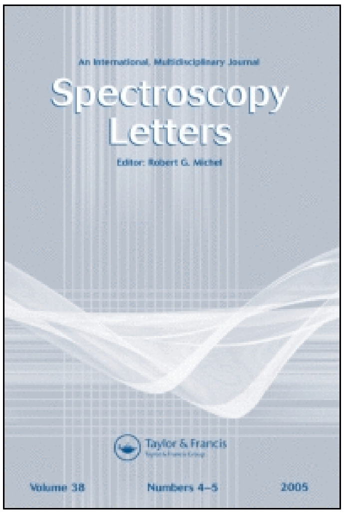

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SYNTHESIS AND SPECTROSCOPIC STUDIES IN SOME NEW SCHIFF BASES

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SYNTHESIS AND SPECTROSCOPIC STUDIES IN SOME NEW SCHIFF BASES

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ABSTRACT

Infrared, ^{1}H-NMR and UV-visible spectra of a series of substituted 2-hydroxy-1-naphthaldehyde Schiff bases were used to investigate enol-imine and keto-amine tautomeric equilibrium. They were synthesised and studied by elemental analysis. From the IR spectra of the model compounds it was possible to assign the IR absorption for the C=O and the C=N groups in both the keto-amine and enol-imine forms. It was possible to assign other absorptions which were either specific to the keto-amine or the enol-imine forms. Specific pattern was observed for all the studied compounds. The UV-visible spectra of compounds have been investigated in different solvent, acidic and basic media. The compounds were in tautomeric equilibrium (enol-imine O-H···N, keto-amine O···H-N forms) in polar and non-polar solvents. The keto-amine form was observed in basic solutions of DMSO, ethanol, chloroform, benzene, cyclohexane and in acidic solutions of chloroform and benzene, but not in acidic solutions of DMSO and ethanol.

Key Words: Schiff bases; Keto-enol tautomerism; Solvent effect; Basic solutions; Spectroscopy

INTRODUCTION

Compounds of the type Ar-CH=N-Ar, commonly referred to as N-benzylidenaniline Schiff bases, have been the object of considerable interest. It has long been known that several of these compounds exhibit thermochromism and photochromism[1]. Studies on the photochromic compounds have been increased ever since the potential applications of photochromic materials were realised in various areas such as the control and measurement of radiation intensity, optical computers and display systems. Tautomerism in 2-hydroxy Schiff bases both in solution and in solid state was investigated using spectroscopy[2–6]. 2-Hydroxy Schiff base ligands are of interest mainly due to the existence of (O-H···N and O···H-N) type hydrogen bonds and tautomerism between enol-imine and keto-amine forms[7–8].

The UV-visible spectra of some 2-hydroxy Schiff bases have been studied in both polar and non-polar solvents. A new band at greater than 400 nm has been observed in polar solvent and in acidic media of some solvents, but this band has not been observed in some non-polar solvents. The results indicate that the absorption band at greater than 400 nm belongs to the keto-amine form of the Schiff base.

We concerned with the keto-enol equilibrium in Schiff bases derived from N^{15}-methyl-amine and several carbonyls compounds; it was shown that intramolecular proton exchange between the oxygen and nitrogen is rapid. The observed spin coupling therefore provides a good measure of the residence time of the proton on nitrogen. This technique has now been extended to Schiff bases derived from N^{15}-aniline to determine the effect of the N-phenyl group upon the keto-enol equilibrium. Some studies on the basicity of aliphatic Schiff base anilines have appeared, but the results are ambiguous.

EXPERIMENTAL

Reagents and Techniques

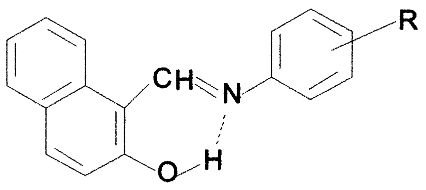
2-Hydroxy-1-naphthaldehyde, 2-fluoroaniline, 2-chloroaniline, 2-bromoanilin 2-iodoanilin, 4-fluoroaniline, 2-4 dichloroaniline, 2-5 dichloroaniline, benzene, dimethylsulfoxide (DMSO), chloroform ($CHCl_3$), ethanol, cyclohexane, triethylamine, and CF_3COOH were purchased from Merck (Germany). Melting points were measured on a Gallonkamp apparatus using a capillary tube. The elemental analyses were performed on a LECO CHNS-932 C-, H-, N- analyser. Infrared absorption spectra were obtained from a Mattson 1000 FTIR spectrometer in KBr discs and reported in cm^{-1}. 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 internal standard).

Preparation of Ligands Schiff Base

Compound (1) was prepared by condensation of naphthaldehyde (0.005 mol) and 2-floro aniline (0.005 mol) in 100 mL of ethanol. The reaction mixture was stirred for 4 h and then placed in a freezer for 18 h. The yellow precipitate was collected by filtration and then washed with cold ethanol. After recrystallization, yellow crystals were harvested and dried in vacuo, m.p. 107°C, 2.65 g (82%) yields. Found: C, 76.88; H, 4.90; N, 5.23. $C_{17}H_{12}NOF$; C, 76.97; H, 4.56; N, 5.28%. IR (KBr, cm^{-1}): ν(C=N) 1624 s, ν(C=C) 1584 s, ν(C-O) 1454 s, 1319 s. ^{1}H-NMR ($CDCl_3$); δ ppm, 15.10 (s, 1H, OH); 9.26 (s, 1H, CH-N); 8.37–6.82 (m, 10H, Ar-H).

Another Schiff base ligands were obtained same method (Scheme 1). For all compounds analytical and experimental details were given in Table 1, some selected IR bands in Table 2, ^{1}H-NMR data in Table 3 and effect of solvent, acid and base on the UV-spectra of compounds in Table 4.

The following Schiff bases were investigated:



R:2-F(1),2-Cl(2), 2-Br(3), 2-I(4), 4-F(5),2-5Cl(6), 2-4Cl(7)

Scheme 1.

RESULTS AND DISCUSSION

IR, ^{1}H-NMR, and UV-Visible Spectroscopy

The observed vibrational bands in the 500–3500 cm^{-1} in all Schiff bases studied are listed in Table 2. Absorption bands with the wave numbers of 1620–1624 cm^{-1} ($\nu_{C=N}$), 3020–3094, ($\nu_{C\text{-}H}$, Ar-H), 1425–1625 cm^{-1} ($\nu_{C=C}$) were observed[9]. The observation of phenolic $\nu_{C\text{-}O}$ at 1156–1328 cm^{-1}

Table 1. Analytical and Experimental Details

Formula		Color	m.p. (℃)	M (g/M)	Elemental Analyses (%) Calc. (Found) C	H	N
(1)	$C_{17}H_{12}NOF$	Yellow	107	265.3	76.97(76.88)	4.56(4.90)	5.28(5.23)
(2)	$C_{17}H_{12}NOCl$	Yellow	137	281.7	72.47(72.32)	4.29(4.32)	4.97(4.93)
(3)	$C_{17}H_{12}NOBr$	Brown	145	326.2	62.60(62.43)	3.71(3.82)	4.29(4.20)
(4)	$C_{17}H_{12}NOI$	Yellow	150	373.2	54.71(54.65)	3.24(3.44)	3.75(3.65)
(5)	$C_{17}H_{12}NOF$	Yellow	129	265.3	76.97(76.92)	4.56(4.50)	5.28(5.18)
(6)	$C_{17}H_{11}NOCl_2$	Brown	165	316.9	66.44(66.12)	3.50(3.67)	4.42(4.44)
(7)	$C_{17}H_{11}NOCl_2$	Yellow	170	316.9	66.44(66.35)	3.50(3.75)	4.42(4.50)

for compound is the evidence for the existence of the keto-amine form (N-H···O) intramolecular hydrogen bonding only in the solid state.

In the solution state of compounds, the existence of the intra molecular hydrogen bonding (N-H···O) has been confirmed by NMR spectroscopy in some Schiff base ligands[10–11]. The entire compounds studied the azomethine proton resonance is a single broad signal. Spectroscopic data suggest that these compounds exist mainly in the enol-imine form in a weakly polar solvent ($CDCl_3$) and in the solid state, but the equilibrium shifts in favour of the keto amine form in a polar protic solvent ($CDCl_3$)[10].

The UV-visible spectra of the compounds were studied in polar, non-polar solvents both in acidic and basic media. The calculated keto-amine form is given in Table 4. Compounds show absorption in the range greater than 400 nm in DMSO, ethanol, chloroform, benzene and cyclohexane. It is point out that the new band (greater than 400 nm) belongs to the keto amine form of the 2-hydroxy Schiff bases in polar and non-polar solvents both in acidic and basic media[1–2]. The band was observed at greater than 400 nm in polar (DMSO, ethanol and chloroform) and non-polar (benzene and cyclohexane) solvents and in acidic (CF_3COOH) solutions of chloroform and benzene and basic [$(C_2H_5)_3N$] solutions of DMSO, ethanol, chloroform, benzene and cyclohexane but it is not observed in acidic solutions of DMSO and ethanol.

The enol-imine tautomer is dominant only in the acidic solutions of DMSO and ethanol for compound, while it is dominant in polar and non-polar solvents and in both polar acidic solutions of chloroform and benzene and basic solutions of DMSO, ethanol, chloroform, benzene and cyclohexane. On the contrary, keto-amine tautomer was increased by 58, 21, 44, 56, 70% and 65, 82% for (1), by 43, 11, 27, 19, 35% and 63, 66% for (2), by 61, 29, 47, 38, 51% and 51, 73% for (3), by 66, 37, 28, 58, 62% and 60, 81% respectively

Table 2. Vibrational Assignments of Some Selected Infrared Regions (cm^{-1})

	C-C (arom.)	$\nu_{\text{O-H}}$	$\nu_{\text{C-O}}$	$\nu_{\text{1-2,1-4,2-5,2-4}}$ (disubst.)	$\nu_{\text{C-X}}$	$\nu_{\text{C-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C-N}}$	$\nu_{\text{C=O}}$
(1)	1450–1618	3407 mb	1186 m 1311 s	1050–1275	946–1251	3066–3068	1620 s	1375 mw	1580–1600 v
(2)	1422–1621	3408 mb	1187 mw 1309 sb	1054–1268	620–739	3070–3072	1621	1381 m	1561–1622 vs
(3)	1421–1619	3402 vwb	1166 m 1321 s	1040–1250	435–467	3069–3071	1623 s	1371 m	1555–1605 s
(4)	1412–1610	3415 vwb	1182 m 1326 s	1020–1260	434–466	3062–3064	1624 vs	1380	1569–1599 vs
(5)	1440–1616	3420 mb	1180 m 1328 sb	980–1222	946–1251	3066–3068	1625 s	1384 m	1557–1609 s
(6)	1442–1611	3422 wb	1181 m 1322 sb	698–808	620–739	3061–3063	1620 s	1373 m	1541–1610 s
(7)	1446–1602	3410 wb	1187 m 1327 sb	798–858	620–739	3063–3067	1622 s	1376 m	1551–1607 s

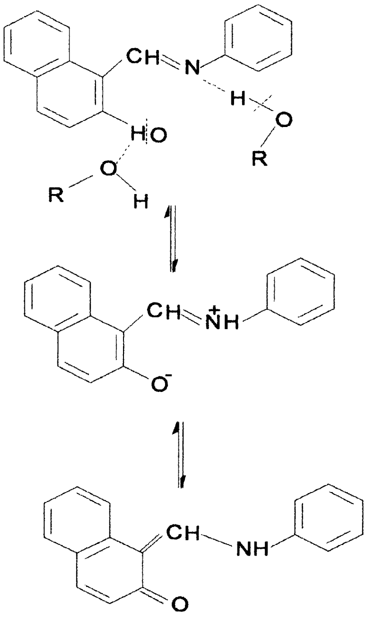
s: strong, m: medium, mb: medium and broad, sb: strong and broad, mw: medium and weak, wb: weak and broad , vwb: very weak and broad, vs: very strong.

Table 3. ^{1}H-NMR Data (δ ppm)

	$\delta_{NH\text{-}CH}$	$\delta_{CH\text{-}N}$	$\delta_{C=C\text{-}H}$	Form	Solvent
(1)	15.10 s 1 H	9.26 s 1 H	6.82–8.37 (arom.) s 10 H	Keto-amine	$CDCl_3$
(2)	15.22 s 1 H	9.18 s 1 H	6.90–8.22 (arom.) s 10 H	Keto-amine	$CDCl_3$
(3)	15.18 s 1 H	9.26 s 1 H	6.84–8.18 (arom.) s 10 H	Keto-amine	$CDCl_3$
(4)	15.24 s 1 H	9.32 s 1 H	6.82–8.14 (arom.) s 10 H	Keto-amine	$CDCl_3$
(5)	15.28 s 1 H	9.30 s 1 H	6.78–8.10 (arom.) s 10 H	Keto-amine	$CDCl_3$
(6)	15.20 s 1 H	9.30 s 1 H	6.76–8.25 (arom.) s 9 H	Keto-amine	$CDCl_3$
(7)	15.18 s 1 H	9.22 s 1 H	6.81–8.10 (arom.) s 9 H	Keto-amine	$CDCl_3$

for (4), by 66, 37, 28, 58, 62% and 60, 81% for (5), by 66, 37, 28, 58, 62% and 60, 81% for (6), by 66, 37, 28, 58, 62% and 60, 81% for (7), respectively, in the basic solutions of DMSO, ethanol, chloroform, benzene, cyclohexane and in the acidic solutions of chloroform and benzene with respect to the pure solvent media. Absence of the keto-amine form in the acidic solutions of DMSO and ethanol may be explained by the hydrogen bonding to CF_3COOH.

On the basis of the results obtained, the interaction of the solvent and the Schiff base molecules conceivably proceeds as in the following process (Scheme 2):



Scheme 2.

Table 4. Effect of Solvent, Acid, and Base on the UV-Spectra of Compounds

			Keto-amine Isomer (%)		
	Solvent	λ, nm (ε, M^{-1} $cm^{-1}.10^4$)	Solvent Media	Acidic Media[a]	Basic Media[b]
(1)	DMSO	322(1.3), 444(1.1)	40	–	65
	Ethanol	346(1.5), 440(1.8)	53	–	61
	$CHCl_3$	376(1.4), 438(1.3)	48	72	60
	Benzene	386(1.4), 428(1.0)	43	70	59
	Cyclohexane	322(1.6), 430(1.2)	36	Not measured	58
(2)	DMSO	340(1.4), 442(1.3)	42	–	66
	Ethanol	318(1.6), 432(1.8)	55	–	62
	$CHCl_3$	374(1.7), 436(1.6)	49	70	60
	Benzene	382(1.4), 430(1.2)	47	68	58
	Cyclohexane	342(1.5), 432(1.2)	40	Not measured	57
(3)	DMSO	388(1.3), 446(1.1)	43	–	66
	Ethanol	344(1.6), 448(1.9)	55	–	61
	$CHCl_3$	372(1.8), 434(1.7)	49	74	59
	Benzene	388(1.7), 432(1.6)	48	73	57
	Cyclohexane	384(1.4), 440(1.2)	43	Not measured	57
(4)	DMSO	382(1.3), 442(1.1)	43	–	69
	Ethanol	342(1.6), 438(1.9)	50	–	63
	$CHCl_3$	370(1.8), 424(1.7)	40	74	62
	Benzene	380(1.7), 442(1.6)	47	70	56
	Cyclohexane	324(1.4), 446(1.2)	46	Not measured	55
(5)	DMSO	382(1.3), 444(1.1)	41	–	66
	Ethanol	316(1.5), 436(1.9)	53	–	65
	$CHCl_3$	376(1.2), 414(1.7)	45	61	63
	Benzene	378(1.5), 432(1.6)	48	59	63
	Cyclohexane	342(1.4), 436(1.2)	42	Not measured	58
(6)	DMSO	344(1.3), 442(1.1)	42	–	69
	Ethanol	320(1.6), 432(1.9)	53	–	61
	$CHCl_3$	342(1.8), 424(1.7)	43	73	62
	Benzene	318(1.7), 442(1.6)	48	72	60
	Cyclohexane	318(1.4), 440(1.2)	43	Not measured	60
(7)	DMSO	386(1.3), 438(1.1)	43	–	68
	Ethanol	342(1.6), 436(1.9)	55	–	62
	$CHCl_3$	322(1.8), 414(1.7)	44	72	62
	Benzene	382(1.7), 452(1.6)	41	73	58
	Cyclohexane	320(1.4), 442(1.2)	40	Not measured	58

[a] CF_3COOH, pH:3., [b] $[(C_2H_5)_3N]$, pH:9., [c] cyclohexane and acid in separate phases.

For the o-hydroxy derivatives of course an additional role in the process is played by intra molecular hydrogen bonding[12]. In contrast with the formation of the keto form, the possibility of formation of a zwitterionic structure has been proposed by a number of authors in their interpretations of the solvent effect[13–15], but this possibility has not been confirmed unambiguously. We consider that the two types of interpretation according to the above process do not exclude, but rather presuppose one another: the molecules pass from the enol form to the quinone form via a zwitterionic structure. As concerns the positions of the above equilibrium, it must also be taken into account that formation of the quinoid structure is inhibited by the conjugation of the Schiff base molecule. In conclusion, structural analysis using IR and 1H-NMR show that the keto tautomeric form is favoured over enol form. Besides, UV results denote that the keto form dominates in ethanol solution state of compounds.

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