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Spectroscopic Study and Semi-empirical Calculations of Tautomeric Forms of Schiff Bases Derived from 2-hydroxy-1-naphthaldehyde and Substituted 2-aminothiophene

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Abstract: New Schiff bases derivative were synthesized by reaction of 2-aminothiophene derivatives and 2-hydroxy-1-naphthaldehyde. The compounds exhibit intra-molecular hydrogen bonding and keto-enamine tautomerism were conformed by using IR and UV-Visible spectral data. The UV-Visible spectra of these compounds have been investigated in different solvents mainly 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. The keto-amine form was observed in both solutions of toluene and acetonitrile for some derivative. 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 solution. The molecular structures of Schiff bases 4a–d enol and 5a–d keto semi-empirical AM1, PM3, MNDO and *ab initio* quantum mechanical (RHF/3–21G* and RHF/6–31G* basis set) was calculated in the gas phase. The relative energy of the keto-enol tautomeric equilibrium in the most methods of calculation in the gas phase is shifted toward the ketone form.

Keywords: schiff base, tautomerism, keto-enamine, enol-imine, solvent effect, semi-empirical, *ab initio*

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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 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). 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 naphthalidines both forms are possible and O–H...N or N–H...O intramolecular hydrogen bonds can occur.^{2,3,14,19,22} 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-naphthaldehyde³ and in solution.²³ 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-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.

Results and Discussion

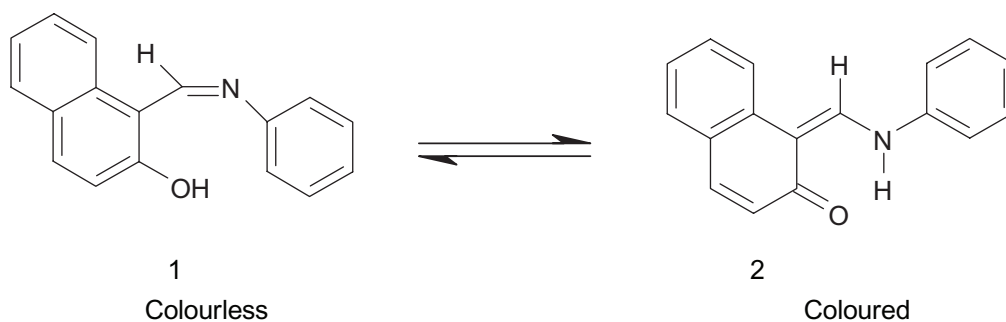
Thiophene based Schiff bases 4a–d were prepared by condensation of 2-Aminothiophene 3 and 2-hydroxy-1-naphthaldehyde as shown in Scheme 2. In the FT-IR spectra of compounds 4a–d, weak and broad absorption bands are observed in the 3400–3200 cm^{-1} region. This is interpreted to be a sign of the enol form 4. The wave numbers between 1710–1590 cm^{-1} arise due to stretching vibrations of C=N and C=O bands. In this region two bands were observed for compounds 4a–d. The FT-IR data indicated that compound 4a crystallized as a mixture of both Enol and ketoforms 4a and 5a respectively. On the other hand compounds 4b came as completely enol form, where compounds 4c–d were crystallized as keto forms 5c–d. The enol form was followed from the presence of weak absorption in the region of 3400–3200 cm^{-1} for O–H band. On the other hand the keto form was followed from the strong absorption in the region of 1660–1700 cm^{-1} for C=O band. (Scheme 2).

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 4a–d 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.

Electronic absorption spectral properties

The UV-Visible spectra of the compounds (4a–4d) were studied in polar acetonitrile and non-polar toluene solvents. The spectra are presented in Figures 1–4 and are summarized in Table 1. Some of the compounds show one absorption bands in the range 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



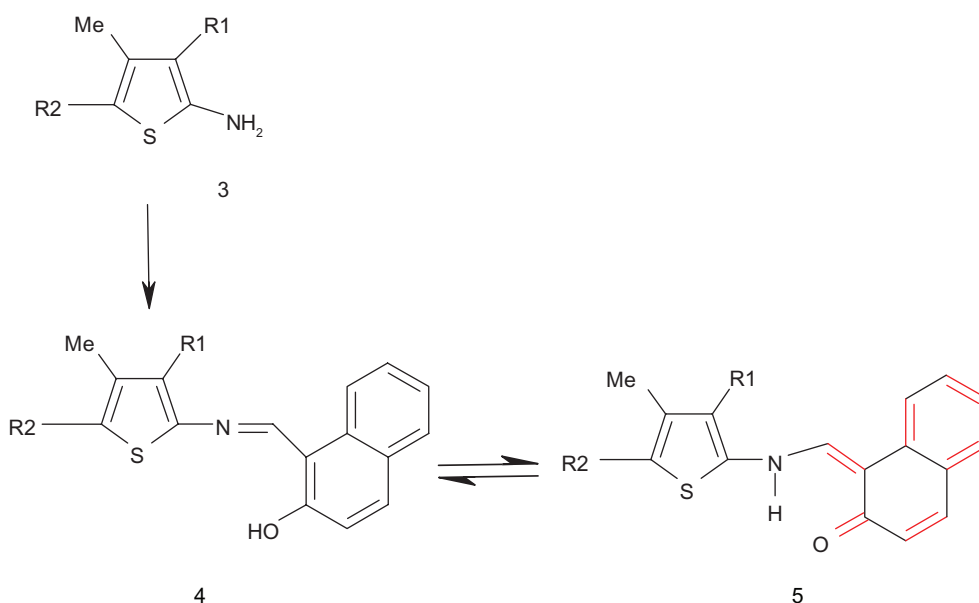
Scheme 1. Tautomerism in 2-hydroxy Schiff bases 1.

solvents. The enol-imine tautomer is dominant only in the polar solutions of acetonitrile.²⁴

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 2). 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.

It is shown in the literature that in Schiff bases the phenyl ring is twisted, and their substituents are



	R1	R2
a;	COOC ₂ H ₅	COCH ₃
b;	COOCH ₃	COCH ₃
c;	CN	COC ₂ H ₅
d;	COOCH ₃	COOC ₂ H ₅

Scheme 2. Synthesis of anils 4a–d.

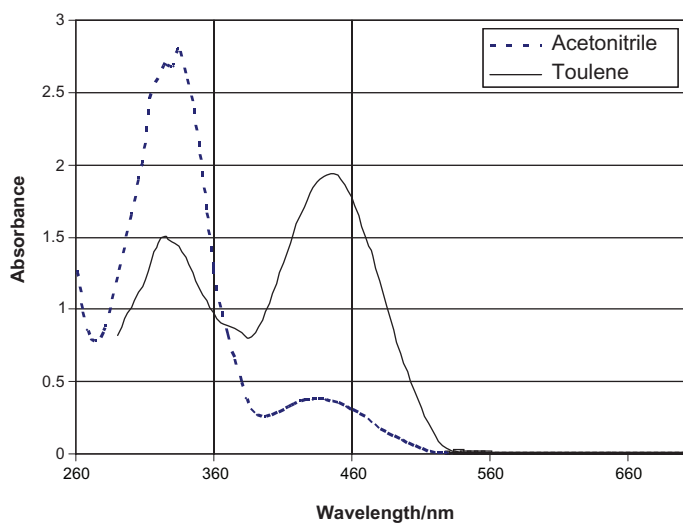


Figure 1. UV visible absorption spectrum of 4a.

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

The investigation of 2-amino substituted thiophene revealed that there is no significant effect of substituents on the thiophene moiety on the keto-enol ratio.

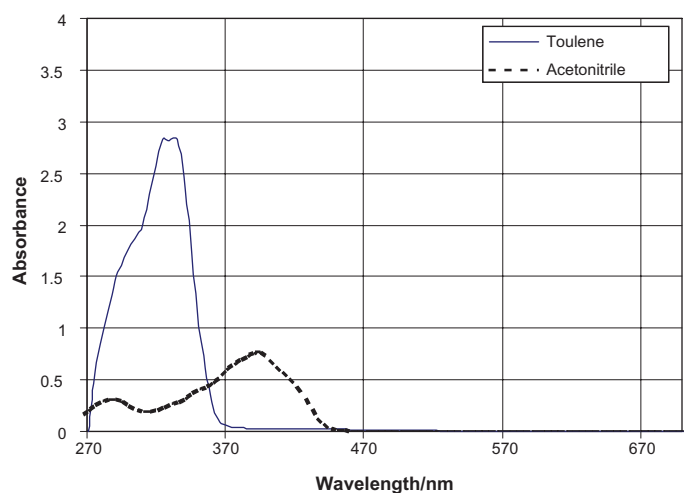


Figure 2. UV visible absorption spectrum of 4b.

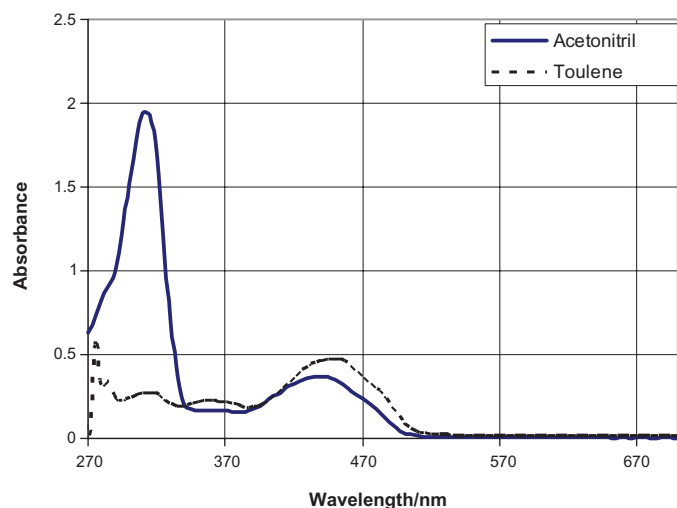


Figure 3. UV visible absorption spectrum of 4c.

The electron withdrawing groups on the thiophene 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 thiophene 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 situation.

Computational methods

Optimized molecular structures calculations for anils derivatives 4a–d keto and 5a–d enol forms in the gas phase were performed using semi-empirical AM1,

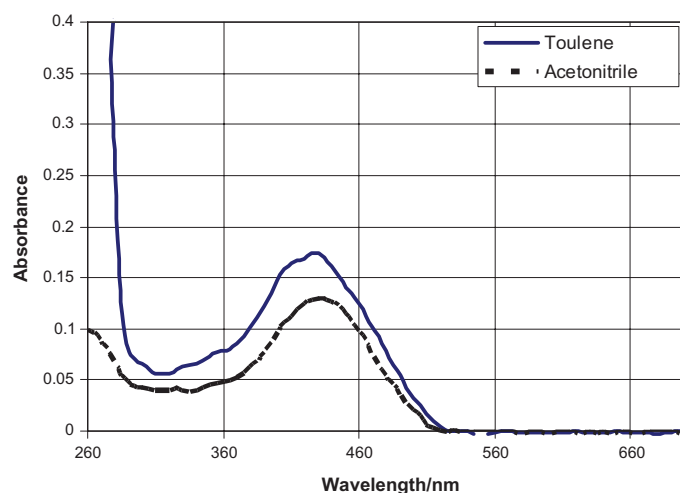


Figure 4. UV visible absorption spectrum of 4d.

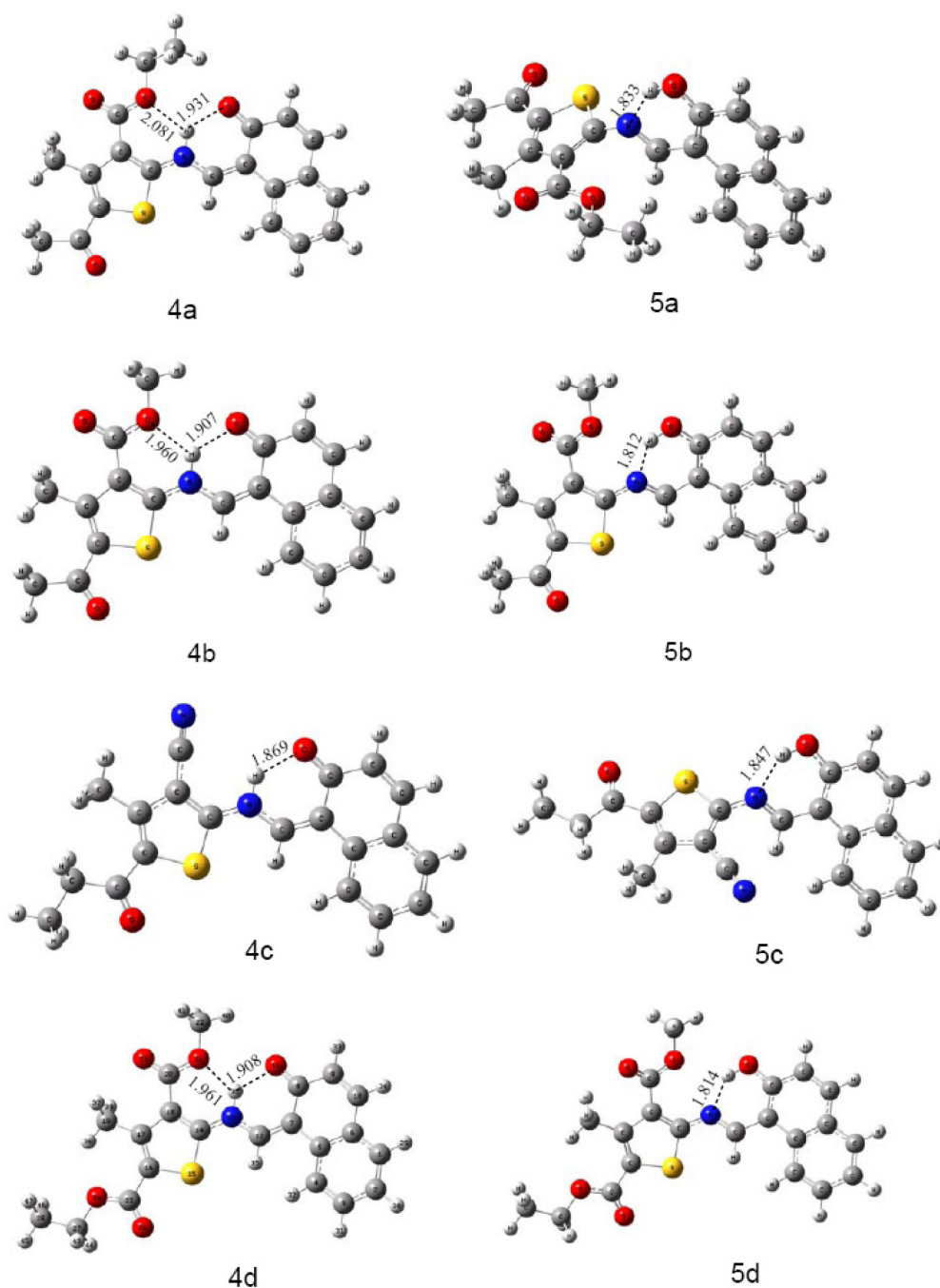


Figure 5. Optimized geometries based on the HF/6-31G* basis set of the studied anils derivatives **4a-d** (Keto form) and **5a-d** (enol form) showing intermolecular H-bond (in A°).

PM3 and MNDO methods and *ab initio* (HF/3-21G* and HF/6-31G* basis set), using the GAUSSIAN 98 program.²⁶ Structures, numbering and the hydrogen bonding geometry of anils derivative for both tautomers are depicted in Figure 5 and the results of Calculation total energies at 3-21G* and 6-31G* (Hartree) and relative stability (in kcal.mol⁻¹) in the

gas phase is given in Table 2. Formation enthalpies (ΔH_f°) and relative stabilities ($\Delta\Delta H_f^\circ$) determined by semi-empirical AM1, PM3, MNDO methods are summarized in Table 3. The data in Table 2 show that the relative energies of tautomers 4a-d and 5a-d obtained in HF/3-21G* and HF/6-31G* in gas phase calculations variations value dependent upon

**Table 1.** The electronic absorption data of the compounds 4a–d.

Compound	Toluene		Acetonitrile		Enol/Keto ratio
	λ_{\max} (nm)	λ_{\max} (nm)	λ_{\max} (nm)	Molar coefficient	
4a	325	225	225	61875.6	70:30
	440	330	330	41953.3	
		445	445	5792.4	
4b	325	220	220	26281.0	40:60
		245	245	19746.1	
		335	335	29919.2	
4c	315	235	235	69781.1	80:20
	360	310	310	48390.1	
	440	445	445	9149.2	
4d	425	215	215	27240.8	0:100
		430	430	13065.2	

nature of the substituent. The results clearly indicate that the ketone is usually more stable in the keto-enol tautomerization for all anils derivatives studies except the tautomer **c** in the case of the HF/6–31G* calculation; the enol form exist predominant, by taking into account the difference between the various structures (see Table 2).

Semiempirical calculation, MNDO and PM3 lead to the same result that the keto form has more heat of formation value than the enol form. The negative sign of the relative stability ($\Delta\Delta H^{\circ}_f$) indicates that the enol form is more stable. The AM1 level calculations provide similar results to that obtained in *ab initio* calculation (HF/6–31G*). Thus, while the AM1 data indicate preference for the keto form in three tautomers (a, b and d), while the tautomer c enol form is predominant (Table 3).

Conclusion

Structural analysis using IR and UV-VIS visible spectroscopy show that the Schiff bases prepared from 2-amino substituted thiophene are exist in both enol and keto tautomeric form. The UV-VIS results

have the keto absorption above 400 nm in polar and non-polar solvents, where as the enol form showed absorption band below 400 nm.

Experimental Section

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, ^1H NMR were recorded in CDCl_3 on a Bruker DPX 400 spectrometer using TMS as internal standard. UV-visible spectra were recorded on a Shimadzu 260 spectrometer for solutions.

General procedure for preparation of anils derivatives

A solution of 1.00 mmol of the appropriate 2-aminothiophene derivatives in pure ethanol was heated to the boiling temperature, and then 1.00 mmol of 2-hydroxy-1-naphthaldehyde was dissolved in hot ethanol, and added to the amine solution then refluxed for 3 hur. Cooling the mixture, filtering the precipitate and recrystallization from ethanol.

Table 2. Calculation total energies at 3–21G* and 6–31G* (Hartree) and relative stability (in kcal mol⁻¹) in the gas phase.

Compounds	3–21G*			6–31G*		
	Enol (a.u)	Keto (a.u)	ΔE Kcal.mol ⁻¹	Enol (a.u)	Keto (a.u)	ΔE Kcal.mol ⁻¹
a	-1549.407491	-1549.423550	10.1	-1557.725030	-1557.730024	3.1
b	-1510.588642	-1510.599595	6.9	-1518.687937	-1518.691837	2.5
c	-1415.248680	-1415.250805	1.3	-1422.816538	-1422.814392	-1.4
d	-1623.876345	-1623.886327	6.3	-1632.602429	-1632.606146	2.3

$\Delta E = E(\text{Enol}) - E(\text{Keto})$.

**Table 3.** Heat of formation (ΔH_f°) and energy difference ($\Delta\Delta H_f^\circ$) in kcal mol⁻¹ of tautomeric form.

Compound	AM1			MNDO			PM3		
	Enol	Keto	$\Delta\Delta H_f^\circ$	Enol	Keto	$\Delta\Delta H_f^\circ$	Enol	Keto	$\Delta\Delta H_f^\circ$
	ΔH_f°	ΔH_f°		ΔH_f°	ΔH_f°		ΔH_f°	ΔH_f°	
a	-67.86	-69.42	1.56	-91.09	-77.21	-13.88	-83.01	-78.07	-4.94
b	-61.98	-63.03	1.05	-85.34	-71.86	-13.48	-78.14	-73.22	-4.92
c	45.78	46.74	-0.96	20.57	35.29	-14.72	33.95	38.39	-4.44
d	-113.11	-114.22	1.11	-132.64	-119.35	-13.29	-119.78	-115.21	-4.57

$$\Delta\Delta H_f = \Delta H_f(\text{Enol}) - \Delta H_f(\text{Keto}).$$

Ethyl 5-acetyl-2-[(1E)-(2-hydroxy-1-naphthyl)met-hylene]amino}-4-methylthiophene-3-carboxylate 4a

Read Crystals, m.p. 87.5 °C, yield 66.74%; IR ν (cm⁻¹): 1707.2 (C=O_{keton}), 1668.5 (C=N), 1570 (C=C), 1227.7 (C-O) and 1080.3 (C-N); ¹H NMR (CDCl₃) δ : 14.56 (s, OH), 9.29 (s, 1H, CH_{olefinic}), 8.35–7.06 (m, 6H_{aromatic}), 4.28 (q, 2H, COOCH₂), 2.66 (s, 3H, Ar-CH₃), 2.16 (s, 3H, COCH₃) and 1.43 (s, 1H, R-CH₃).

Methyl 5-acetyl-2-[(1E)-(2-hydroxy-1-naphthyl)methylene]amino}-4-methylthiophene-3-carboxylate 4b

Red crystals, m.p. 164.8, yield 25.11%; IR ν (cm⁻¹): 3413.7 (OH), 1667.7 (C=O_{keton}), 1586.8 (C=N), 1446.3 (C=C), 1259.4 (C-O) and 1099.9 (C-N); ¹H-NMR (CDCl₃) δ : 14.81 (s, OH), 8.87 (s, 1H, CH_{olefinic}), 8.55 (d, CH_{aromatic}), 8.17 (d, CH_{aromatic}), 7.76 (dd, CH_{aromatic}), 7.67 (dd, CH_{aromatic}), 7.59 (d, CH_{aromatic}), 6.93 (d, CH_{aromatic}), 3.88 (s, 3H, COOMe) and 2.50 (s, 3H Ar-Me).

Ethyl 2-[(1E)-(2-hydroxy-1-naphthyl)methylene]amino}-4-methylthiophene-5-carboxylate-3-carbonitrile 4c

Orange crystals, mp: 202.1 °C, Yield: (58.36%); IR ν (cm⁻¹): 2209.5 (CN), 1452.8 (C=C) and 1267.5 (C-O); ¹H NMR (CDCl₃) δ : 14.81 (s, OH), 9.52 (s, 1H, CH_{olefinic}), 8.55 (d, CH_{aromatic}), 8.17 (d, CH_{aromatic}), 7.76 (dd, CH_{aromatic}), 7.67 (dd, CH_{aromatic}), 7.59 (d, CH_{aromatic}), 6.93 (d, CH_{aromatic}), 4.30 (q, 2H, COOCH₂), 2.50 (s, 3H, Ar-Me) and 1.28 (t, 3H, Me).

4-Ethyl-2-methyl 5-[(1E)-(2-hydroxy-1-naphthyl)methylene]amino}-3-methylthiophene-2,5-dicarboxylate 4d

Orange crystals, mp: 180.6 °C, Yield: (43.68%); IR ν (cm⁻¹): 1705.2 (C=O), 1575.9 (C=N), 1450.5 (C=C), 1248.4 (C-O)

and 1099.8 (C-N); ¹H NMR (CDCl₃) δ : 14.81 (s, OH), 8.87 (s, 1H, CH_{olefinic}), 8.55 (d, CH_{aromatic}), 8.17 (d, CH_{aromatic}), 7.76 (dd, CH_{aromatic}), 7.67 (dd, CH_{aromatic}), 7.59 (d, CH_{aromatic}), 6.93 (d, CH_{aromatic}), 4.31 (q, 2H, COOCH₂), 3.87 (s, 3H, COOMe), 2.52 (s, 3H, Ar-Me), and 1.37 (t, 3H, Me).

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Disclosures

This manuscript has been read and approved by all authors. This paper is unique and is not under consideration by any other publication and has not been published elsewhere. The authors report no conflicts of interest.

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