

Full Paper

Synthesis of Some New Anils: Part 1. Reaction of 2-Hydroxy-benzaldehyde and 2-Hydroxynaphthaldehyde with 2-Aminopyridene and 2-Aminopyrazine

Abdullah M. Asiri* and Khadija O. Badahdah

Chemistry Department, Faculty of Science, King Abdul Aziz University, Jeddah 21413, P. O. Box 80203, Saudi Arabia

* Author to whom correspondence should be addressed; E-mail: aasiri2@kaau.edu.sa

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Abstract: New Schiff bases derived from 2-aminopyridene and 2-aminopyrazine have been synthesized. The UV-Visible spectra of the compounds have been investigated in acetonitrile and toluene. The compounds were in tautomeric equilibrium (enol-imine O–H···N, keto-amine O···H–N forms) in polar and nonpolar solvents. For some derivatives the keto-amine form was observed in both toluene and acetonitrile. ¹H-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 deuteriochloroform.

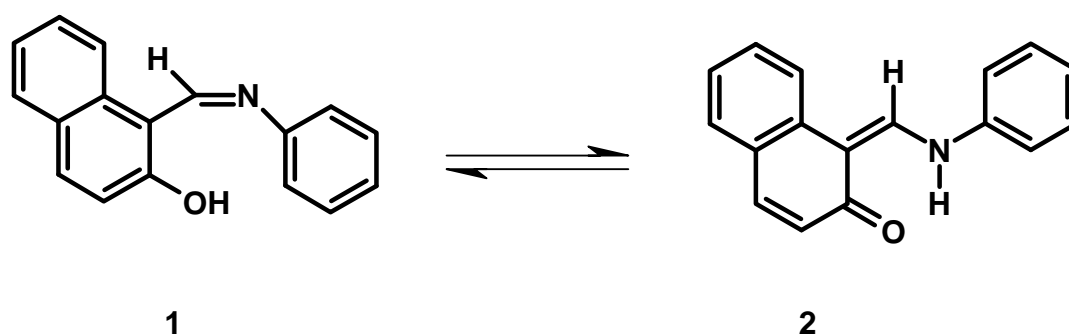
Keywords: Schiff base, Tautomerism, Keto-enamine, Enol-imine, Solvent effect

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 the 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 in 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). 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. In the solid state, salicylideneanilines exist mostly in the enol-imino 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 for the Schiff base formed by 3-haloanilines and 2-hydroxy-1-naphthaldehyde [3]. The Schiff base compounds can be classified according to their photo- 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-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.

Scheme 1. Tautomerism in 2-hydroxy Schiff bases 1.

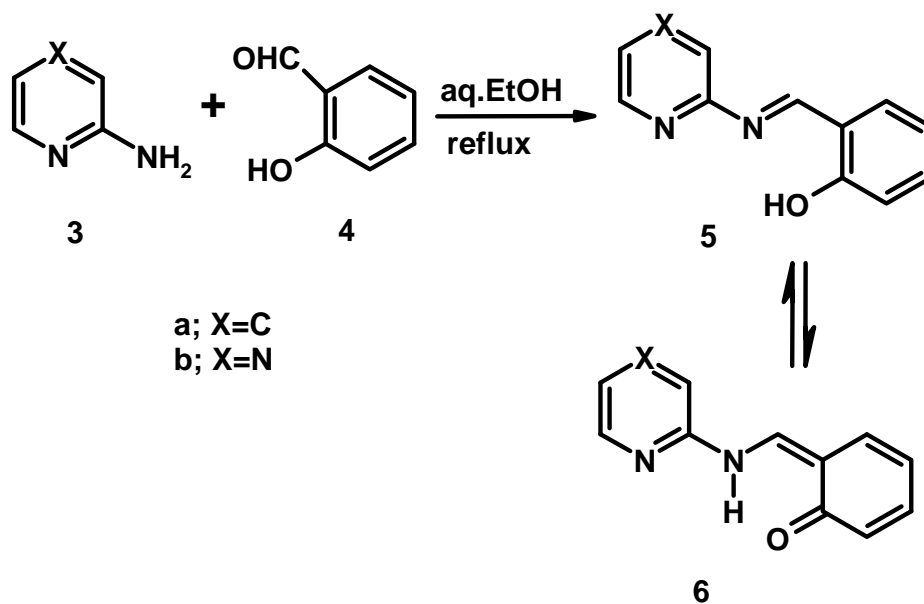


Results and Discussion

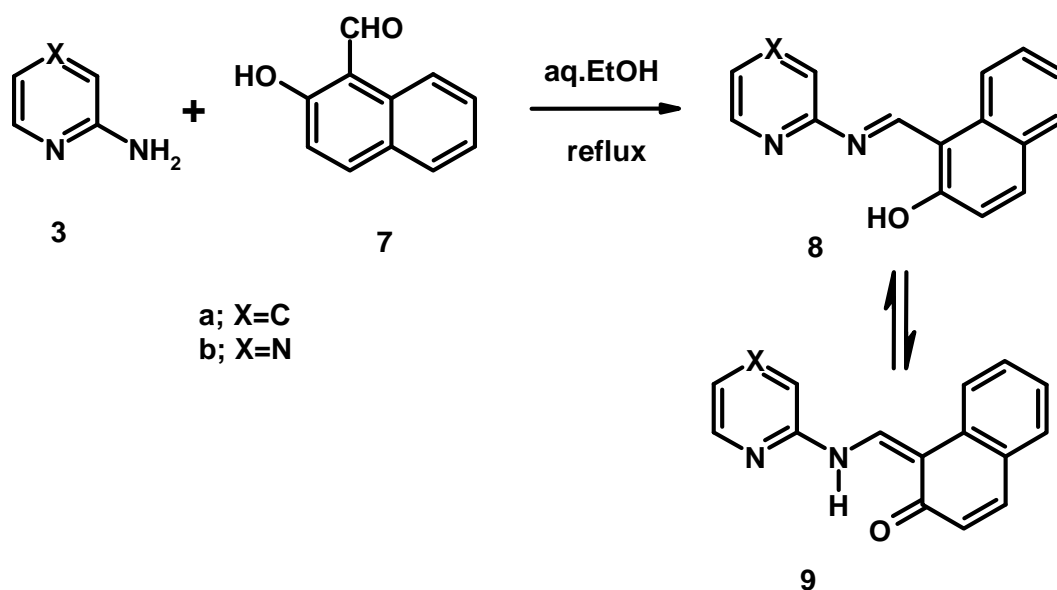
The Schiff bases studied were prepared as shown in Schemes 2 and 3. FT-IR spectra for compounds **5a-b** and **8a-b** showed weak and broad absorption bands in the 3400–3200 cm^{-1} region.

This is interpreted to be a sign of the presence of the enol forms **6a-b** and **8a-b**. The peaks with wave numbers between $1710\text{--}1590\text{ cm}^{-1}$ arise due to stretching vibrations of $\text{C}=\text{N}$ and $\text{C}=\text{O}$ bands. In this region one band was observed for compounds **5a-b** and **8b**, indicating a fully enol form. The FT-IR data indicated that compound **7a** crystallized as a mixture of both enol and keto forms **8a** and **9a**, respectively. The enol form was inferred from the presence of strong absorption in the region of $3400\text{--}3200\text{ cm}^{-1}$. On the other hand, the keto form was suggested by the strong absorption in the $1660\text{--}1700\text{ cm}^{-1}$ region (Scheme 3).

Scheme 2. Synthesis of Schiff bases **5a-b** and **6a-b**.



Scheme 3. Synthesis of Schiff bases **5a-b** and **8a-b**.



From the $^1\text{H-NMR}$ spectra of compounds **5a-b** and **8a-b** it was possible to assign the value of the chemical shifts of the labile hydroxyl group protons. This proton exists in the spectra of all four compounds, which indicated the presence of the enol form of these compounds. On the other hand compound **8a** exists as a mixture of both enol and keto forms.

Electronic absorption spectral properties

The UV-Visible spectra of the compounds were studied in polar acetonitrile and non-polar toluene solvents. The spectra are presented in Figures 1-4 and summarized in Table 1. Some of the compounds studied show one absorption band in the range of less than 400 nm in toluene. The new band (greater than 400 nm) belongs to the keto form of the 2-hydroxy Schiff bases in polar and non-polar solvents [1-2]. The band was observed in some cases at greater than 400 nm in both polar acetonitrile and non-polar toluene solutions. The enol-imine tautomer is dominant only in the polar solutions of acetonitrile, in contrast to the keto-enamine tautomer **6**.

Solvent effects can be explained in term of the capability of solvents to form hydrogen bonding both as proton donors and as proton acceptors, thereby permitting 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 a non-bonding electron pair is no longer available, a solvent effect will not be observed.

Table 1. Electronic Spectral Data of Compounds **5a-b** and **8a-b**.

Compound	Toluene		Acetonitrile	
	λ_{max} (nm)	λ_{max} (nm)	λ_{max} (nm)	Molar coefficient
5a	315	315		5956.4
	435	430		67867.7
	455	455		65277.6
5b	315	220		415219.1
	360	270		289652.8
		310		340425.5
		350		310710.8
8a	285	235		47667.5
	385	270		48247.6
		340		43482.6
8b	345	230		441340.0
	410	400		125780.3

The spectroscopic data suggest that these compounds exist mainly in the enol-imine form in solid state for compounds **5a-b**, and a mixture of enol and the keto form for compounds **8b**. The new compounds prepared in this work showed no photochromic nor thermochromic properties in both solution and solid rigid polymer matrices.

Figure 1. UV-Visible spectra of compound **5a** in toluene.

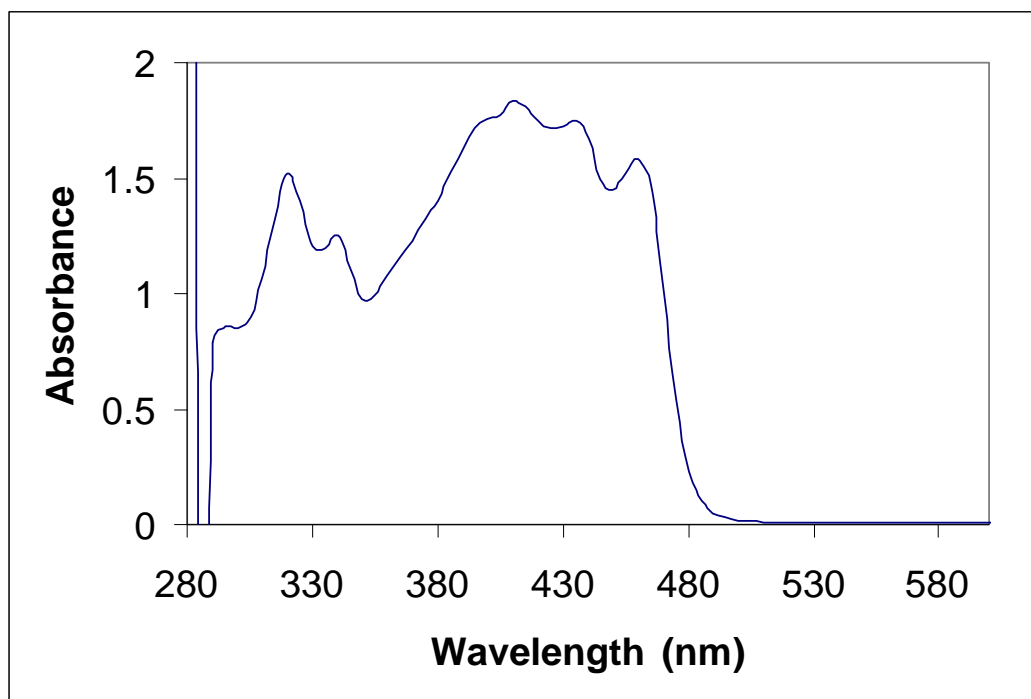


Figure 2. UV-Visible spectra of compound **5b** in toluene.

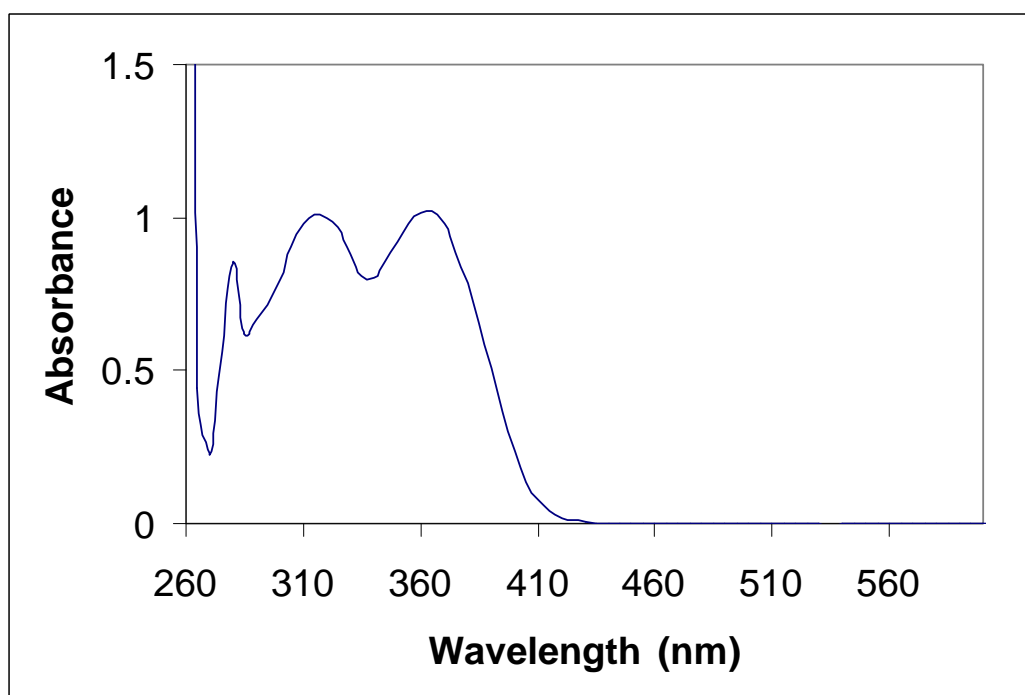
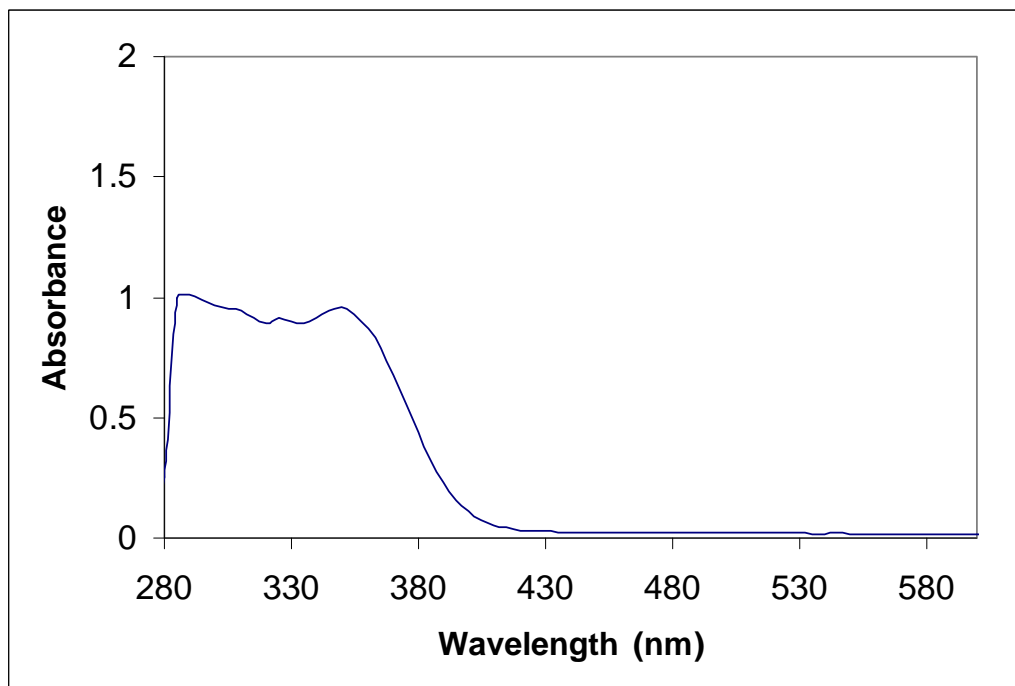
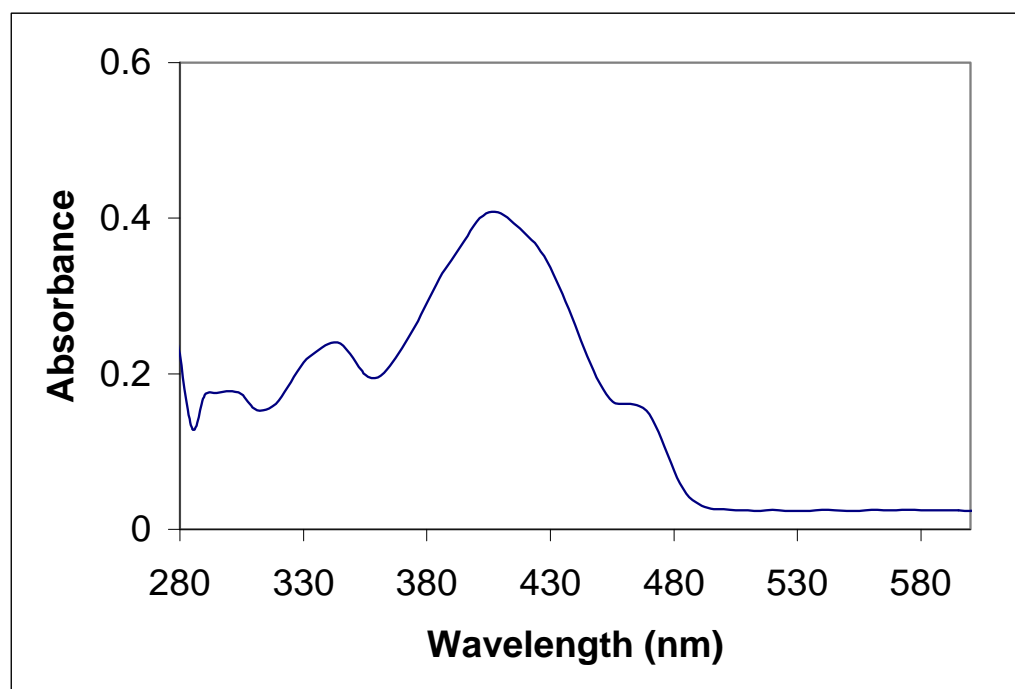


Figure 3. UV-Visible spectra of compound **8a** in toluene.**Figure 4.** UV-Visible spectra of compound **8b** in toluene.

Conclusions

In summary, structural analysis using IR, $^1\text{H-NMR}$ and UV-visible spectroscopy show that the anils prepared from 2-amino substituted pyridine and pyrazine exist mainly in enol forms and mixture of both enol and keto tautomeric form in some instances.

Experimental

General

Melting points were recorded on a Thomas-Hoover capillary melting apparatus without correction. IR spectra were taken as KBr disk on a Nicolet Magna 520 FTIR spectrometer, $^1\text{H-NMR}$ were recorded in CDCl_3 on a Bruker DPX 400 spectrometer using TMS as internal standard. Mass spectra were obtained on a Varian MAT CH5 Spectrometer using EI technique. UV-visible spectra were recorded on a Shimadzu 260 spectrometer for solutions. All reagents and chemicals were obtained from Aldrich Chemical Company (USA) and were used as received unless otherwise noted.

General procedure for preparation of anil derivatives:

A solution of amine (1 mol) in pure ethanol was heated to its boiling temperature, and then aldehyde (1 mol) dissolved in hot ethanol was added to the amine solution and the resulting mixture was then refluxed for 3 hrs. Cooling the mixture, filtering the precipitates and recrystallization from ethanol gave the pure products.

2-(2-Hydroxybenzylidene)aminopyridine: Yield: 64.6 %; mp: 172.9 °C; colour: yellow; IR ν (cm^{-1}); 1612.5 (C=N), 1474.3 (C=C), 1322.9 (C-O) and 1141 (C-N); $^1\text{H-NMR}$ (CDCl_3) δ : 12.92 (s, OH), 8.64 (s, 1H, CH_{olef}) and 8.07-6.92 (m, 8H, CH_{arom}).

2-(2-Hydroxynaphthylidene)aminopyridine: Yield: quantitative; mp: 273.4 °C; colour: yellow; IR ν (cm^{-1}); 1685.5 (C=N), 1495.2 (C=C), 1291.3 (C-O) and 1180.3 (C-N); $^1\text{H-NMR}$ (CDCl_3) δ : 15.44 (s, OH), 9.97 (s, 1H, CH_{olef}), and 8.52-6.93 (m, 10H, CH_{arom}).

2-(2-Hydroxybenzylidene)aminopyrazine: Yield: 33.9 %; mp: 96.6 °C; colour: yellow; IR ν (cm^{-1}); 1594.9 (C=N), 1470 (C=C) and 1191.9 (C-N); $^1\text{H-NMR}$ (CDCl_3) δ : 12.67 (s, OH), 8.80 (s, 1H, CH_{olef}), 8.67 (d, CH_{arom}), 8.51 (s, CH_{arom}), 8.50 (d, CH_{arom}), 7.69 (d, CH_{arom}), 7.27 (dd, CH_{arom}), 6.92 (d, CH_{arom}) and 6.84 (dd, CH_{arom}); Analysis for $\text{C}_{11}\text{H}_9\text{N}_3\text{O}$ (199.21) % Calcd: C: 66.32, H: 4.55, N: 21.09; % Found: C: 66.05, H: 4.43 N: 21.14.

2-(2-Hydroxynaphthylidene)aminopyrazine: Yield: 49.7 %; mp: 177.2°C; colour: orange; IR ν (cm^{-1}); 1607 (C=N), 1507 (C=C), 1298.7 (C-O) and 1141.4 (C-N); $^1\text{H-NMR}$ (CDCl_3) δ : 14.81 (s, OH), 9.31 (s, 1H, CH_{olef}), 8.67 (d, CH_{arom}), 8.55 (d, CH_{arom}), 8.50 (m, 2CH_{arom}), 8.17 (d, CH_{arom}), 7.76 (dd, CH_{arom}), 7.67 (dd, CH_{arom}), 7.59 (d, CH_{arom}) and 6.93 (d, CH_{arom}). Analysis for $\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}$ (249.27) Calcd: C: 72.28; H: 4.45; N: 16.86; % Found: C: 72.28; H: 4.53; N: 16.79.

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*, 25-27.
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-naphthalimine. *J. Chem. Crystallogr.* **1996**, *26*, 23-28.
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*, 359-364.
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. Chem. Soc., Dalton Trans.* **1981**, 559-566.
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*, 197-2007.
6. Antonov, L.; Fabian, M. F.; Nedeltcheva, D.; Kamounah, F. S. Tautomerism of 2-hydroxy-naphthaldehyde Schiff bases, *J. Chem. Soc., Perkin Trans. 2* **2000**, 1173-1179.
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*, 2245-2249.
8. Nagy, P.; Harzfeld, R. Study of enol-keto tautomerism of N-(2-hydroxy-1-naphthylidene)anils. *Spectr. Lett.* **1998**, *31*, 221-232.
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*, 1557-1567.
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-hydroxy-benzaldehydes. *J. Mol. Struct.* **1999**, *475*, 233-240.
11. Rospenk, M.; Król-Starzomska, I.; Filarowski, A.; Koll, A. Proton transfer and self-association of sterically modified Schiff bases. *Chem. Phys.* **2003**, *287*, 113-124.
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**, 329-334.
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*, 2303-2308.
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 naphthalimine 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*, 39-47.
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*, 183-191.
 16. Herzfeld, R.; Nagy, P. Studies of the solvent effect observed in the absorption spectra of certain types of Schiff bases. *Curr. Org. Chem.* **2001**, *5*, 373-394.
 17. Dudek, G. O.; Dudek, E. P. Spectroscopic studies of keto-enol equilibria. VII. N¹⁵ substituted substituted Schiff bases. *J. Am. Chem. Soc.* **1964**, *86*, 4283-4287.
 18. Dudek, G. O.; Dudek, E. P. Spectroscopic studies of keto-enol equilibria. IX. ¹⁵N-substituted anilides. *J. Am. Chem. Soc.* **1966**, *88*, 2407-2412.
 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*, 67-87.
 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*, 57-71.
 21. Salman, S. R.; Saleh, N. A. I. Infrared study of tautomerism in some Schiff bases. *Spectr. Lett.* **1997**, *30*, 1289-1300.
 22. Hadjoudis, E.; Vitterakis, M.; Maustakali-Marridis, I. Photochromism and thermochromism of Schiff bases in the solid state and rigid glasses. *Tetrahedron* **1987**, *43*, 1345-1360.
 23. Kletskii, M. E.; Millov, A. A.; Metelitsa, A. V.; Knyazhansky, M. I. Role of structural flexibility in the fluorescence and photochromism of salicylideneaniline: the general scheme of the phototransformations. *J. Photochem. Photobiol. A: Chem.* **1997**, *110*, 267-270.
 24. 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*, 241-250.

Sample availability: Contact the authors.