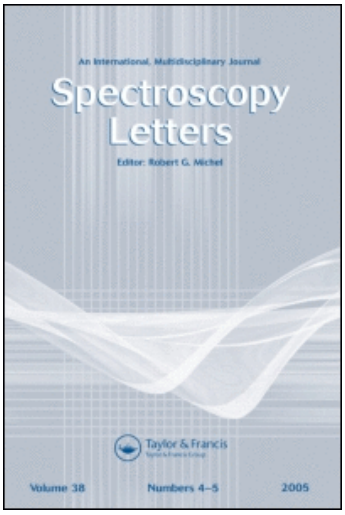

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Study of Enol-Keto Tautomerism of N-(2-Hydroxy-1-Naphthylidene)anils

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STUDY OF ENOL–KETO TAUTOMERISM OF N–(2–HYDROXY–1–NAPHTHYLIDENE)ANILS

Key words: Schiff bases, tautomerism, substitution effect, UV-visible spectroscopy

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ABSTRACT

The enol-keto tautomerism of N-(2-hydroxy-1-naphthylidene)anilines was studied. In response to the action of salts (e.g. $CaCl_2$), in ethanolic solution the equilibrium is shifted extensively in the direction of the keto form; this allows determination of the concentration of the keto form and of the equilibrium constant of the process. In accordance with the Hammett equation, the equilibrium constant varies as a function of the constants σ of the substituents on the aniline ring.

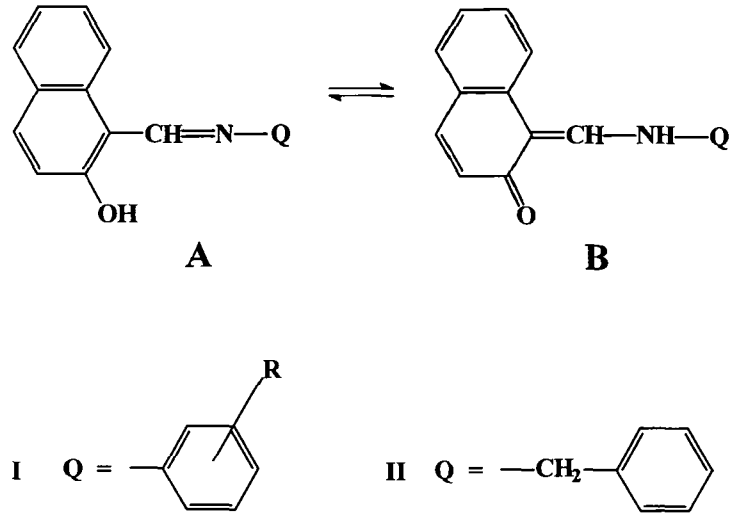
INTRODUCTION

It has long been known that a characteristic solvent effect can be observed in the absorption spectra of Schiff bases containing an *o*- or *p*-OH group on the aromatic aldehyde component; this effect is primarily induced by protic solvents[1,2]. There is a very extensive literature on investigations of this phenomenon[3-10], and it is now generally accepted that the solvent dependence to be observed in the spectrum may be interpreted in terms of an enol $\rightleftharpoons$ keto tautomeric equilibrium (Scheme 1), though the possibility of formation of a zwitterion structure cannot be excluded[11-13].

Direct quantitative study of the equilibrium by means of spectroscopy is not possible, as the molar absorbances of the tautomers are not known. NMR spectral data on the quantity of the keto form have been reported for the N-(2-hydroxy-1-naphthylidene)anilines[3,14-17]. In order to determine the quantity of the keto form, we have made use of the observation that in ethanolic solution, in response to the action of various salts, and particularly $CaCl_2$, the equilibrium is shifted to such a degree in the direction of the keto form that the limiting value of the 440 nm band (ascribed to the keto form) can be extrapolated. The present article compares the results obtained in this way with the literature data resulting from NMR spectral studies.

EXPERIMENTAL

The investigated compounds were prepared by the condensation of 2-hydroxy-1-naphthaldehyde with substituted anilines or



Scheme 1

benzylamine. After recrystallization, their purities were checked by means of m.p. measurement, and the absorbances in the visible and ultraviolet ranges were examined in various solvents. Measurements were made with a VSU-2P spectrophotometer at 25 °C. The applied solvents and the $CaCl_2$ were of spectroscopic purity and were free of water.

RESULT AND DISCUSSION

In solution in various organic solvents, in the absence or in the presence of $CaCl_2$, the absorption spectra of the investigated compounds exhibit well-defined isosbestic points, in accordance with an equilibrium of type A $\rightleftharpoons$ B (Figs 1 and 2).

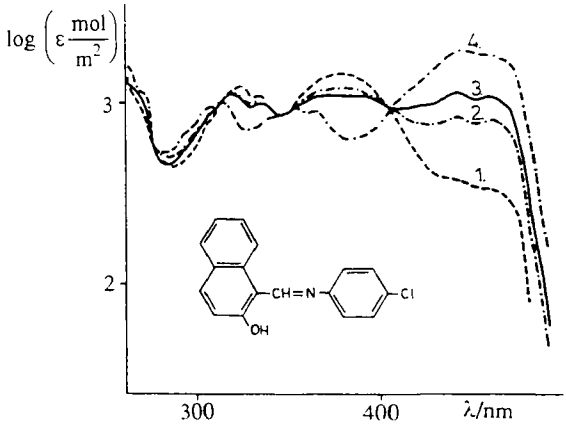


Fig. 1 Absorption spectra of N-(2-hydroxy-1-naphthylidene)-4-chloroaniline in (1) ethanol-hexane (1:9), (2) ethanol-hexane (1:1), (3) absolute ethanol, and (4) 0.9 mol dm^{-3} $CaCl_2$ in absolute ethanol.

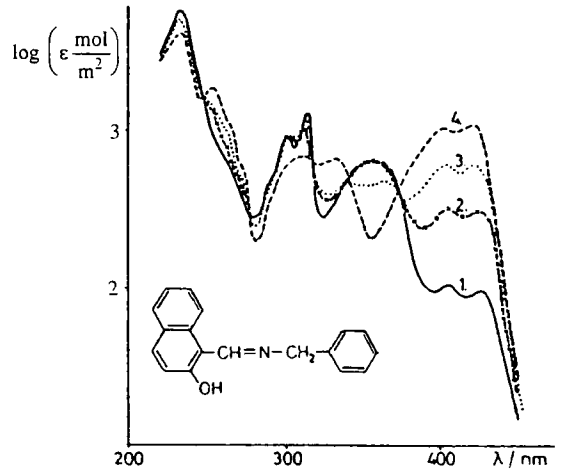


Fig. 2 Absorption spectra of N-(2-hydroxy-1-naphthylidene)-benzylamine in (1) cyclohexane, (2) ethanol-cyclohexane (1:49), (3) ethanol-cyclohexane (1:9), and (4) 0.9 mol dm^{-3} $CaCl_2$ in absolute ethanol.

The individual bands in the spectra can generally be ascribed either to form A or to form B, as their intensities vary in opposite ways in accordance with the position of the equilibrium. The band at 400-460 nm, for example, can be ascribed to the keto form; the enol form has no appreciable absorbance in this region. Using the method of Berstein[18], we confirmed this from the data of the absorption spectra recorded in the various solvents[19].

Figures 1 and 2 reveal that, in response to the action of $CaCl_2$, the equilibrium is shifted significantly in the direction of the keto form. If the $CaCl_2$ concentration is increased, the intensity of the 440 nm band tends towards the limiting value. This is illustrated as an example in Fig. 3.

The curves can be described well by the relation

$$\Delta\varepsilon = \frac{[\text{salt}]}{a + b[\text{salt}]} \tag{1}$$

This can be rewritten as

$$\frac{1}{\Delta\varepsilon} = \frac{a}{[\text{salt}]} + b \tag{2}$$

and Fig. 4 demonstrates that a plot of $\frac{1}{\Delta\varepsilon}$ versus $\frac{1}{[\text{salt}]}$ for the experimental data is linear.

The intercepts of these linear plots on the ordinate (obtained graphically or by the method of least squares) give the value of *b*, i.e. the limiting value of $\frac{1}{\Delta\varepsilon}$. From this, the molar absorption coefficient

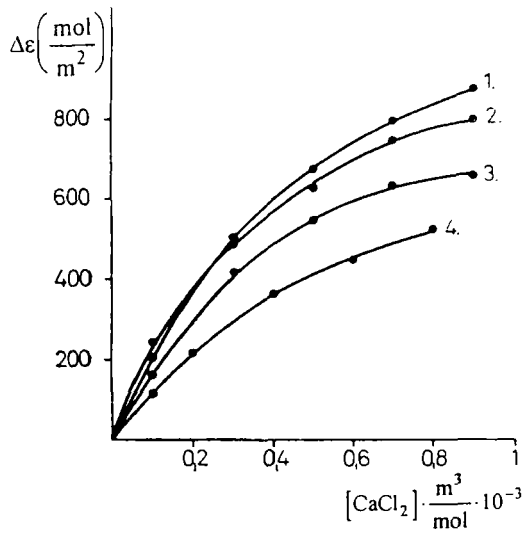


Fig. 3 Change in intensity of the 440 nm keto band ($\Delta\varepsilon = \varepsilon_{CaCl_2} - \varepsilon_{ethanol}$) at the band maximum as a function of [$CaCl_2$] for N-(2-hydroxy-1-naphthylidene)anilines. Substituents: (1) *p*-Cl, (2) *p*-OCH_3, (3) *m*-OH, and (4) H.

of the keto form (ε_k) may be obtained at the band maximum:

$$b = \frac{1}{\Delta\varepsilon_l} \; ; \quad \varepsilon_k = \Delta\varepsilon_l + \varepsilon_{ethanol}$$

where $\Delta\varepsilon_l$ is the limiting value of $\Delta\varepsilon$. Data calculated in this way are to be seen in Table 1. It is noteworthy that the nature of the substituents has little influence on the value of ε_k.

For compound I(4), G. O. Dudek and E. P. Dudek determined the quantity of the keto form and the value of ε_k by study of the NMR, ultraviolet and visible spectra[3]. Their data are given in Table 2 (in $\varepsilon_k/m^2\ mol^{-1}$).

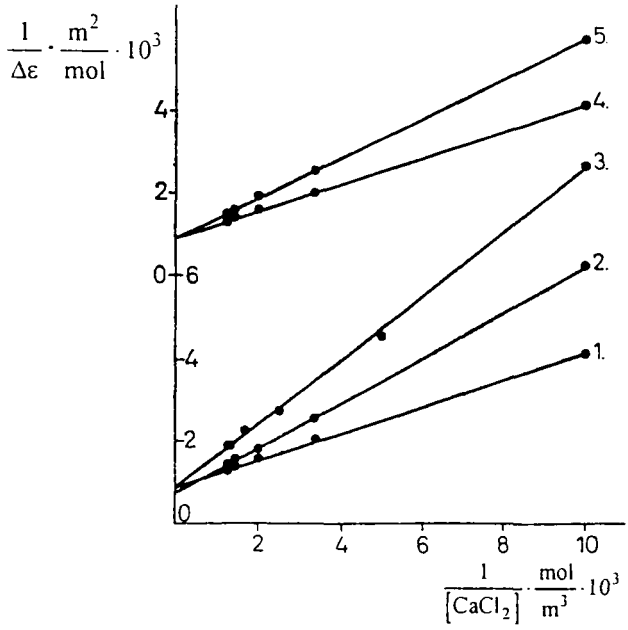


Fig. 4 Plots of the experimental data on N-(2-hydroxy-1-naphthylidene)anilines according to Eq. (2). Substituents: (1) *p*-OCH_3, (2) *m*-OH, (3) H, (4) *p*-OH, and (5) *p*-CH_3.

TABLE 1

ε_k values of the keto form for N-(2-hydroxy-1-naphthylidene)anils in absolute ethanol at 25 °C.

Compound	R	λ_{max}/nm	ε_k/m^2 mol^{-1}
I (1)	*p*-OH	450	2480
I (2)	*p*-OCH_3	445	2440
I (3)	*p*-CH_3	440	2430
I (4)	H	440	2350
I (5)	*m*-OH	440	2550
I (6)	*p*-Cl	440	2650
I (7)	*m*-Cl	440	2550
II	-	420	1086

TABLE 2

ε_k values for compound I(4) in various solvents[3].

solvent	λ_{max}/nm	ε_k/m^2 mol^{-1}
CCl_4	435	2240
$CHCl_3$	438	2250
CH_3CN	433	2340

It may be seen that these data agree well with those that we determined, and it may also be stated that the molar absorption of the keto form at 440 nm is not influenced appreciably by the solvent applied.

Salman et al. determined the quantity of the keto form of the same compound by measurement of the proton-proton coupling constant ^3J(CH-NH)[14-16]. The percentage of the keto form measured in chloroform, in proportion to the molar absorbance of the long-wave band, was used to calculate the quantity of the keto form in various solvents for five *p*-substituted derivatives[17].

In order to compare the experimental data obtained with the different methods, from the data reported by Kamounah and Salman we calculated the molar absorption coefficients for the maximum of the long-wave keto band (Table 3).

The data in Table 3 reveal that the values calculated for the methyl and bromo derivatives agree with those in Tables 1 and 2. The other values, however, and particularly those for the unsubstituted derivatives, appear improbably high. It is possible that the coupling

TABLE 3

Molar absorption coefficient of the keto form (ε_k) for N-(2-hydroxy-1-naphthylidene)anilines substituted on the aniline ring, calculated from data reported for methanolic solutions[17].

R	λ_{max}/nm	ε_k/m^2 mol^{-1}
p-OCH_3	444	4122
p-CH_3	439	2293
H	437	11770
p-Br	439	2660
p-NO_2	450	3850

constant of 11.6 Hz[15] calculated for the methyl derivative in the determination of the keto percentage requires correction for other substituents.

Kamounah and Salman[17] did not observe a clear-cut connection between the keto percentage and the elektron-attracting effect of the substituent. In contrast, our investigations indicated that the equilibrium constant can be calculated in the knowledge of the quantity of the keto form:

$$K = \frac{[\text{keto}]}{[\text{A}]_0 - [\text{keto}]} \qquad (3)$$

In accordance with the Hammett equation, K varies as a function of the constant σ (Table 4, Fig. 5) and also as a function of the basicity of the corresponding substituted aniline[20] (Fig. 6).

This experience corresponds to the expectation that the formation of the keto form is promoted by the electron-donating

TABLE 4

Percentage of the keto form and equilibrium constant of the process for compounds I (1-7).

R	abs. ethanol		50% ethanol-50% hexane	
	% keto	K	% keto	K
p-OH	58.3	1.40	49.2	0.968
p-OCH_3	55.9	1.27	45.1	0.821
p-CH_3	55.9	1.27	45.7	0.841
H	51.7	1.07	40.6	0.683
m-OH	47.7	0.911	39.2	0.644
p-Cl	42.4	0.736	32.1	0.472
m-Cl	39.4	0.650	27.1	0.372

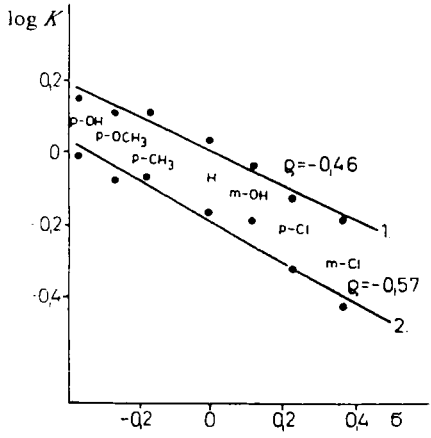


Fig. 5 Variation in log K as a function of the constant σ of the substituent in (1) absolute ethanol and (2) a 1:1 ethanol-hexane mixture.

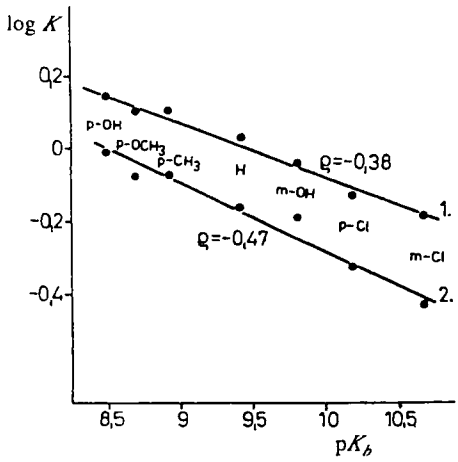


Fig. 6 Variation in log K as a function of the value of pK_b^{20} of the corresponding substituted aniline.

nature of the substituent on the aniline ring, i.e. by increasing basicity of the amine component of the Schiff base. In ethanolic solution, compound II is present as the keto form to an extent of 90%, for example, in accordance with the fact that benzylamine is essentially more basic than the aniline derivatives.

This work has demonstrated that the action of $CaCl_2$ dissolved in ethanol allows a quantitative study of the enol-keto tautomerism of Schiff bases. An interpretation of this "salt effect" has so far not been discovered. It is possible that the zwitterion structure[11-13] must be taken into consideration in the explanation of the phenomenon, for it is probable that in ethanolic solution the zwitterion structure is stabilized by the field of the undissociated salt molecules. Formally, the interactions of the salt and these Schiff bases can be described in accordance with a complex equilibrium.

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