Solvent Effect On Tautomerism In Some
2-Hydroxynaphthilidene-4-/methoxyaniline
Schiff Base

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The UV-Visible spectra of 2-hydroxynaphthilidene-4′-methoxyaniline Schiff base were recorded in sixteen solvents of different physical properties. It was observed that molar extinction coefficient of keto form is decreased in the following order: protic>polar(aprotic)>nonpolar. This may suggest that proton donor-acceptor behaviour of solvents play a significant role in increasing the keto tautomeric percentage through hydrogen bonding. The molar extinction coefficients of enol and keto forms were also correlated with some solvent parameters such as proton acceptor number (ANG), donor number (DN), dielectric constant (C) and dipole moment (μ) of the solvents.

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INTRODUCTION

Several studies have been published concerning the influence of factors affecting the tautomeration of some Schiff bases derived from the reaction of salicylaldehyde and 2-hydroxynaphthaldehyde with aniline such as temperature, substituents and solvent polarity [1-7]. The evidence for the existence of the keto-enol tautomerism in above kind of Schiff bases was proved through the study of their UV-Visible and NMR spectra [8-12]. Generally three UV absorption bands were characterized in the spectra of substituted naphthilidenes aniline bases, the first band occurred in the region 360-395 nm which belong to the enol form (I), while the other two bands occurred in the region 400-500 nm which belong to the keto form II [13-17].
Previous investigations have shown that the keto-tautomer bands in \( p \)-substituted naphthilidene Schiff base have the highest extinction coefficient in methanol [7]. These findings and the lack of information concerning the solvent effect on the keto-enol equilibrium in this new kind of Schiff bases promoted our interest to study the behaviour of 2-hydroxy naphthilidene-4'-methoxyaniline in different solvents, protic, aprotic and nonpolar, to verify the effect of polarity of the solvents on this equilibrium. We have also investigated the correlations of the molar extinction coefficients of both enol and keto forms in sixteen solvents with some solvents parameters such as Gutmann proton acceptor number (AN\(_G\)), donor number (DN\(_G\)), dielectric constant (\( \varepsilon \)) and dipole moment (\( \mu \)) of the solvents to follow the behaviour of the solvent effect on tautomerism.

**EXPERIMENTAL**

This compound was prepared through condensation of 2-hydroxynaphthaldehyde with \( p \)-methoxyaniline as previously described [7]. All solvents used were spectral grade solution. The UV spectra were run with Shimatzu UV-visible recorder spectrophotometer UV-160 using an optimum concentrations of \( 5 \times 10^{-5} \) mole in a quartz cell of 1 cm path length.

**RESULTS AND DISCUSSION**

The 2-hydroxynaphthilidene-4'-methoxyaniline was used as a probe for studying solvent effect (III).
III

Table (1) list the main UV-visible absorption bands with their molar extinction coefficient ($\xi$). Table (2-4) show the correlations of molar extinction coefficients of enol and keto bands with proton acceptor number* ($AN^G$), donor number ($DN^G$) [18], dielectric constant ($C$) and dipole moment ($\mu$) of the solvent and their function were illustrated in figures (1-4).

It was assumed that the band at 360-395 nm belongs to the enol form, while the bands above 400 nm belong to the keto form [7,14]. It is evident from the above data that:

1- The correlation coefficient between proton acceptor number, $AN^G$, of the solvents and the molar extinction coefficient of the enol band 1 was fair (ca. 0.82) while a good value was obtained for keto band 2 (ca. 0.93). The correlation coefficient values for proton donor, $DN^G$, were poor for the two bands 1&2 (Table 2) ranging from 0.4760-0.5149.

* To differentiate them from normalized proton acceptor and donor number, $AN^N$ and $DN^N$. 
Fig.: (1): Acceptor number against molar extinction coefficient of the enol band 1.

Fig.: (2): Acceptor number against molar extinction coefficient of the keto band 2.
Fig.: (3): Dielectric constant against molar extinction coefficient of all bands.

Fig.: (4): Dielectric constant against molar extinction coefficient of enol and keto bands.
2- The slope of the regression line is negative for the enol band 1 (Fig 1.), and positive for the keto bands 2&3 (Fig.2) These data provide an evidence that band 1 belongs to enol form, while bands 2&3 belong to the keto form. Table (1) also showed that the values of the extinction coefficients of the keto form (band 2) decreased through protic, polar (aprotic) and non polar solvent respectively and that was clearly evident in Figures (3 & 4 ) through the effect of the dielectric constant or dipole moment of the solvent, because these solvent parameters declare the effect of the solvent polarity and polarizability respectively on the molecular conformations during solvation mechanism.

These results may suggest that molecular structure of this kind of Schiff base prefers the keto form in most protic solvents. A previous proton NMR data for similar series showed that the tautomeric equilibrium favors the keto-amine or nonaromatic form in polar solvents but shifts to the hydroxy-imine form in nonpolar solvents [11].

It seems that hydrogen bonding between the solvent and the hydroxyl group of the molecule plays a major role in enhancing the keto form , further work is in progress to verify this aspect and this is currently under investigation.
REFERENCES


