Pakistan Journal of Applied Sciences 2(4): 491-493, 2002

^{1}H NMR Supported Analysis of the UV-vis Spectra of (*Z*) 2-(2-hydroxy-2-phenyl vinyl)-pyridines

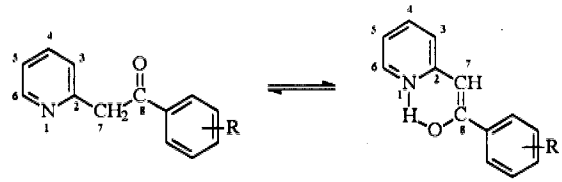
B. Osmialowski and R. Gawinecki
Department of Chemistry, Technical and Agricultural University, Seminaryjna 3, PL-85-326, Bydgoszcz, Poland

Abstract: UV-vis spectral parameters are predicted for fourteen (*Z*) 2-(2-hydroxy-2-phenyl-vinyl)pyridines being in the tautomeric equilibrium with 2-phenacylpyridines (solutions in chloroform). Evaluation of the band intensities is based on content of the enolimine form determined by ^{1}H NMR spectroscopy. Effect of the substituent on both position and intensity of the absorption band as well as on tautomeric equilibrium is discussed.

Key words: Tautomerism, Enolimines, Hydrogen Bond, UV-vis Spectra, Substituent Effect

Introduction

Interconversion of labile species causes that different forms are present in the reaction mixture at the same time. If this process is relatively slow, spectrum of the mixture is a superposition of the spectra of all forms present (Kolehmainen *et al.*, 2000). In consequence, direct recording of the spectrum of individual tautomer is usually not possible. The so-called fixed tautomers, *e.g.* methylated derivatives of the respective tautomeric forms, can be often used to distinguish the absorption bands of the individual form (Kolehmainen *et al.*, 2000; Gawinecki *et al.*, 1999 and 2000). One should bear in mind, however, that due to drastic changes in population of the conformers, comparison of the spectral data for the tautomeric mixture with those for the fixed tautomers may lead to wrong conclusions (Gawinecki *et al.*, 2000 and More O' Ferrall and Murray, 1994). Quantitative analysis of the two-component mixtures with unknown absorption spectra of the pure species is usually the time consuming procedure (Antonov and Stoyanov, 1995). Support from two different spectroscopies can sometimes be helpful. This refers to prediction of the spectra of tautomers, which are stabilized by intermolecular hydrogen bond. No reliable fixed tautomers are known for them (Gawinecki *et al.*, 2000). The present paper deals with determination of the UV-vis spectral parameters of (*Z*) 2-(2-hydroxy-2-phenyl vinyl)pyridines, which are in equilibrium with 2-phenacylpyridines (Scheme 1).



K	R	O	R
1	*p*-N(CH$_2$)$_4$	8	*p*-F
2	*p*-NMe$_2$	9	*p*-Br
3	*p*-NH$_2$	10	*p*-Cl
4	*p*-OMe	11	*m*-F
5	*p*-Me	12	*m*-Br
6	*m*-Me	13	*p*-CF$_3$
7	H	14	*p*-NO$_2$

Scheme 1

Results and Discussion

2-Phenacylquinolines (Kolehmainen *et al.*, 2000) reveal weak absorption in the 300-325 nm region and are practically transparent at $\lambda > 325$ nm. In solution these compounds are in equilibrium with (*Z*) 1,2-dihydro-2-benzoylmethylenequinolines (Kolehmainen *et al.*, 2000). On the other hand, 2-phenacylpyridines equilibrate with (*Z*) 2-(2-hydroxy-2-phenyl vinyl)pyridines (Scheme 1) (Kolehmainen *et al.*, 2000). The UV-vis spectra of mixtures of these two tautomers are shown in Fig. 1.

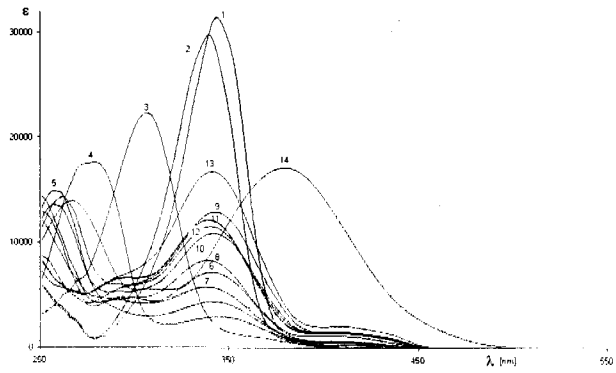


Fig. 1: UV-vis Absorption Spectra of Tautomeric Mixtures K + O in Chloroform

UV-vis spectra of tautomeric mixtures **K** + **O** (Scheme 1) differ from each other both quantitatively and qualitatively. It is known (Kolehmainen *et al.*, 2000) that at 24°C a chloroform solution contains 58.1 and 41.9 % of **7K** and **7O**, respectively (content of the tautomer is based on integral intensity of the H7 signal in its ^{1}H NMR spectrum). Since the **K** forms do not absorb at $\lambda > 325$ nm (Kolehmainen *et al.*, 2000), the band at $\lambda \approx 340$ nm is that of **7O**. The same conclusion refers to solutions **4-13.** The minor effect of the substituent on λ_{max} in the spectra of **4O-13O** seems noteworthy (Table 1).

Content of the **O** form (Table 1) is dependent on substituent. It seems interesting that the **O** (%) *vs.* the Hammett σ substituent constants (Hansch, 1991) relationship is linear in character:

O (%) = (59.9 ± 3.5)σ + 43.5 ± 1.5

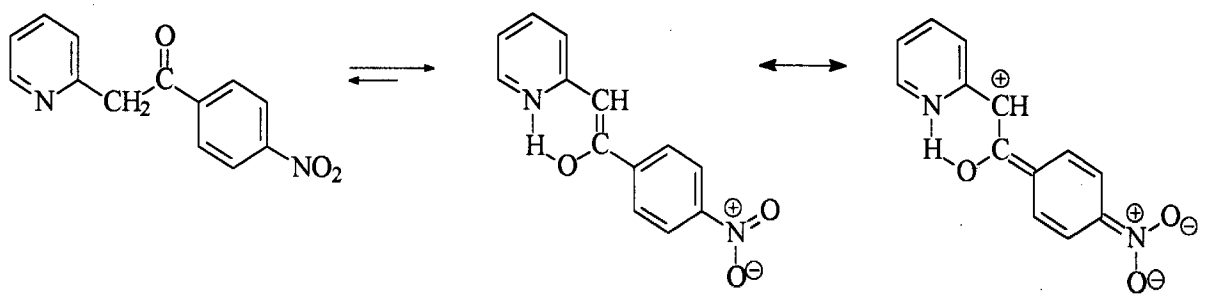
[*p*-N(CH$_2$)$_4$ excluded, correlation coefficient = 0.982]

The main absorption band (λ_{max} = 380.5 nm) in the UV-vis spectrum of **14** is red shifted (with respect to the

Table 1: UV-vis Spectra of Tautomeric Mixtures 1-14 (Solutions in Chloroform)

Tautomeric mixture	λ_{max}[a] [nm]	ε[a] [10^4 l mol^{-1} cm^{-1}]	λ_{max} [nm]	ε [10^4 l mol^{-1} cm^{-1}]	λ_{max} [nm]	ε [10^4 l mol^{-1} cm^{-1}]	O (%)[b]
1	-	-	343.5	3.14	-	-	1.7
2	-	-	339.5	2.97	-	-	3.3
3	-	-	307	2.23	-	-	3.9
4	410sh	0.02	344.5	0.29	279.5	1.76	14.0
					296sh	0.90	
5	410sh	0.04	341.5	0.43	296sh	0.33	33.3
6	410sh	0.06	341.5	0.71	296	0.48	39.3
7	410sh	0.05	338.5	0.57	296sh	0.44	41.9
					257.5	1.49	
8	410sh	0.11	338.5	0.83	296sh	0.46	47.1
9	410	0.15	338.5	0.83	296sh	0.46	56.6
10	410	0.13	341.5	1.08	296sh	0.53	52.2
					257.5	1.35	
11	410	0.14	339.5	1.21	296	0.66	67.9
12	410	0.15	340.5	1.15	296sh	0.58	67.9
13	410	0.20	341.5	1.67	296sh	0.70	78.7
14	380.5	1.71	-	-	296sh	0.57	93.2

[a]Very wide band.
[b] Content of the **O** form at 24° C based on integral intensities of H7 signals in the ^{1}H NMR spectrum Accuracy: ± 0.5 %.



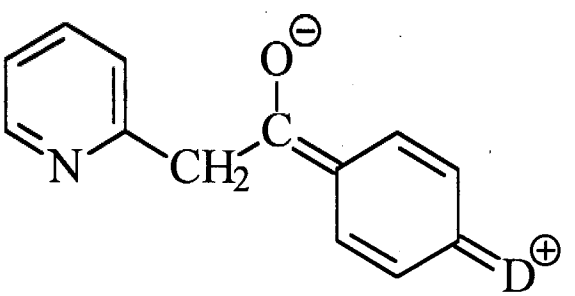
Scheme 2

bands of enolimines **4O-13O**). The charge-transfer resonance structure is responsible for that behaviour: This is also supported by the downfield shift of C7 signal in the ^{13}C NMR spectrum of **14O** (as compared to similar signals in the spectra of other enolimines) (Kolehmainen *et al.*, 2000).

Except a very weak absorption band at 345 nm, there is also another strong one at 280 nm present in the spectrum of **4**. Electron excitation in **4K** is supposed to be responsible for that absorption. Other strong electron-donor substituents cause intensity of this band to increase. It is subjected to the batochromic shift when substituent is getting stronger donor.

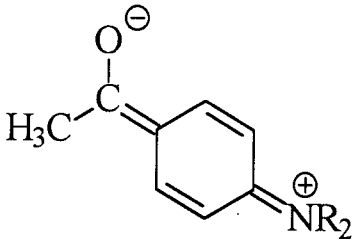
Absorption at 343.5 nm in the spectrum of **1** is typical for **1K** (according to data in Table 1 there is no **1O** practically present in solution). Decrease in contribution of the **K** form in solutions **1-3** (Table 1) is responsible for the observed hypsochromic effect of that band (Branch *et al.*, 1963).

Scheme 3



If there is no resonance interaction between the phenacyl and pyridyl parts of the molecule, the spectra of the **K** forms at $\lambda > 300$ nm should resemble these for respectively substituted acetophenones. It is noteworthy that weak long-wavelength band in the spectra of the

latter compounds has the *n* → π* nature (Silverstein *et al.*, 1991). However, if there is a very strong electron-donor substituent in position *para* with respect to the acetyl group, this band becomes very strong and has the π → π*nature (Nicolet and Laurence, 1986; McClelland *et al.*, 1994; Doub and Vandelbelt, 1947 and 1947):



Scheme 4

Thus, the long-wavelength bands in the spectra of solutions **1-3** are those resulting from the local electron excitation in the phenacyl part of the molecule ($CH_2COC_6H_4R$). The less electron-donor is the substituent the more hypso- and hypochromic effect of the band is observed. In the same time, intensity of the band at ~340 nm in the spectra of solutions **4-13** increases (its position is almost independent on substituent). λ_{max} of this band is comparable to that of the π → π* band in the spectra of acetophenones but its intensity is increased (Olivato *et al.*, 1988). Thus, the band at ~340 nm in the spectra of solutions **4-13** results from the more or less effective π → π* excitations in **4O-13O**. Parameters of this band are supposed to be dependent on the resonance interactions in the **O** form. Its position is almost constant which means that extent of the conjugation in **4O-13O** is also constant. **14O** is exceptional and this results in different shape of its spectrum. There is also a band at ~410 nm in the spectra of **4-13**. Its intensity is dependent on substituent: it is weak in the spectrum of **4O** (*n* → π*) and becomes stronger for more electron-withdrawing (acceptor) substituents. One may assume that ε_{max} of that band increases as the hydrogen bond in the **O** form is getting stronger. This band in the spectrum of **14O** appears at 380.5 nm and is very intense.

Content of the **O** form in the tautomeric mixture (Table 1) which is based on integration of its ^{1}H NMR spectra, can be used to obtain the UV-vis spectral parameters of (*Z*) 2-(2-hydroxy-2-phenylvinyl)pyridines (Table 2). Thus, analysis of the UV-vis spectra of tautomeric mixtures supported by their ^{1}H NMR spectra enables determination of the absorption spectra of labile species, *e.g.* tautomers.

Table 2: UV-vis Spectra of (*Z*) 2-(2-hydroxy-2-phenyl-vinyl)pyridines

	Band II		Band I	
	λ_{max}[nm]	ε_o[$M^{-1}cm^{-1}$]	λ_{max}[nm]	ε_o[$M^{-1}cm^{-1}$]
4O	344.5	20700	410	1400
5O	341.5	12900	410	1200
6O	341.5	18100	410	1500
7O	338.5	13600	410	1200
8O	338.5	17600	410	2300
9O	338.5	14700	410	2700
10O	341.5	20700	410	2500
11O	339.5	17800	410	2100
12O	340.5	16900	410	2200
13O	341.5	21200	410	2500

Experimental: Synthesis of compounds was described in our recent paper (Kolehmainen *et al.*, 2000). Conditions for recording the UV-vis spectra (in chloroform at 24° C) were these specified earlier (Gawinecki and Trzebiatowska, 2000).

Conclusion

^{1}H NMR spectra were found to be helpful in calculating the UV-vis spectral parameters of the individual species being in equilibrium (usually it is not possible to see the separate absorption bands in the spectrum of the tautomeric mixture). The procedure may be applied in quantitative evaluation of the equlibria between interconverting components. This was exemplified for the series of (Z)-(2-hydroxy-2-phenylvinyl)pyridines and 2-phenacyl-pyridines.

References

C. Hansch, A. Leo, R.W. Taft, 1991. *Chem. Rev.* 91 165.

E. Kolehmainen, B. Osmialowski, T.M. Krygowski, R. Kauppinen, M. Nissinen, R. Gawinecki, 2000. J. Chem. Soc., Perkin Trans. 2: 1259.

E. Kolehmainen, B. Osmialowski, M. Nissinen, R. Kauppinen, R. Gawinecki, 2000. J. Chem. Soc., Perkin Trans. 2 2185.

L. Antonov, S. Stoyanov, 1995. Anal. Chim. Acta 314 225.

L. Doub, J.M. Vandelbelt, 1947. J. Am Chem. Soc, 69: 2714.

L. Doub, J.M. Vandelbelt, 1947. J. Am Chem. Soc. 71: 2414.

P. Nicolet, Ch. Laurence, 1986. J. Chem. Soc., Perkin Trans. 2: 1071.

P.R. Olivato, S.A. Guerrero, P.S. Santos, Spectrochim, 1988. Acta 44A: 677.

R. Gawinecki, E. Kolehmainen, B. Osmialowski, P. Palkovic, M. Nissinen, Heterocycl, 1999. Comm. 5: 549.

R. Gawinecki, B. Osmialowski, E. Kolehmainen, M. Nissinen, 2000. J. Mol. Struct., 525: 233 and references cited therein.

R.A. More O'Ferrall, B.A. Murray, 1994. J. Chem. Soc., Perkin Trans. 2: 2461.

R.F. Branch, A.H. Beckett, D.B. Cowell, Tetrahedron, 1963. 19: 401.

R.M. Silverstein, G.C. Bassler, T.C. Morrill, 1991. Spectrophotometric Identification of Organic Compounds, 5th ed., Wiley, New York, pp. 289-315.

R.A. McClelland, K.M. Engell, T.S. Larsen, P.E. Sørensen, 1994. J. Chem. Soc., Perkin Trans. 2: 2199.

R. Gawinecki, K. Trzebiatowska, 2000. Dyes Pigm. 45: 103.