Keto-Enol Tautomerism of Schiff-bases derived from 2-Hydroxy naphthaldehyde and substituted aniline with LSR $Pr(fod)_3$

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Abstract: A series of naphthylidene substituted anilines (2-hydroxy-1-naphthylidene aniline, para-Chloroaniline, 3,4,5-trimethoxyaniline, o,m and p-toluidine) were synthesized and were studied with the lanthanide shift reagent $Pr(fod)_3$ in cyclohexane. The spectra of the compounds show a decrease in the major band (enol) and increase in the minor keto band with observance of a nice isobestic point as the amount of $Pr(fod)_3$ increases which causes in a change in the tautomeric equilibrium. K_T values were calculated at normal temperature and at different temperatures. The thermodynamic parameters were calculated ΔH^o, ΔS^o, ΔG^o, values were all negative. The results obtained in this research indicate that $Pr(fod)_3$ causes a shift in the tautomeric process towards the keto form, several experiments were performed to confirm the above results.

Keywords: keto-enol tautomerism, Schiff-bases, $Pr(fod)_3$.

Introduction

Schiff-bases that contain hydroxyl group in their ortho position to the aldehyde group are characterized by the precence of two forms which are in equilibrium , the keto and enol forms, their ratio depend on the conditions. Schiff-bases derived from 2-OH-1-naphthaldehyde has been studied extensively from the experimental and theoretical point of view by different spectroscopic methods[1-5]. The spectra of different schiff-bases have been studied in polar and nonpolar solvents and mixed solvents, it was established that the tautomeric equilibrium in 2-hydroxy-1-naphthylideneaniline schiff-bases depend on the polarity of the solvent, the acidity of the medium, the temperature and the strength of the hydrogen bond[6-8]. Earlier[9] we have repoted the effect of the shift reagent $Eu(fod)_3$ on the cis-trans isomerization of benzylideneaniline and their substituents. Also we reported the stability constant of charge transfer complexes of a number of salicylideneanilines with $Eu(fod)_3$ in different solvents through UV-spectroscopy studies[10-12] and theoretical studies[13]. Later we reported the effect of $Pr(fod)_3$ on the tautomeric equilibrium of 2-hydroxy-1-naphthylideneaniline (HNA) by UV-spectroscopy. In this work we would like to present the effect of $Pr(fod)_3$ on the tautomeric equilibrium of Schiff-bases derived from 2-hydroxy-naphthaldehyde and substituted anilines which have the following structures.
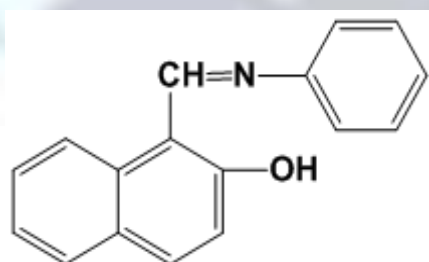
1- 2-hydroxy-1-naphthylideneaniline[*(14)] ....(HNA)
2- 2-hydroxy-1-naphthylidene-p-Chloro aniline.........................(HN-p-ClA)
3- 2-hydroxy-1-naphthylidene-(3,4,5)trimethoxy aniline..........(HN-tmA)
4- 2-hydroxy-1-naphthylidene-o-toluidine.............................(HN-o-T)
5- 2-hydroxy-1-naphthylidene-m-toluidine............................(HN-m-T)
6- 2-hydroxy-1-naphthylidene-p-toluidine...............................(HN-p-T)

*= The tautomerism of the Schiff –bases (HNA) have been reported earlier and have been placed here for the sake of comparison.

EXPERIMENTAL

1- Materials:

2-hydroxy-1-naphthaldehyde, p-Cl-aniline, 3,4,5-trimethoxyaniline, o,m,p-toluidine were purchased from BDH, Laboratory reagent and were distilled at their boiling points before use. Lanthanide shift reagent $Pr(fod)_3$ 99.9% was purchased from Flukaand was used with out purification. Cyclohexane was purified by distillation at its boiling point.

2- Preparation of the Schiff-bases of 2-OH- naphthylidene substituted anilines:

10^{-3} M of 2-hydroxy naphthaldehyde was dissolved in absolute ethanol (10 ml), to this solution 10^{-3} M of each aniline (freshly distilled) in absolute ethanol was added dropwise with continuous stirring. The mixtures were refluxed for 2 hr then were left to cool, the precipitate was separated and dried then recrystallized from ethanol/H_2O to yield crystals with m.p. , IR and NMR results given in Table-1.

Table-1: Physical and spectroscopic data for the Schiff-bases.

S.B	m.p C°	IR			NMR(ppm)		
		υ(O-H) cm^{-1}	υ(C=N) cm^{-1}	υ(C-O) cm^{-1}	HC=N	O-H	N-H
HN-A	90-92	3444	1621	1330	8.1	9.3	15.5
HN-p-Cl A	153-154	3447	1618	1331	8.15	9.37	15.5
HN-t-m A	103-104	3437	1635	1329	8.15	9.3	15.5
HN-o-T	116-117	3443	1621	1324-1346	8.1	9.33	15.8
HN-m-T	96-97	3442	1626	1311-1353	....	....	......
HN-p-T	134-135	3460	1632	1326	....	....	......

3- Preparation of solutions:

Stock solutions of $(5*10^{-5})$M of the Schiff-bases and $(5*10^{-4})$M of $Pr(fod)_3$ were prepared in cyclohexane. 2ml of the Schiff-bases solutiont was placed in a silica cell $(1*1*3)$cm and 2ml of the solvent was placed in the blank cell. Several additions (100-μl) of $Pr(fod)_3$ were performed on the sample cell and the blank cell. The absorption spectra after each addition at room temperature and at higher temperatures (10-50˚) were recorded on shimadzu UV-1800 spectrophotometer equipped with a water bath SB-11 EYRLNTT.

RESULTS & DISCUSSIONS

The UV-spectra of $(5*10^{-5})$M of the Schiff-bases in cyclohexane generally show two bands the first one (strong band) which is located tothe low wave length is related to the enol from, the second which is located at the high wave length is a weak band and is attributed to the keto form.

The non polar solvent cyclohexane has been chosen in this study for the following reasons:

1. The %keto in the absence of $Pr(fod)_3$ was too small ,so that the main band considered in this study is attributed to the enol form.
2. In order to observe the effect of $Pr(fod)_3$ in the absence of a polar solvent, since the polar solvents compet with the shift reagent i-e to avoid the factor of polarity.
3. It is known that polar solvents effect the tautomeric equilibrium and result in an increase in the keto form even thought no other factor is present.

Addition of the LSR $Pr(fod)_3$ ($5*10^{-4}$M) in cyclohexane to the solutions of the mentionel schiff-bases resulted in a decrease in the enol band accompanied by an increase in the keto band and the observance of an isobestic point (IP) Fig-1.
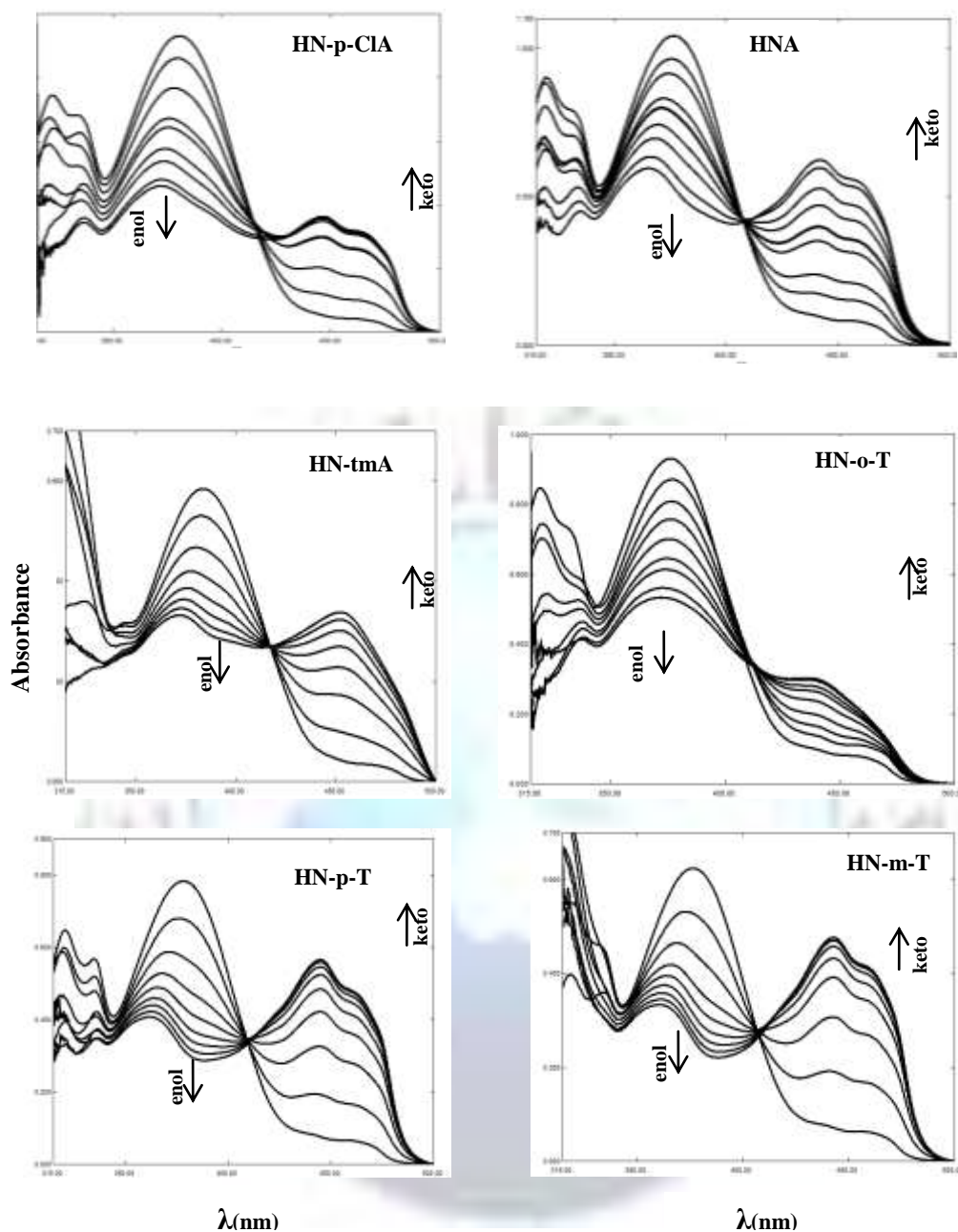

Fig-1: The UV-spectra of Schiff-bases with $Pr(fod)_3$ in cyclohexane at normal temperature

The spectroscopic data obtained from the above spectra including the wave lengths of the keto and enol bands, the absorbance and λ_{max} at the isobestic points and the %keto aresummarized in Table-2.

Table-2: The spectroscopic data and %keto for the Schiff-bases in cyclohexane at normal temperature

S.B	$\lambda_{(max)nm}$		IP		%keto		
	enol	keto	$\lambda_{(nm)}$	Abs	(a)	(b)	Δ%
HN-A	376	441	410	0.417	8.4	51.15	42.8
HN-p-Cl A	379	446	418	0.304	5.1	44	38.9
HN-t-m A	383	452	422	0.278	6.4	52	45.6
HN-o-T	376	435	413	0.331	9.9	36.2	26.3
HN-m-T	376	443	407	0.273	10.5	58.9	48.4
HN-p-T	378	445	410	0.337	8.7	58.13	49.4

a- %keto in the absence of $Pr(fod)_3$.
b- %keto in the presence of $Pr(fod)_3$.
Δ%= the difference between (b-a).

From Table-2 it can be seen that the wave length of the enol form is between (383-376)nm, the keto bands λ values were between (435-452)nm .

The %keto in the absence of $Pr(fod)_3$ was between (5.1-10.5%), however after addition of $Pr(fod)_3$ the %keto values were between (36.2-58.9%). Δ% values are high (38.9-49.39) (except for(HN-o-T)) which indicates that the effect of addition $Pr(fod)_3$ in cyclohexane on the tautomeric equilibrium is great under these conditions and that addition of $Pr(fod)_3$ accelerates the process enol $\rightarrow$ keto through the migration of the hydroxyl proton towards the nitrogen.

The average K_T values (=[keto]/[enol]) were calculated and are tabutated in Table-3.

Table-3: $K_T$values for the Schiff-bases with $Pr(fod)_3$ in cyclohexane at normal temperature

S.B	HN-A	HN-p-ClA	HN-tmA	HN-o-T	HN-m-T	HN-p-T
Ave. K_T	0.7418	0.986	0.985	0.788	1.298	1.304

From Table-3 it can be seen that K_T values are very close for compounds (HN-p-ClA) ana (HN-tmA), but they are higher for (HN-m-T) and (HN-p-T). Also it can be seen that the electron donating group in the p-position prefers the keto form as in (HN-p-T) which can be seen clearly from the high value of (K_T= 1.304) which means that electron donating groups increase the electron density around the CH=N, which accelerates the process of tautomerization.

However the electron with drawing group (HN-p-ClA) prefers the enol form which can be seen from its K_T value (0.986) , (HN-o-T) has low K_T value may be due to the steric effect of the CH_3 group in the ortho position. Thus it can be seen for the above results that substitutents has an effect on the tautomeric equilibrium . The UV-spectra for the Schiff-bases in cyclohexane were studied after additions of $Pr(fod)_3$ at different temperatures (10-50C°) (see Fig-2).

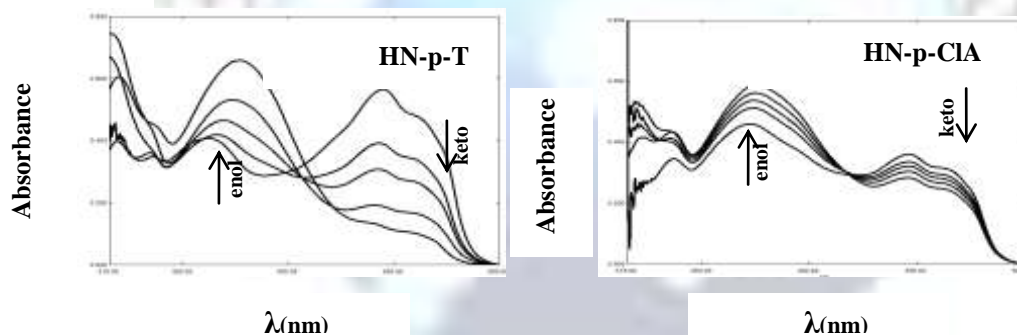**Fig-2: The UV-spectra of Schiff-bases with $Pr(fod)_3$in cyclohexane at different temperatures(10,20,30,40,50C°)**

From these figures it can be seen that increasing the temperature result in a decrease in the absorbance of the keto band and an increase in the enol band, and the isobestic points were observed. K_T values are calculated at the different temperatures, and plots were performed between $\ln K_T$ vs $1/T$ (Fig-3), from the slope ΔH^o values were calculated, ΔS^o values were obtained from the intercept. ΔG^o values were calculated (ΔG^o= -$RT\ln K_T$). The thermodynamic parameters for the Schiff-bases are give in Table-4.
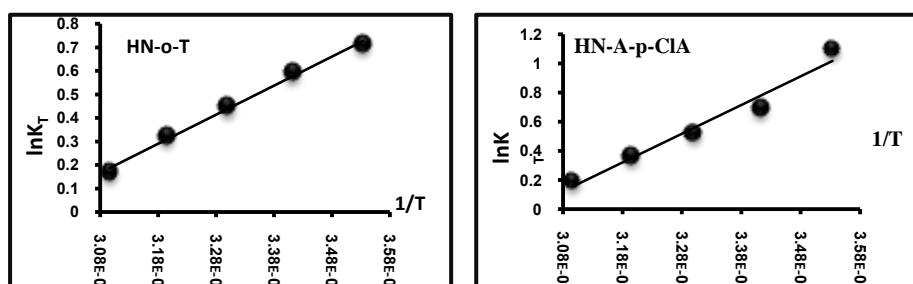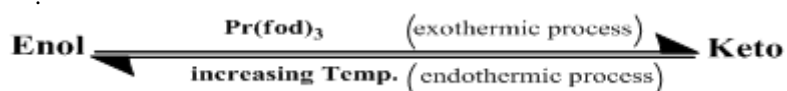

Fig-3: plot of $\ln K_T$ vs $1/T$ for Schiff-bases

Table-4: The thermodynamic values for Schiff-bases studied with Pr(fod)$_3$ in cyclohexane

S.B	ΔH^o (KJ/mol)	ΔS^o (J/mol. K^O)	ΔG^o (KJ/mol)
HN-A	-23.34	-77.29	0.054
HN-p-Cl A	-16.37	-49.41	-1.403
HN-t m A	-46.82	-157.85	-1.01
HN-o-T	-11.42	-35.08	-0.789
HN-m-T	-26.95	-85.96	-0.904
HN-p-T	-40.14	-130.41	-0.626

It can be seen from(Table-4) that ΔH^o values are all –ve which indicate that the tautomeric equilibrium is exothermic, whilst the reverse processwhich is observed on heating the samples (keto $\rightarrow$ enol) is endothermic, this is in consistence with the earlier researches[14] .

$$\text{Enol} \underset{\text{increasing Temp.} \left(\text{endothermic process}\right)}{\overset{\text{Pr(fod)}_3 \quad \left(\text{exothermic process}\right)}{\rightleftharpoons}} \text{Keto}$$

ΔS^o values all were negative which means that the products are less ordered than the reactants .ΔG^o were all negative except for (HNA) which show a small positive values, this indicates that the tautomerism occurs simultaneously in the presense of Pr(fod)$_3$ .From the above results it can be seen that addition of Pr(fod)$_3$ to the Schiff-bases resulted in a change in the tautomeric equilibrium, which is confirmed through the following points.

1- Addition of Pr(fod)$_3$ to the Schiff-bases does not results in observance of a new band like those observed on studying charge transfer complexes, i.e no indication of complex formation.
2- Increasing the temperature results in a decrease in the keto band and increase in the enol band i-e the compound tries to return back to its original form and no change was observed in the shape of the bands but only a change in their absorbance which could be attributed to the decrease in the polarity of the solvent as a result of the increase in the temperature, a situation which prefers the less polar form(the enol).
3- An experiment was performed for (HNA) in which Pr(fod)$_3$ was exchanged by the solvent cyclohexane in order to observe the effect of the solvent alone. The result was a decrease in both the keto and enol bands but the decrease in the enol band was greater, this experiment confirm the effect of Pr(fod)$_3$ on the process of tautomerization.
4- Other experiment was performed in which acetic acid (Fig-4) and formic acid were added to HNA in two separate experiments instead of Pr(fod)$_3$. The results show adecrease in the enol band and increase in the keto band similar to that observed on adding Pr(fod)$_3$ but the effect is weaker, this experiment may explain that the acidity of Pr(fod)$_3$ is responsible for the tautomerism in a way similar to those two acids.
5- Another experiment was performed using Eu(fod)$_3$instead of Pr(fod)$_3$, similar results were obtained as with Pr(fod)$_3$ (Fig-5). From this experiment it can be seen that the metal in the LSR dose not play a role in the tautomerism process and the effect is attributed to the acidic hydrogen in the shift reagent. The above results lead to a conclusion that the effect of LSR on the tautomeric process is attributed to the acidity of Pr(fod)$_3$ especially with the presence of electron with drawing flourines which increase its acidity.
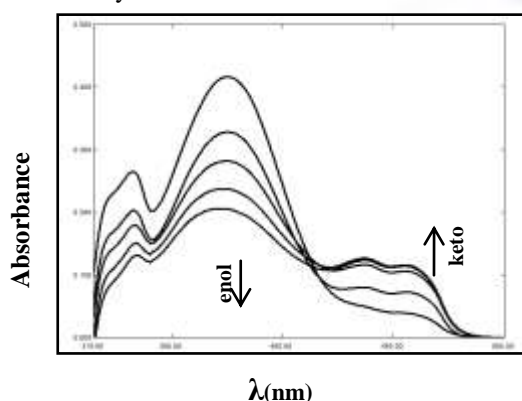

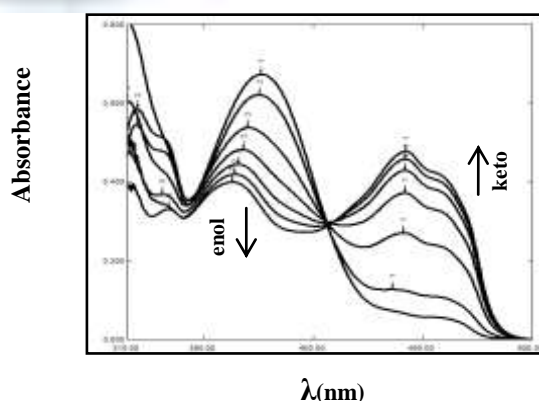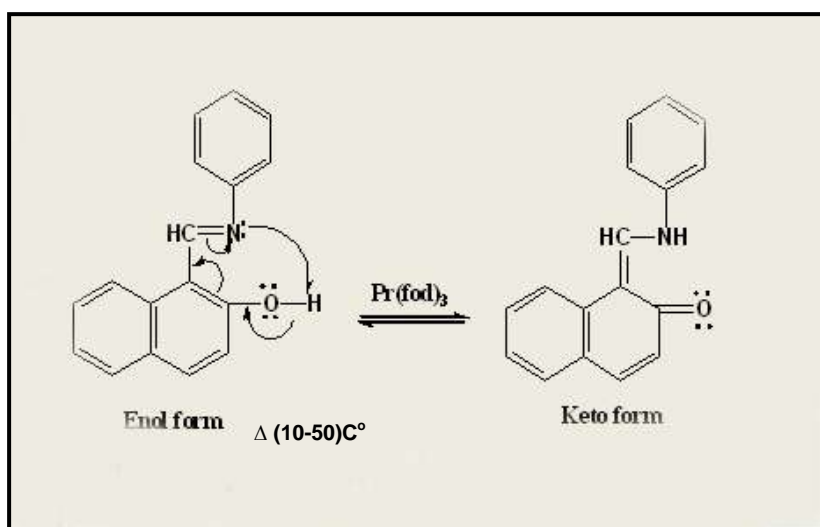**Fig-4: The uv-spectra of HNA on adding acetic acid in cyclohexane**

Fig-5: The uv-spectra of HNA on adding Eu(fod)$_3$in cyclohexane

Finally the process of tautomerization with $Pr(fod)_3$ can be represented by the following scheme-1.

Scheme-1: The process of tautomerization process of HNA in the presence of $Pr(fod)_3$

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