	330.2 (0.9)	315.0 (0.9)

The compounds investigated here exhibit solvatochromism in the solvents with different polarities (Figs. 2–4), *i.e.*, maximal absorption peaks of all the compounds show bathochromic behaviour with band shift < 400 nm and all the

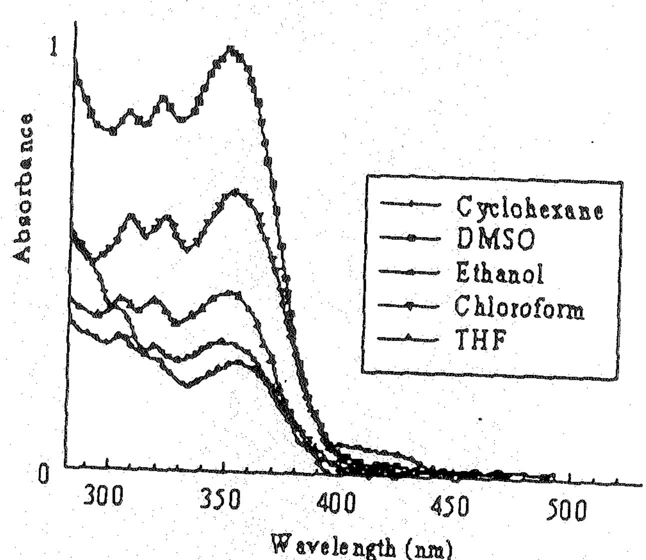

Fig. 2. UV-Vis absorption spectra of the compound **5** in cyclohexane, DMSO, ethanol, chloroform and THF

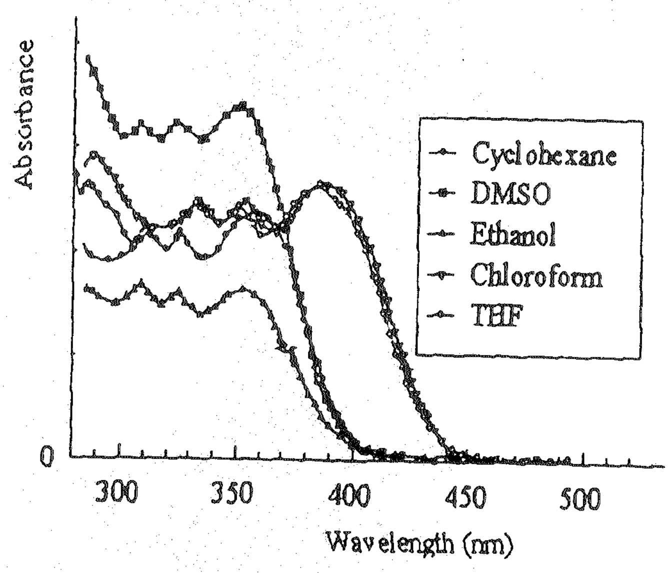

Fig. 3. UV-Vis absorption spectra of the compound 6 in cyclohexane, DMSO, ethanol, chloroform and THF

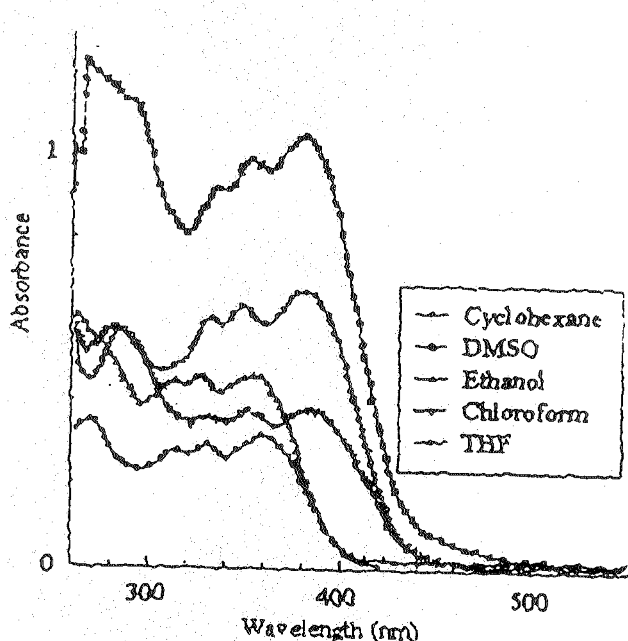

Fig. 4. UV-Vis absorption spectra of the compound 8 in cyclohexane, DMSO, ethanol, chloroform and THF

transitions are $\pi \rightarrow \pi^*$. Because there is no absorption above 400 nm in all the solvents, these UV-visible results indicate that such compounds could exist mainly in the enol form[1, 27]. Moreover, increasing conjugation over the whole compound will cause the equilibrium to shift in favour of the enol form. Quinoid tautomer generally increases with the electron-donating ability of the substituent. The amine group being electron-donating increases the electron-withdrawing power in the order of IBrClF and thus a bathochromic shift occurs in the band.

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