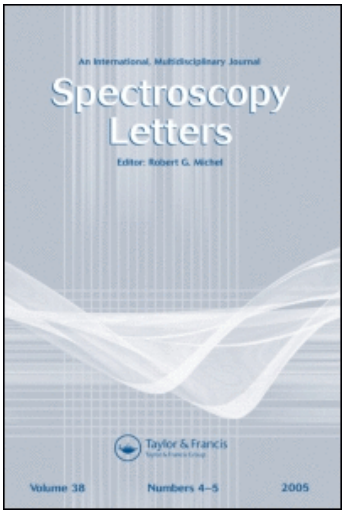

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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Online publication date: 09 August 2003

To cite this Article Ünver, H. , Polat, K. , Uçar, M. and Zengin, D. M.(2003) 'Synthesis and Keto-Enol Tautomerism in N-(2-Hydroxy-1-Naphthylidene)Anils', Spectroscopy Letters, 36: 4, 287 — 301
To link to this Article: DOI: 10.1081/SL-120024579
URL: http://dx.doi.org/10.1081/SL-120024579

SPECTROSCOPY LETTERS
Vol. 36, No. 4, pp. 287–301, 2003

Synthesis and Keto-Enol Tautomerism in N-(2-Hydroxy-1-naphthylidene)anils

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ABSTRACT

New ligands of Schiff bases [($C_{17}H_{12}NOX$), X = F, Cl, Br, I] have been synthesised. Intra-molecular hydrogen bonding and keto-enamine tautomerism have been studied using IR, ^{1}H-NMR, ^{13}C-NMR (DEPT), UV-Visible and GC-MS techniques. The UV-Visible spectra of the compounds have been investigated in different solvents, acidic and basic media. The compounds were in tautomeric equilibrium (enol-imine O—H···N, keto-amine O···H—N forms) in polar and nonpolar solvents. The keto-amine form was observed in basic solutions of DMSO, ethanol, chloroform, benzene, and cyclohexane, and in acidic

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DOI: 10.1081/SL-120024579 0038-7010 (Print); 1532-2289 (Online)

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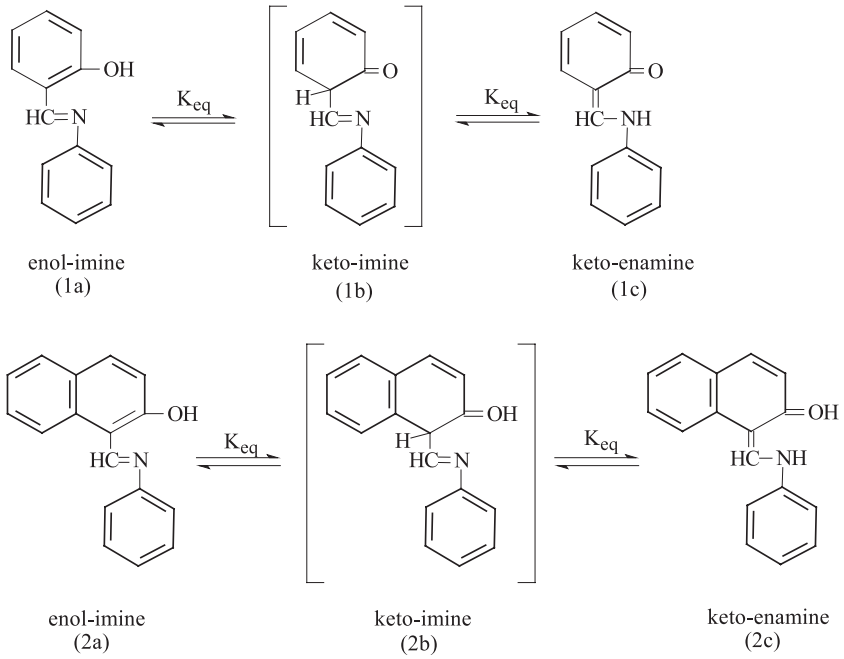
solutions of chloroform and benzene, but not in acidic solutions of DMSO and ethanol. ^{1}H-NMR and ^{13}C-NMR and IR results showed that all Schiff bases studied favor the enol-imine form over the keto form in a weakly polar solvent such as deuterochloroform solution.

Key Words: Schiff base; Tautomerism; Keto-enamine; Enol-imine; Solvent effect.

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.[1–6] 2-Hydroxy Schiff base ligands are of interest mainly due to the existence of (O—H···N and N—H···O) type hydrogen bonds and tautomerism between enol-imine and keto-enamine forms (Scheme 1). Tautomerism in 2-hydroxy Schiff bases both in solution and in the solid state was investigated using different spectroscopic techniques.[7–23] In the spectra of solutions of these compounds different Schiff bases have been studied in both polar and non-polar solvents.[5,6,8,9,11,13,16,20] A new band at greater than 400 nm has been observed in polar solvents, and in acidic media of some solvents, but this band has not been observed in hydrocarbon solvents. The results indicate that the absorption band at greater than 400 nm belongs to the keto-enamine form of the Schiff base; the enol form has no appreciable absorbance in this region. Different explanations for the source of this band have been proposed.[5,8,15,17,20] It was suggested that this new band is due to the keto form in salicylidene anilines (Scheme 1, 1b and 1c). It was also observed that *ortho*-hydroxy naphthalidene anilines show two bands in the visible region located above 400 nm.[8] These two bands were assigned to the keto form (Scheme 2b and 2c). In the solid state, salicylideneanilines exist mostly in the enolimino tautomeric form. In naphthaldimines both forms are possible and O—H···N or N—H···O intramolecular hydrogen bonds can occur.[2,3,14,19,22] The hydrogen bonding and tautomerism of Schiff bases, and the tautomeric forms at 50% abundance, have been reported in the crystalline state of the Schiff base formed by 3-haloaniline and 2-hydroxy-1-naphthaldehyde.[3] The Schiff base compounds can be classified by their photochromic and thermochromic characteristics.[24,25] Thermochromism is due to a change in the π-electron configuration induced by proton transfer, which can occur in the ground state and requires a planar molecular system. Non-

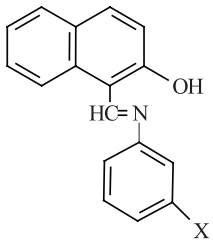


Scheme 1. Tautomerism of salicylidene and naphthylidene anilines.

planar molecules exhibit photochromism. Studies on the photochromic compounds have been increasing ever since the potential applications of photochromic materials were realized in various areas such as the control and measurement of radiation intensity, optical computers and display systems.

EXPERIMENTAL

2-Hydroxy-1-naphthaldehyde, 3-fluoroaniline, 3-chloroaniline, 3-bromoaniline, 3-iodoaniline, benzene, dimethylsulfoxide, chloroform, ethanol, cyclohexane, triethylamine, tetrahydrofuran and trifluoroacetic acid were purchased from Merck (Germany) and used without further purification. Melting points were determined with a Gallonkamp apparatus without correction. The elemental analyses were performed on a LECO CHNS-932 C-, H-, N-analyzer. Infrared absorption spectra were obtained from a Mattson



1-{(Z)/(E)-[3-halophenyl)imino]methyl}-2-naphthol

X	Comp. No.	m.p (^{o}C)
F	I	113
Cl	II	115
Br	III	140
I	IV	163

Scheme 2. Melting points of the compounds.

1000 FT-IR spectrometer using KBr pellets and reported in cm^{-1}. UV-visible spectra were measured using a Perkin Elmer Lambda 2 series spectrophotometer. ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker DPX 400-MHz FT-NMR spectrometer operating at a proton frequency 400.5 MHz and a carbon frequency of 100.7 MHz using $CDCl_3$ solvent and tetramethylsilane (TMS) as an internal standard. Mass spectra for all compounds were obtained for a solid sample using an Agilent GC-MSD, and Micromass Platform 2 mass spectrometer model in EI mode as an ionization technique.

The compounds (Scheme 2) were synthesized by standard procedures and characterized by spectroscopic and elemental analysis data. The spectral and element analysis data are as follows:

Compound (**I**); found: C, 76.97; H, 4.56; N, 5.28. Cal. for $C_{17}H_{12}NOF$; C, 77.42; H, 4.44; N, 5.29%. MS (EI 1.15 e5) M/z (%) 264 $(M\text{-}1(H))^{+}$ 47.77; 266 $(M+1)^{+}$ 30.36; 95 $(M\text{-}C_6H_5F^{+})$ 100; 248 (M-OH) 2.32; 128 $(C_{10}H_8^{+})$ 2.97; 127 $(M\text{-}C_{10}H_7^{+})$ 2.9; 77 $(M\text{-}C_6H_5^{+})$ 2.39 and 76 $(M\text{-}C_6H_4^{+})$ 5.92.

Compound (**II**); found: C, 72.47; H, 4.29; N, 12.58. Cal. for $C_{17}H_{12}NOCl$; C, 73.12; H, 4.14; N, 4.97%. MS (EI 1.15 e5) M/z (%) 281 $(M^{+\cdot})$ 73; 280 $(M\text{-}1)^{+\cdot}$ 100; 282 $(M+1)^{+\cdot}$ 42.4; $(M+2)^{+\cdot}$ 23.2; 284 $(M+3)^{+\cdot}$ 3.8; 170 $(M\text{-}C_6H_5Cl^{+})$ 4.8; 264 (M-OH) 14; 265 (M-16) 2.8; 246 (M-Cl) 1.5; 128 $(C_{10}H_8^{+})$ 1.5; 77 $(M\text{-}C_6H_5^{+})$ 2.1 and 76 $(M\text{-}C_6H_4^{+})$ 1.5.

Compound (**III**); found: C, 62.60; H, 3.71; N, 4.29. Cal. for $C_{17}H_{12}NOBr$; C, 62.42; H, 3.84; N, 4.19%. MS (EI 1.15 e5) M/z (%) 326 $(M^{+\cdot})$ 100; 327 $(M+1)^{+\cdot}$ 73; 324 $(M\text{-}2)^{+\cdot}$ 96; 325 $(M\text{-}1)^{+\cdot}$ 79.2; 310 (M-16) 13.4; 308 (M-OH) 14; 246 (M-Br) 3; 168–170 $(M\text{-}C_6H_5Br^{+})$ 4.7; 128 $(C_{10}H_8^{+})$ 4; 77 $(M\text{-}C_6H_5^{+})$ 3.5 and 76 $(M\text{-}C_6H_4^{+})$ 5.1.

Compound (**IV**); found; C, 54.71; H, 3.24; N, 3.75. Cal. for $C_{17}H_{12}NOI$; C, 54.32; H, 3.02; N, 3.35%. MS (EI 1.15 e5) M/z (%) 373 $(M^{+\cdot})$ 100; 374 $(M+1)^{+\cdot}$ 17.5; 375 $(M+2)^{+\cdot}$ 1.7; 372 $(M\text{-}1)^{+\cdot}$ 87; 356 (M-OH) 12.1; 204 $(M\text{-}C_6H_5I^{+})$ 1.1; 128 $(C_{10}H_8^{+})$ 3.8; 246 (M-I) 10.95; 77

Table 1. Selected FT-IR bands (cm^{-1}) for compounds.

Comp.	$\nu_{O—H}$ or $\nu_{N—H}$	Ar-OH bend or $\nu_{(C—OH)}$	ν_{1-3} disubst.	$\nu_{C—X}$	$\nu_{C=O}$	$\nu_{C—NH}$	$\nu_{C=C(ext.)}$ and $\nu_{C=N}$
I	3062	1319mb	691–726	946–1251	1624s	1188m	1584s 1605s
II	3070	1324vs	627–781	620–739	1622vs	1178m	1569vs 1612w
III	3067	1325vs	671–778	435–467	1622vs	1156m	1565vs 1607w
IV	3064	1325vs	675–778	434–466	1622vs	1180m	1561vs 1604vs

s: strong, **m**: medium, **mb**: medium and broad, **vs**: very strong, **ext**: external double band, **w**: weak, **wb**: weak and broad.

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Table 2. ^{1}H-NMR data (δ ppm).

Comp.	$\delta_{OH—NH}$	$\delta_{CH—N}$	$\delta_{C=C—H}$	Solvent
I	15.20 singlet	9.16 singlet	6.88–8.27	$CDCl_3$
II	15.22 singlet	9.18 singlet	6.90–8.22	$CDCl_3$
III	15.18 singlet	9.26 singlet	6.84–8.18	$CDCl_3$
IV	15.24 singlet	9.32 singlet	6.82–8.14	$CDCl_3$

($M\text{-}C_6H_5^+$) 2.92 and 76 ($M\text{-}C_6H_4^+$) 5.5. UV, IR and ^{1}H-NMR data were given in Tables 1–3 respectively.

RESULTS AND DISCUSSION

Data obtained from the FT-IR spectrum of all Schiff bases are listed in Table 1 and an example of a spectrum is given in Figure 1. In the FT-IR spectra for the compounds, weak and broad absorption bands are observed in the 3100–3000 cm^{-1} region. This is interpreted to be a sign of the formation of an intra-molecular hydrogen bond. The wave numbers between 1700–1600 cm^{-1} arise due to stretching vibrations of C═N and C═O bands. In this region two bands were observed for compounds **I**–**IV**. The sharp and strong first band at 1624 and 1622 cm^{-1} ($\nu_{C=N}$) for compound **I** and compound **II**–**IV** respectively, and a second band as a shoulder with weak intensity was located near the first band. The assumption that this new band is due to $C=NH^+$ stretching motion of a zwitterionic structure (Scheme 3) has been pointed out by Aton.[21] This indicates that the keto tautomer of these compounds exists in appreciable amounts compared to the enol form.

The absorption bands in the 1561–1584 cm^{-1} region must be related to the keto structure (C═C external double bond). In other words these bands occur only if there is a considerable amount of the keto tautomer.[21] However, broad bands were observed at 1350–1300 cm^{-1}, in the phenolic C—OH stretching region, which is evidence for the imine form in the solid state.

From the FT-IR spectra of compounds **I**–**IV** it was possible to assign the IR absorption for the C═O and C═N group in both the keto and the enol form. It was also possible to assign other absorptions, which were specific either to the keto or the enol forms.

In solution the existence of intra-molecular hydrogen bonding (N—H···O) has been confirmed by ^{1}H-NMR spectroscopy in some Schiff base ligands.[17,19,22] All compounds studied illustrated that the enol-imine form dominates in $CDCl_3$ (Table 2). The signals at the proton of the OH or

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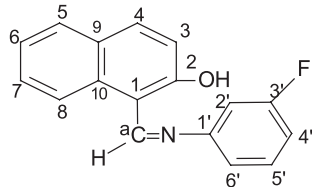
NH group which is involved in intra-molecular hydrogen bonding [δ(xH)] appear in the 15.20–15.24 ppm. The methine proton resonance is a single signal which indicates these compounds exist mainly in the enol-imine form in a weakly polar solvent ($CDCl_3$).

The peaks located at between 14–15 ppm and 9–10 ppm are singlet and there is no observed CH—NH coupling. These show that in deutero-chloroform solution all compounds studied exist mainly in enol-imine tautomeric form.

Further evidence for the identity of the compounds **I**–**IV** comes from the ^{13}C-NMR (decoupled and DEPT techniques) and ^{1}H-NMR data. As an example, ^{13}C-NMR data relating to compound **I** are given below



δ (ppm): 148.20 (C-a); 136.95 (C-1); 162.69 (C-2); 127.43 (C-3); 119.56 (C-4); 120.96 (C-5); 121.77 (C-6); 126.86 (C-7); 128.60 (C-8); 135.77 (C-9); 127.98 (C-10); 139.48 (C-1′); 137.10 (C-2′); 144.17 (C-3′); 138.16 (C-4′); 133.49 (C-5′); 129.82 (C-6′).

DEPT (45, 90, 135) δ (ppm): 148.20 (C-a); 127.43 (C-3); 119.56 (C-4); 120.96 (C-5); 121.77 (C-6); 126.86 (C-7); 128.60 (C-8); 139.48 (C-1′); 137.10 (C-2′); 133.49 (C-5′); 129.82 (C-6′).

The ^{13}C-NMR signal in the Schiff bases studied occurs between 158–162 ppm (C-2) indicating that the proton is bonded to the OH group. This indicates that the keto-enol equilibrium is in favor of enol in weak protic media. The ^{13}C-NMR data obtained are in accordance with information about 2-hydroxynaphthaldehyde type Schiff bases in the literature.[5,10,19]

In conclusion ^{1}H and ^{13}C-NMR results indicate that, in deuterochloro-form solution, all Schiff bases studied exist in the imine form.

The UV-Visible spectra of the compounds were studied in polar and non-polar solvents both in acidic and basic media. The spectra are presented in Figures 2 and 3 and the calculated keto-enol ratio is given in Table 3.[26] All the compounds studied show two absorption bands in the range greater than 400 nm in DMSO, ethanol, chloroform, benzene and cyclohexane. The new band (greater than 400 nm) belongs to the keto 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,

Table 3. Effect of solvent, acid, and base on the UV-spectra of compounds.

Comp.	Solvent	λ, nm (ε, M^{-1} cm^{-1} 10^4)	Keto-enamine isomer (%)		
			Solvent media	Acidic media[a]	Basic media[b]
I	DMSO	318(1.3), 444(1.1)	40	–	63
	Ethanol	380(1.5), 440(1.8)	53	–	64
	$CHCl_3$	346(1.4), 420(1.3)	48	79	69
	Benzene	316(1.4), 418(1.0)	43	78	67
	Cyclohexane	320(1.6), 438(1.2)	36	Not measured	61
II	DMSO	314(1.4), 440(1.3)	42	–	60
	Ethanol	378(1.6), 438(1.8)	55	–	61
	$CHCl_3$	344(1.7), 422(1.6)	49	80	62
	Benzene	312(1.4), 416(1.2)	47	78	56
	Cyclohexane	322(1.5), 434(1.2)	40	Not measured	54
III	DMSO	310(1.3), 438(1.1)	43	–	69
	Ethanol	372(1.6), 442(1.9)	55	–	71
	$CHCl_3$	342(1.8), 414(1.7)	49	74	72
	Benzene	318(1.7), 412(1.6)	48	83	66
	Cyclohexane	324(1.4), 440(1.2)	43	Not measured	65
IV	DMSO	316(1.3), 430(1.1)	41	–	68
	Ethanol	370(1.5), 448(1.6)	51	–	70
	$CHCl_3$	348(1.1), 408(1.2)	47	75	72
	Benzene	316(1.5), 412(1.4)	43	78	68
	Cyclohexane	322(1.3), 448(1.0)	39	Not measured	63

[a]CF_3COOH, pH: 2.0.
[b]$[(C_2H_5)_3N]$, pH: 9.0.
[c]Not mixture cyclohexane and acid.

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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 compounds, while it is dominant in polar and non-polar solvents and in both acidic solutions of chloroform and benzene and basic solutions of DMSO, ethanol, chloroform, benzene and cyclohexane. In contrast, 58, 21, 44, 56, 70%, and 65, 82% for compound **I** increased the keto-enamine tautomer by 43, 11, 27, 19, 35% and 63, 66% for compound **II**, by 61, 29, 47, 38, 51% and 51, 73% for compound **III**, by 66, 37, 28, 58, 62% and 60, 81% respectively for compound **IV**, in basic solutions of DMSO, ethanol, chloroform, benzene, cyclohexane, and in acidic solutions of chloroform and benzene with respect to the pure solvent media. Absence of the keto-enamine form in the acidic solutions of DMSO, and ethanol, may be explained by hydrogen bonding with CF_3COOH. On the other hand, an appreciable quantity of the keto form is present only in solvents capable of hydrogen bonding.[9,10]

Solvent effects can be explained, which are capable of hydrogen bonding both as proton donors and as proton acceptors, thereby permitting the proton transfers that result in formation of the keto form (Scheme 3). As a proton donor, the solvent interacts with the non-bonding electron pair of the azomethine nitrogen. Thus, it may be assumed that, in those Schiff base derivatives where non-bonding electron pair is no longer available, a solvent effect will not be observed.

The investigation of halogens at the *metha* position revealed that there is no significant effect on the keto-enol ratio. However, the ratio was observed to change in the order of $I > II \geq III > IV$ (Table 3). The electron withdrawing groups on the aniline ring decrease the electron density of the N atom, and it makes the proton transfer from the solvent extremely difficult. Proton uptake by the azomethine nitrogen is the more probable, the more electron-repelling the aniline ring substituent and the more basic the amine constituent of the Schiff base. The proton transfer necessary for the development of the keto form explains this.

It is shown in the literature that in Schiff bases the phenyl ring is twisted, and their substituents are not fully conjugated with the rest of the molecule. Therefore, the tautomeric ratio does not depend, in general, on the electron action (donor or acceptor) of the substituents. Thus the tautomeric process is localized on the naphthylmethylidene moiety.[13] It is claimed that the presence of electron acceptor or donating substituents, on 2-hydroxynaphthaldehyde Schiff bases acceptor substituents, shifts the equilibrium towards the phenolic form, while donors favor the keto form and donating groups at the aniline ring does not have a significant effect on keto-enol tautomerism.[6]

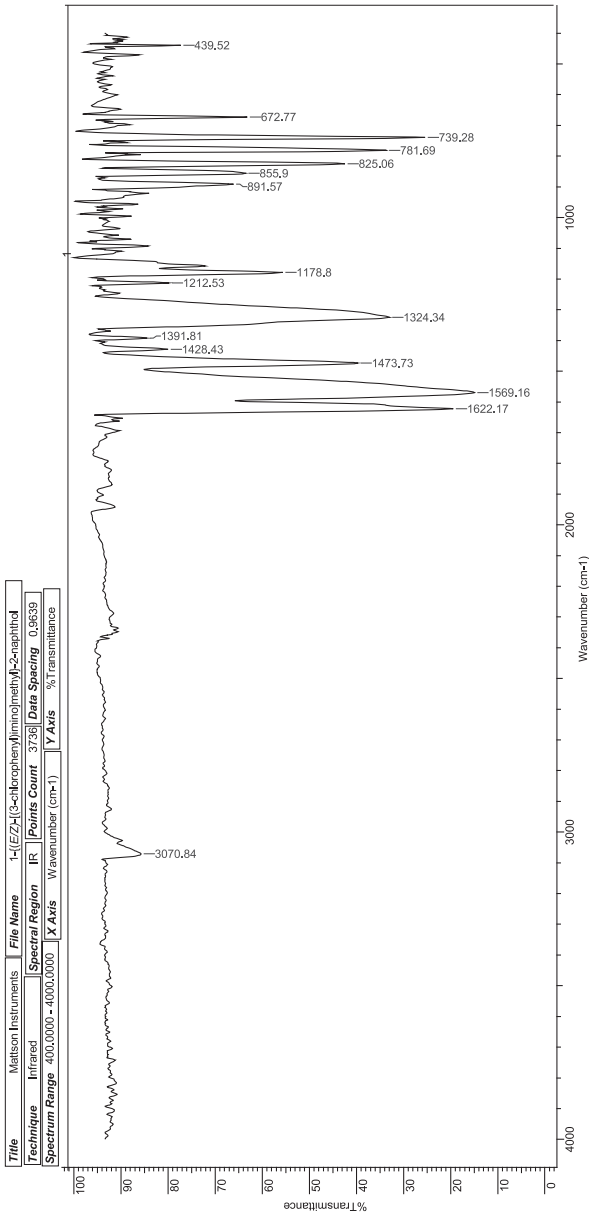

Figure 1. IR spectrum of the compound **I**.

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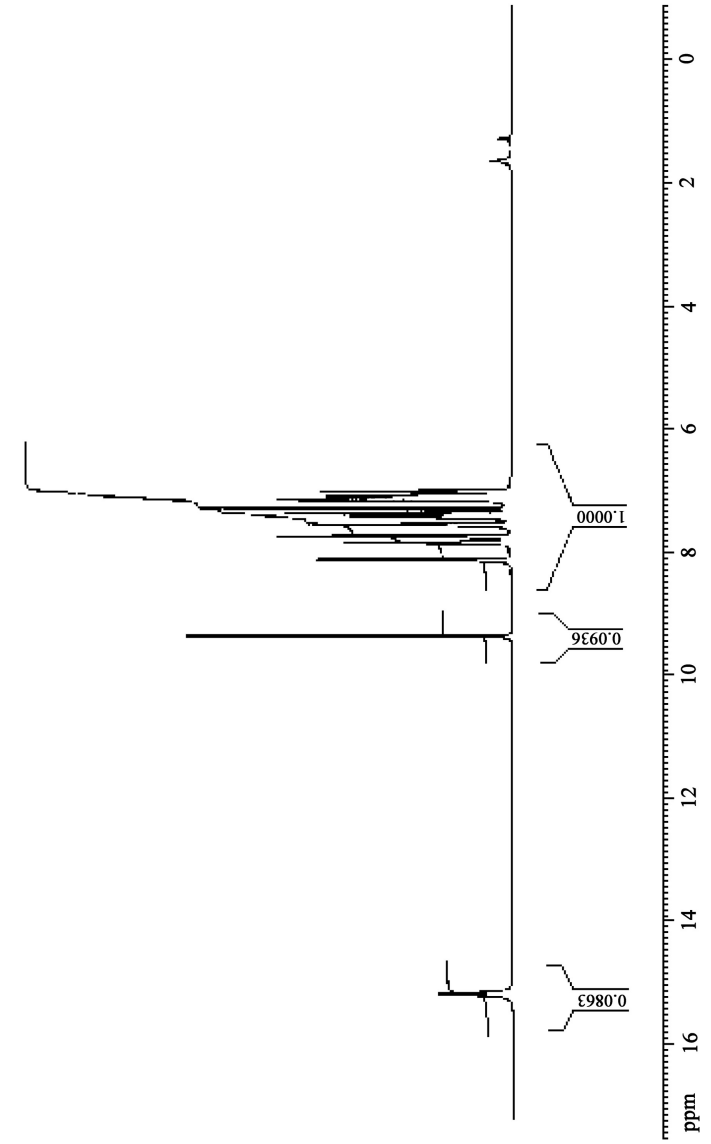

Figure 2. ^{1}H-NMR spectrum of compound **I**.

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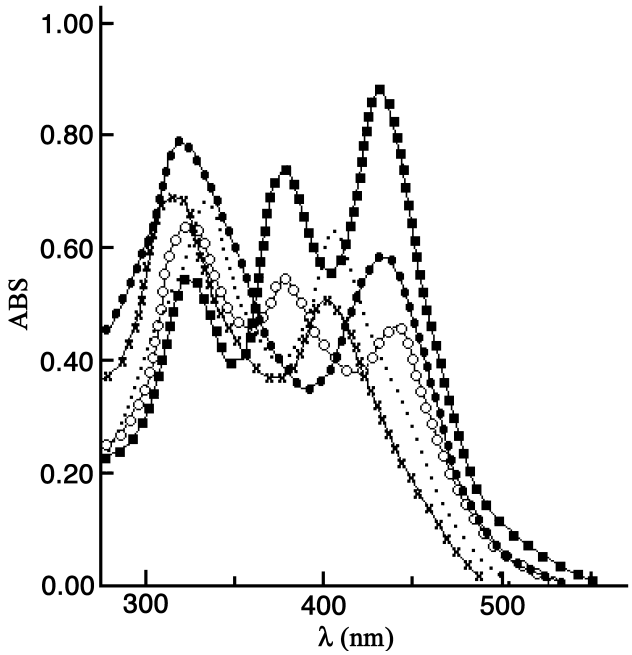
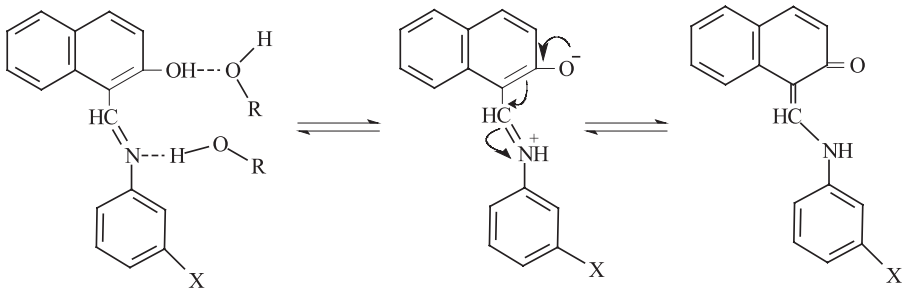


Figure 3. The solvent effect on compound **I**. [DMSO (-○-○-○;-), ethanol (-■-■-■-), chloroform (- - - - - - - -), benzene (-x-x-x-), cylohexane (-●-●-●-); Schiff base concentration 5×10^{-5} M].



Scheme 3. The mechanism of the enol ⇄ zwitterion tautomerism.

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The spectroscopic data suggest that these compounds exist mainly in the enol-imine form in weakly polar solvents, and in the solid state, but the equilibrium shifts in favor of the keto-amine form in a polar protic solvent[8] (ethanol) for all compounds studied.

In conclusion, structural analysis using IR and ^{1}H-NMR and ^{13}C-NMR show that the enol tautomeric form is favored over the keto form. The UV results have the keto absorption above 400 nm in polar and non-polar solvents, indicating that the compounds studied exist mainly in the keto form. Moreover, the intensity of the keto band increased with increasing solvent polarity. They were in good agreement with the results obtained in these studies by other workers' measurements.[7–9,20]

ACKNOWLEDGMENTS

The authors wish to acknowledge the financial assistance of the Ankara University Research Fund, Grant Number CHE 2001 07 05 039.

REFERENCES

1. Salman, S.R.; Shawkat, S.H.; Al-Obaidi, G.M. Tautomerism in o-hydroxy Schiff bases: effect of alkyl group. Can. J. Spectr. **1990**, *35*, 25.
2. Gavranić, M.; Kaitner, B.; Mestrović, E. Intramolecular N—H···O hydrogen bonding, quinoid effect, and partial p-electron delocalisation in N-aryl Schiff bases of 2-hydroxy-1-naphthaldehyde: the crystal structures of planar N-(α-naphthyl)- and N-(β-naphthyl)-2-oxy-1-naphthaldimine. J. Chem. Crystallogr. **1996**, *26*, 23.
3. Ünver, H.; Zengin, D.M.; Güven, K. Intramolecular hydrogen bonding and tautomerism in 1-[N-(4-bromophenyl)] aminomethylidene-2(1H)naphthalonene. J. Chem. Crystallogr. **2000**, *30*, 359.
4. Cannor, J.A.; Fine, D.J. Studies of chelation. Part 9. Cobalt complexes of 1-[(substituted phenyl)azo]-2-naphthol and 1-[(substituted phenylimino)methyl]-2-naphthol ligands. Tautomerism and Reactivity J.C.S. Dalton **1981**, 559.
5. Fernández-G, J.M.; del Rio-Portilla, F.; Quiroz-García, B.; Toscano, R.A.; Salcedo, R. The structures of some ortho-hydroxy Schiff base ligands. J. Mol. Struct. **2001**, *561*, 197.
6. Antonov, L.; Fabian, M.F.; Nedeltcheva, D.; Kamounah, F.S.

Tautomerism of 2-hydroxynaphthaldehyde Schiff bases. J. Chem. Soc., Perkin Trans. 2 **2000**, 1173.
7. Ledbetter, J.W. Spectroscopic evidence for the enol imine-keto enamine tautomerism of N-(o- and p-hydroxybenzylidene)anils in solution. J. Phys. Chem. **1966**, *70*, 2245.
8. Nagy, P.; Harzfeld, R. Study of enol-keto tautomerism of N-(2-hydroxy-1-naphthylidene)anils. Spectr. Lett. **1998**, *31*, 221.
9. Kamounah, F.S.; Salman, S.R.; Mahmoud, A.A.K. Substitution and solvent effect of some substituted hydroxy Schiff bases. Spect. Lett. **1998**, *31*, 1557.
10. Alarcón, S.H; Pagani, D.; Bacigalupo, J.; Olivieri, A.C. Spectroscopic and semi-empirical MO study of substituent effects on the intramolecular proton transfer in anils of 2-hydroxybenzaldehydes. J. Mol. Struct. **1999**, *475*, 233.
11. Rospenk, M.; Król-Starzomska, I.; Filarowski, A.; Koll, A. Proton transfer and self-association of sterically modified Schiff bases. Chem. Phys. **2003**, *287*, 113.
12. Cohen, M.D.; Flavian, S.; Leiserowitz, L. Topochemistry. Part XXVI. The absorption spectra of some thermochromic N-salicylideneanilines and hydroxynaphthylideneanilines in the crystal. J. Chem. Soc. B **1967**, 329.
13. Joshi, H.; Kamounah, F.S.; van der Zwan, G.; Gooijer, C.; Antonov, L. Temperature dependent absorption spectroscopy of some tautomeric azo dyes and Schiff bases. J. Chem. Soc., Perkin Trans. 2 **2001**, *12*, 2303.
14. Popović, Z.; Roje, V.; Pavlović, G.; Matković-Čalogović, D.; Giester, G. The first example of coexistence of the ketoamino-enolimino forms of diamine Schiff base naphthaldimine parts: the crystal and molecular structure of N,N′-bis(1-naphthaldimine)-o-phenylenediamine chloroform (1/1) solvate at 200 K. J. Mol. Struct. **2001**, *597*, 39.
15. Joshi, H.; Kamounah, F.S.; Gooijer, C.; van der Zwan, G.; Antonov, L. Excited state intramolecular proton transfer in some tautomeric azo dyes and Schiff bases containing and intramolecular hydrogen bond. J. Photochem. Photobiol. A: Chem. **2002**, *152*, 183.
16. Herzfeld, R.; Nagy, P. Studies of the solvent effect observed in the absoption spectra of certain types of Schiff bases. Curr. Org. Chem. **2001**, *5*, 373.
17. Dudek, G.O.; Dudek, E.P. Spectroscopic studies of keto-enol equilibria. VII. N-15 substituted substituted Schiff bases. J. Am. Chem. Soc. **1964**, *86*, 428.
18. Dudek, G.O.; Dudek, E.P. Spectroscopic studies of keto-enol equilibria. IX. ^{15}N-substituted anilides. J. Am. Chem. Soc. **1966**, *88*, 2407.

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19. Dziembowska, T.; Rozwadowski, Z.; Filarowski, A.; Hansen, P.E. NMR study of proton transfer equilibrium in Schiff bases derived from 2-hydroxy-1-naphthaldehyde and 1-hydroxy-2-acetonaphthone. Deuterium isotope effects on 13C and 15N chemical shifts. Magn. Reson. Chem. **2001**, *39*, 67.
20. Herzfeld, R.; Nagy, P. Role of acidity and basicity of the solvent in the solvent effect observed in the absorption spectra of certain types of Schiff bases. Spectrosc. Lett. **1999**, *32*, 57.
21. Salman, S.R.; Saleh, N.A.I. Infrared study of tautomerism in some Schiff bases. Spectr. Lett. **1997**, *30*, 1289.
22. Dudek, G.O.; Dudek, E.P. Spectroscopic studies of keto-enol equilibria. IX. Nitrogen-15 substituted Schiff bases. J. Am. Chem. Soc. **1966**, *88*, 2407.
23. Salman, S.R.; Saleh, N.A.I. Mass spectral study of tautomerism in some Schiff bases. Spect. Lett. **1997**, *30*, 1289.
24. Hadjoudis, E.; Vitterakis, M.; Maustakali-Marridis, I. Photochromism and thermochromism of Schiff bases in the solid state and rigid glasses. Tetrahedron **1987**, *43*, 1345.
25. Kletskii, M.E.; Millov, A.A.; Metelitsa, A.V.; Knyazhansky, M.I. Role of structural flexibility in the fluorescence and photochromisim of salicylideneaniline: the general scheme of the phototransformations. J. Photochem. Photobiol. A: Chem. **1997**, *110*, 267.
26. Nazır, H.; Yıldız, M.; Yılmaz, H.; Tahir, M.N.; Ülkü, D. Intramolecular hydrogen bonding and tautomerism in Schiff bases. Structure of N-(2-pyridil)-2-oxo-1-naphthylidenemethylamine. J. Mol. Struct. **2000**, *524*, 241.

Received January 14, 2003
Accepted May 8, 2003