

ABSORPTION SPECTRA OF NITRONES OF N-(2-HYDROXYBENZYLIDENE)ANILINE AND N-(4-HYDROXYBENZYLIDENE)ANILINE  
IN VARIOUS SOLVENT MIXTURES

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THE ABSORPTION SPECTRA OF THE EXAMINED NITRONES ARE NOT AFFECTED IN THE ESSENTIALS BY THE APPLIED SOLVENTS, WHEREAS THE SPECTRA OF THE CORRESPONDING SCHIFF BASES ARE GREATLY INFLUENCED BY THEM, MAINLY AT AROUND 400 nm.

THIS FINDING IS IN ACCORDANCE WITH THE SUPPOSITION OF BOTH THE ENOL  $\rightleftharpoons$  KETO AND ENOL  $\rightleftharpoons$  "ION-PAIR" EQUILIBRIUM. IT IS POSSIBLE THAT BOTH THE "ION-PAIR" AND THE KETO FORM PLAY A ROLE IN THE GIVEN SOLVENT EFFECT.

*Introduction*

In spite of extensive investigations, there is still no unanimously verified explanation for the characteristic solvent effect observed [1,2] at around 400 nm in the absorption spectra of certain types of Schiff bases.

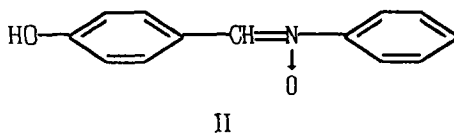
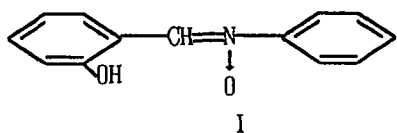
DUDEK [3] and LEDBETTER [4] presume that a quinoline structure is formed on the action of the solvent, with an enol  $\rightleftharpoons$  keto tautomer equilibrium dependent on the solvent. In our opinion, the band at around 400 nm (the "fore-band") in the absorption spectra can be ascribed to the keto form. This explanation corresponds to the observation that this phenomenon can occur in those Schiff bases whose aromatic aldehyde component contains an OH group in the o- or p-position. Numerous experimental results are in accord with this explanation [5-10]. However, LEWIS and SANDORFY have postulated

the possibility of formation of an "ion-pair" structure [11]. The UV-VIS, IR and Raman spectra of *N*-(2-hydroxybenzylidene)aniline, however, did not reveal the presence of a substantial amount of either the quinone form or the "ion-pair" structure. On the basis of the Raman spectra of the amino acid Schiff bases of salicylaldehyde, LEDBETTER [12] explains this solvent effect in terms of the "ion-pair" structure. RANGANATHAN et al. [13] studied the PMR and electronic spectra of Schiff bases originating from substituted salicylaldehydes and 2-aminopyridine. They explained the solvent-dependent absorption band at around 400 nm as due to formation of the quinone structure. From an analysis of the electronic and Raman spectra of *N*-(2-hydroxybenzylidene)methylamine, LEE and KITAGAWA [14] attribute the absorption band at around 400 nm to the "ion-pair" structure. Accordingly, in spite of the fact that the investigations have been carried out with wide-ranging and varied methods, this problem has not been clarified unanimously so far.

The present paper reports on a study of the absorption spectra in various solvent mixtures of the nitrones of *N*-(2-hydroxybenzylidene)aniline and *N*-(4-hydroxybenzylidene)aniline, the two type-compounds as concerns the phenomenon in question. In these compounds, the non-bonding electron-pair of the azomethine N atom is involved in the N → O linkage, and it can therefore be expected that there will be a difference in the solvent effect relative to the corresponding Schiff bases, and that this may provide further data towards a better understanding of this solvent effect. It should be noted that KUBOTA et al. [15] made a detailed study of the spectroscopic behaviour of many nitrones, but they did not investigate Schiff bases originating from 2- and 4-hydroxybenzaldehyde, which are important from the aspect of the solvent effect in question.

### *Experimental*

The following compounds



were prepared by mixing ethanolic solutions of the appropriate aldehyde and phenylhydroxylamine, and were subsequently purified by recrystallization. The analytical data are given in Table I.

*Table I*

Analytical data on compounds I and II

Com- pound	mp. (°C)		C(%)		H(%)		N(%)	
		*	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
I	118	51	73.24	73.30	5.16	5.21	6.57	6.22
II	210	192	73.24	73.32	5.16	5.16	6.57	6.58

\* melting point of the corresponding Schiff base

The applied solvents were purified by means of the methods customary in spectroscopy, and were carefully freed from water. Freshly dried (dehydrated) calcium chloride was used for the investigation of the salt effect. The absorption spectra were recorded with a VSU2-P spectrophotometer at 298 K.

#### *Results and discussion*

The visible and UV spectra of compounds I and II were determined in absolute ethanol, in a 90% cyclohexene – 10% ethanol solvent mixture and in a 0.9 mol/dm<sup>3</sup> CaCl<sub>2</sub> solution in absolute ethanol. The absorption curves, together with those of the corresponding Schiff bases, are illustrated in Figs. 1 and 2. It can be seen that the absorption of the Schiff bases in the region 400–450 nm depends strongly on the solvent

used. On the other hand, the absorption curves of the nitrones are not appreciably influenced by the solvent. This experimental observation proves that conditions for the solvent effect are an OH group in the o- or p-position on the aldehyde ring, and also a non-bonding electron-pair on the azomethine N atom. If this electron-pair is involved in the bonding, the solvent effect is not observed.

This finding was next compared with the assumptions applied to date to explain the solvent effect. For the nitrones, the absence of the solvent effect would be in accord with the explanation that the hydrogen-bond between the solvent and the azomethine N atom causes the appearance of the new band and the change in the absorption spectrum, for this hydrogen-bond can not form in the nitrones. Nevertheless, this explanation is improbable for energetic reasons, and also because the solvent effect should then be observed for all Schiff bases. LEWIS and SANDORFY [11], among other authors, confirmed that a

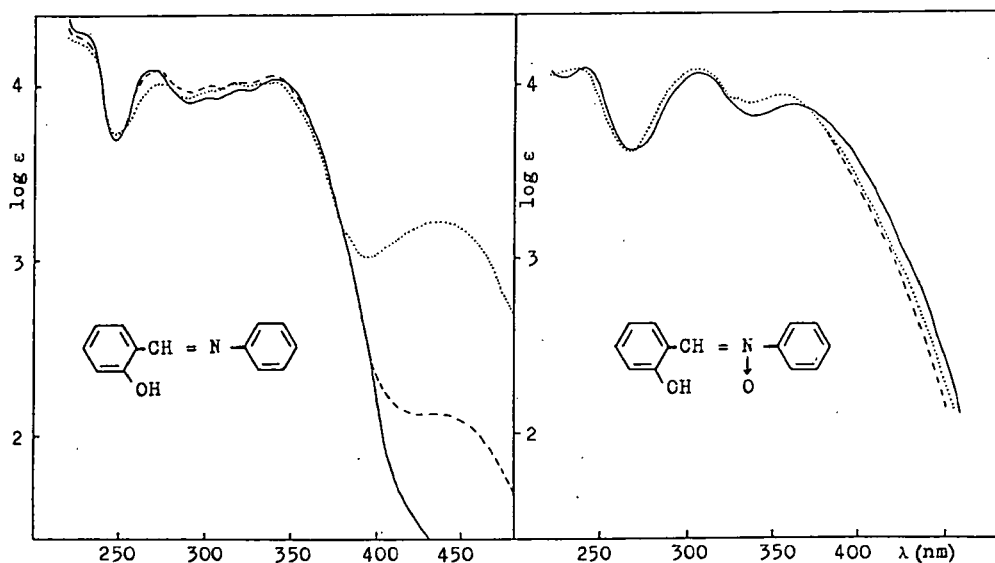


Figure 1: Absorption curves of compound I and the corresponding Schiff base in different solvents. Solvents: 90% cyclohexene - 10% ethanol (—), abs. ethanol(---) and 0.9 mol/dm<sup>3</sup> CaCl<sub>2</sub> in abs ethanol(...)

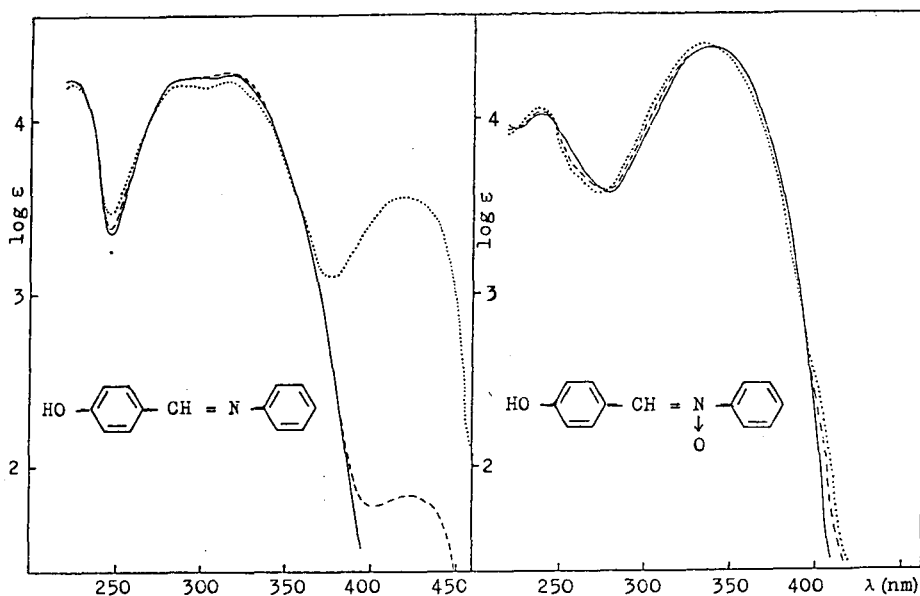


Figure 2: Absorption curves of compound II and the corresponding Schiff base in different solvents. Solvents: 90% cyclohexene - 10% ethanol (—), abs. ethanol(---) and 0.9 mol/dm<sup>3</sup> CaCl<sub>2</sub> in abs ethanol(...)

hydrogen-bond is formed with benzaldehyde, similarly as with N-(2-hydroxybenzylidene)-aniline, but the solvent effect in question can be observed only for the latter compound.

The data in Figs. 1 and 2 are in accord with the interpretation of the solvent effect in terms of either the enol  $\rightleftharpoons$  keto or the enol  $\rightleftharpoons$  "ion-pair" equilibrium. Both explanations correspond to the fact that the non-bonding electron-pair of the N atom plays a decisive role in the solvent effect. This is why the phenomenon is not observed for the nitrones. Via PMR and UV spectroscopic measurements, DUDEK presumed the enol  $\rightleftharpoons$  keto tautomeric equilibrium, on the basis of quantitative determination of the N-H bonding [3]. It is possible, however, that his experimental results can also be explained via the N-H bonds of the "ion-pair" structure. Apparently convincing evidence of the formation of the quinone structure is the fact that the solvent effect can be observed only if there is an OH group in

the o- or p-position on the aldehyde ring of the Schiff base. However, it can also be explained by the formation of the "ion-pair" structure, but less convincingly for the negative K effect of the azomethine group it can be expected that an OH group in the o- or p-position loses a proton more easily than one in the m-position, and therefore this solvent effect can not be observed for the m-derivatives.

The explanation of the phenomenon in terms of the formation of the "ion-pair" structure is in accord with our observation [6,10] that the solvent effect is greatly increased by various salts dissolved in absolute ethanol. Such an effect of  $\text{CaCl}_2$  can be seen in Figs. 1 and 2. In our opinion, the charged particles of salts (in anhydrous solvent the salt molecules are largely non-dissociated) promote the formation of the "ion-pair" structure and therefore the ethanol  $\rightleftharpoons$  "ion-pair" equilibrium shifts as a function of the salt concentration. We cannot explain the role of salts if the solvent effect is interpreted via the quinoidal transformation.

In their IR and Raman spectroscopic study of the solvent effect for N-(2-hydroxybenzylidene)aniline, LEWIS and SANDORFY [11] did not observe a perceptible change in the  $\text{C}=\text{N}$  force constant. Thus, formation of the quinone or "ion-pair" structure was not proved by their experimental data. Their suggested explanation, which they consider unlikely, is that one-two per cent of the molecules have the quinone or "ion-pair" structure in an ethanolic solution of the compound [10]. In contrast, there is a very considerable solvent effect for N-(2-hydroxybenzylidene)aniline, which DUDEK likewise investigated (Fig.3.); about 50 per cent of the molecules have the quinone (or "ion-pair") structure in ethanolic solution [3,10].

The reported results demonstrate that the findings relating to this solvent effect (perhaps with the exception of the role of the salts) can be explained with either the enol  $\rightleftharpoons$  keto or the enol  $\rightleftharpoons$  "ion-pair" equilibrium. However, in our opinion, these two explanations do not exclude, but rather presuppose one another: it is probable that the Schiff base molecules can assume the quinone form through the "ion-pair" structure



The substituents on the aldehyde or amine component greatly influence the position of the above equilibria [5,13], and it must be taken into consideration that conjugation of the Schiff base molecule inhibits formation of the quinone structure. This may result in the solvent effect being perceptibly larger for the Schiff bases formed with aliphatic amines than for the aromatic derivatives [5]. In accordance with the stability difference between the naphthalene and benzene rings, the probability of formation of the quinone structure is larger for the Schiff bases formed with 2-hydroxy-1-naphthaldehyde than for the derivatives of salicylaldehyde. The solvent effect is essentially larger for the former. It is possible that virtually only the first equilibrium plays a role in the slight solvent effect observed for the 2- and 4-hydroxybenzylideneanilines. This would explain why the solvent effect basically occurs only in the "fore-band" region for these latter compounds (Figs. 1 and 2), whereas the whole absorption spectrum changes considerably for N-(2-hydroxy-1-naphthylidene)aniline, *e.g.* see Fig. 3. The change in the spectrum is similarly considerable for the Schiff bases formed with aliphatic amines.

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#### АДСОРБЦИОННЫЕ СПЕКТРЫ НИТРОНОВ N-(2-ГИДРОКСИБЕНЗИЛИДЕН)АНИЛИНА И N-(4-ГИДРОКСИБЕНЗИЛИДЕН)АНИЛИНА В РАЗНЫХ СМЕСЯХ РАСТВОРИТЕЛЕЙ

П.НАДЬ, П.ГЕРЦФЕЛЬД

Адсорбционные спектры изученных нитронов в основном не зависят от применяемых растворителей, но в противоположность этому на спектры соответствующих Шиффовых оснований сильно влияют, в главном, в области 400 нм. Этот результат находится в соответствии с предположением наличия обеих энол  $\rightleftharpoons$  кето и энол  $\rightleftharpoons$  "ионная пара" равновесий. Возможно, что как "ионная пара" так и кето формы играют роль в эффекте растворителей.