

HYDROGEN BONDING EFFECT ON THE ABSORPTION SPECTRUM OF SOME SCHIFF-BASES

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The electronic absorption spectra of *N,N'*-bis/salicylidene/ethylenediamine, *N*-salicylideneaniline and of *N*-salicylidenebenzylamine were determined in ethanol and hexane. In the absorption spectra of these compounds, in ethanol, there appears a long-wave length absorption band. The intensity of the long-wave length absorption bands has been measured also in the mixture of hexan-ethanol. The measures prove that the appearance of these long-wave lengths is to be attributed to the effects of hydrogen bonding between the ethanol and the solved molecules. The long-wave length bands appear also in dioxane and pyridine, however, with a considerably less intensity.

It is well-known that the OH group may produce intramolecular or intermolecular hydrogen bond. In case of the hydrogen bond formation, the stretching vibrations of the infrared absorption spectra due to the OH group are shifted to lower frequencies. The OH group, producing the intermolecular hydrogen bond, shows a broad absorption band at $3445\text{--}3200\text{ cm}^{-1}$. The intermolecular hydrogen bond is broken by dilution, so is the intensity of the characteristic infrared absorption band. If the OH group produces intramolecular hydrogen bond, the intensity of the characteristic bands ($3200\text{--}2500\text{ cm}^{-1}$ and $3570\text{--}3445\text{ cm}^{-1}$) is not broken by dilution.

The effect of the intermolecular hydrogen bond may be seen also on the electronic absorption spectra. This is manifested by the anomalies of the effects of the solvents. It is known from experience that changing the solvent from hexane, heptane cyclohexane to ethanol, pyridine, ether etc. the absorption bands may be shifted relatively to shorter or longer waves, the frequency of other bands remains, its intensity, however, grows. According to the examinations of BABA and NAGAKURA, BREALEY and KASHA, MCCONNEL, HIRT and HALVERSON [1], [2], [3], [4], [5] and of other authors between the molecules having a lone pair of electrons and containing a relative electronegative atom (phenol, cresols, pyridazin, benzophenon) and the molecules of the solvent (pyridine, ethanol, ether etc.) a hydrogen bonding complex may occur. The absorption bands of relatively low intensity which, in ethanol as compared to their position measured in the hexane, are shifted to shorter wave lengths, are called blue-shift bands by MCCONNEL. These blue-shift bands, as experience proves, appear in molecules containing carbonyl, azo, thycarbonyl and other similar groups and their origin is to be attributed to $n\rightarrow\pi^*$ singlet-

singlet transitions. In a planar, conjugated molecule the $n \rightarrow \pi^*$ transition is due to an excitation of an n -electron from an orbital symmetric to the molecular plane, to an antibonding π^* molecular-orbital, antisymmetric to the molecular plane.

If the absorption bands, by changing the solvents (from hexane to ethanol or ether), are shifted to the longer wave lengths, then these bands are called red-shift bands and their appearance is attributed to the $\pi \rightarrow \pi^*$ transitions [7], [8].

According to BREALEY and KASHA in the formation of the hydrogen bond, in blue-shift, the solved molecule plays the role of hydrogen acceptor, while in red-shift that of hydrogen donor.

Discussion

Examining the electronic absorption spectra it was observed that the spectra of Schiff-bases containing OH group on the benzene-ring in ortho or para position to the aldehyde group, a long wave length band of low intensity appears in ethanol, between 420—408 $m\mu$ [8], [9], [10]. However, it was noted if the hydrogen of the OH group is substituted by CH_3 methyl group then this long wave length band of low intensity can not be observed. Thus it is not to be found, in ethanol solution, in the absorption spectra of N-/2-methoxybenzylidene/aniline and of N-/4-methoxybenzylidene/aniline. TSUCHIDA and TSUMAKI [9] drew the conclusion from this observation that this long wave length absorption band is due to the intramolecular hydrogen bond occurring between the hydrogen of OH group and the double bonded nitrogen of the $CH=N$ azomethin. KISS, BÁCSEKAI and VARGA [8] have attributed the band to the arising of the chinoidal and benzoidal mesomer system and to its excitation. In our opinion the band fails to appear in the etherification because the arising of the benzoidal and chinoidal mesomer systems is inhibited.

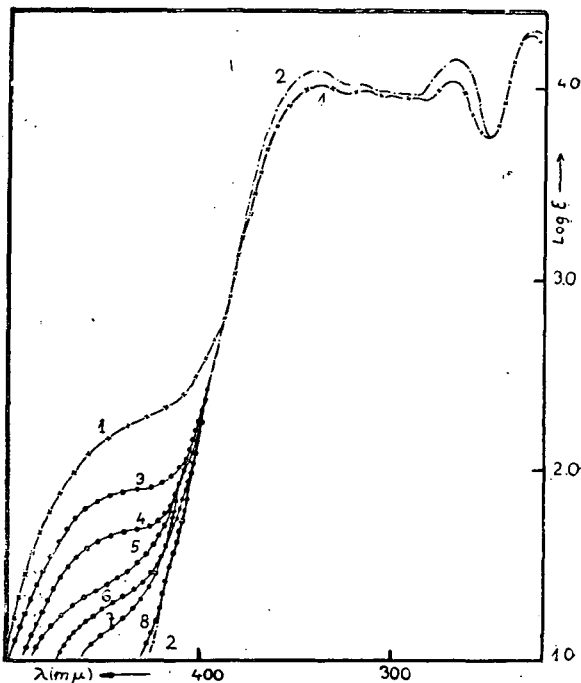


Fig. 1. The absorption spectrum of N-salicylideneaniline in ethanol (curve 1), hexane (curve 2), pyridine (curve 5), dioxane (curve 7) and hexanethanol solvent (curve 3, 4, 6, 8). Ethanol concentrations: Curve 3, 8.44 M; curve 4, 5.11 M; curve 6, 2.00 M; curve 8, 0.29 M.

Papers of H. BABA, G. J. BREALEY and M. KASHA drew our attention to study the absorption spectra of Schiff-bases mentioned above in ethanol, dioxane, pyridine and in the mixture of hexan-ethanol. The measures indicate that the first band of the long wave length is the result of the hydrogen bond formed between the molecules of the solvent and those of the solved Schiff-bases derivatives.

Fig. 1 shows the absorption spectra of the N-salicylideneaniline. In ethanol and hexane the complete absorption spectra were determined while in dioxane, pyridine and in the mixture of hexan-ethanol merely the long wave length band appearing about $440\text{ m}\mu$. It can be stated that the band of $440\text{ m}\mu$ appearing in ethanol, hexane and pyridine fails in hexane (Fig. 1, curve: 1, 2, 5 and 7). The two short wave length bands, in ethanol solution compared to the hexane solution are slightly shifted towards the long wave lengths ($269, 228\text{ m}\mu$ and $267, 225\text{ m}\mu$ respectively). The intensity of the band about $440\text{ m}\mu$ measured in the mixture of hexan-ethanol decreases if the concentration of the ethanol is diminished. This absorption band appears relatively with a slight intensity in the dioxane and pyridine (Fig. 1, curves: 5 and 7). It is noteworthy that the effect of dioxane and pyridine on the absorption spectra hardly differs from that of the mixture of the 2 M ethanol-hexan. As the infrared absorption spectra of N-salicylideneaniline

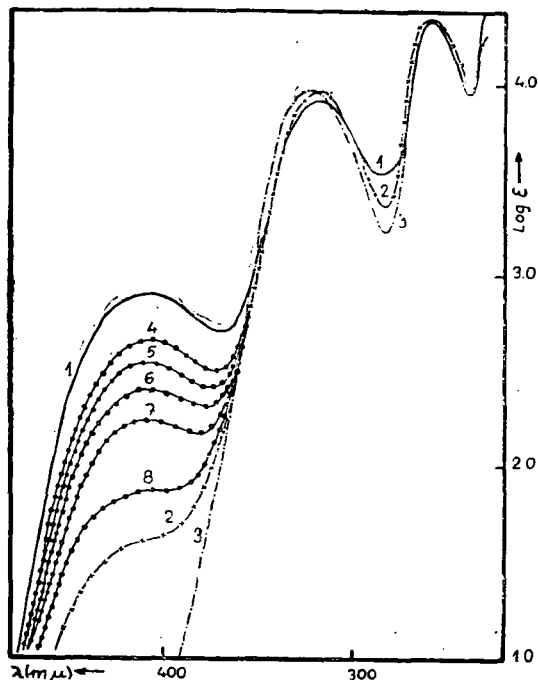


Fig. 2. The absorption spectrum of N-salicylidenebenzylamine in ethanol (curve 1), dioxane (curve 2), hexane (curve 3), pyridine (curve 8) and hexan-ethanol solvent (curve 4, 5, 6, 7). Ethanol concentrations: Curve 4, 10.10 M; curve 5, 8.60 M; curve 6, 5.11 M; curve 7, 2.0 M.

[11], [12], [13] and other methods prove the formation of the intermolecular hydrogen bond between the hydrogen of the OH group and the nitrogen of azomethin, presumably this intermolecular bridge-bond, in ethanol, dioxane and pyridine, is but partly solved due to the effect of the solvent. Between the intramolecular complex and the solvated substance, as well as the intermolecular hydrogen bond formed among the molecules of the solvent an equilibrium occurs. In ethanol, however, the lone pair of electrons of the oxygen of the ortho positioned OH group may produce also another hydrogen bond toward the hydrogen of the OH group of the ethanol, and so such a complex may be formed wherein there are two hydrogen bonds. There is no possibility of such formation in dioxane and pyridine. This assumption may account for the observation that in the present case the effect of the solvent is of a smaller degree than observed by other authors where there is no possibility of a formation of the intramolecular hydrogen bond [7].

A phenomenon entirely analogous with the latter can be noticed on the absorption curves of the N-salicylidenebenzylamine (Fig. 2) and of the N, N'-bis/salicylidene/ethylenediamine (Fig. 3). At both compounds the first band of the long wave lengths appears about 408 $m\mu$ and the diminutive effect of both the pyridine and dioxane on the intensity is less than that of the 2 M ethanol (ethanol in hexane). The bands at shorter wave lengths, however,

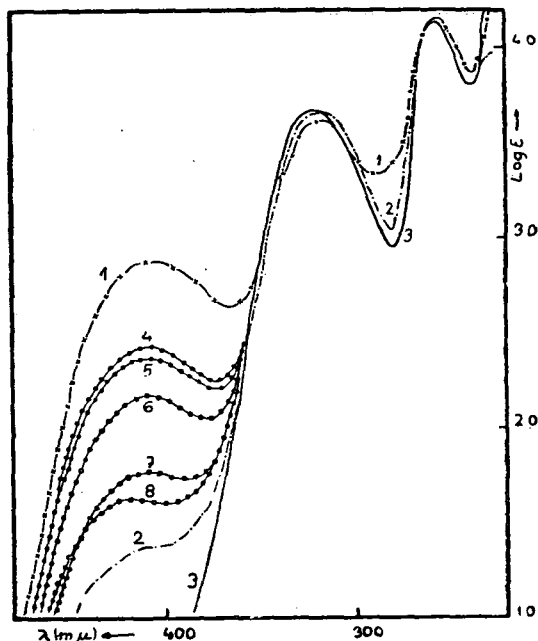


Fig. 3. The absorption spectrum of N,N'-bis/salicylidene/ethylenediamine in ethanol (curve 1), dioxane (curve 2), hexane (curve 3), pyridine (curve 8) and hexan-ethanol solvent (curve 4, 5, 6, 7). Ethanol concentrations: Curve 4, 8.40 M; curve 5, 6.00 M; curve 6, 2.93 M; curve 7, 2.00 M.

behave differently. The maximums of the bands observed in alcohol solution compared to the value measured in the hexane are shifted to the shorter wave lengths.

To study the phenomenon the absorption spectra of several Schiff-bases derivatives will be subjected to examination under identical conditions.

Experimental

The absorption curves were measured with Beckman DU spectrophotometer using 1 cm cell at 25°C. The concentration of the compounds examined ranged from 10^{-3} to 10^{-5} mole/lit. Solvents were purified with the methods described in the literature [14], [15], [16].

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