

SPECTRA OF SCHIFF BASES OF THE TYPE X,Y-BENZYLIDENE-4-Z-ANILINE

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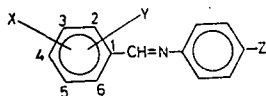
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The ultraviolet, infrared and ¹H NMR spectra of aromatic Schiff bases of the type X,Y-benzylidene-4-Z-aniline (X=H, 5-NO₂, 5-Br; Y=2-OH, 2-NH₂; Z=OH, NO₂) have been investigated. Regarding the formation of the keto-amine tautomeric form, the conclusion is drawn that the aniline-substituents play a determining role, but the aldehyde-substituents also influence the intensity of the visible band.

Several papers deal with the spectra [1—6], with the photochromic and thermochromic properties [7, 8] and with other behaviour [9—12] of the aromatic Schiff bases. In polar solvents a medium-intensity band appears in the 400—450 nm spectral region, which can be interpreted as due to enol-imine/keto-amine tautomeric equilibrium [13—15].

In an earlier paper [16] we reviewed the spectroscopic characteristics of numerous Schiff bases. It was concluded that the visible band appears if the following three conditions are fulfilled: a) the solvent is strongly polar, b) an OH group is present in the aldehyde ring in the *o*- or/and *p*-position, and c) a certain charge-density is attained on the N atom.

In this paper we discuss the spectra of the following compounds:



No.	X	Y	Z	m.p.
I	H	2-OH	OH	139.0
II	H	2-OH	NO ₂	151.0
III	H	2-NH ₂	NO ₂	130.3
IV	5-NO ₂	2-OH	OH	272.8
V	5-NO ₂	2-OH	NO ₂	230.3
VI	5-Br	2-OH	OH	224.6
VII	5-Br	2-OH	NO ₂	200.7

The Schiff bases were prepared from their components in methanolic solution; the compositions were checked by C, N and H analysis. The ultraviolet, infrared and ^1H NMR spectra were recorded with a SPECORD UV—VIS and ZEISS UR—10 spectrophotometers and a JEOL 60 MHz instrument (TMS internal standard).

Table I
The ultraviolet*, infrared** and ^1H NMR spectral data of the Schiff bases

No.	nm and lg ϵ				$\nu\text{C}=\text{N}$	νNO_2	$\nu\text{C}-\text{O}$	γCH	δCHN	δOH
I ^{b)}	430	348	270	~230	1613 s		1278 s	747 m	8.84	13.49
	2.60	4.20	3.91					833 m		9.53
II ^{a)}		358	~320	~220	1607 s	1337 s	1267 s	760 m	8.69	12.58
		4.30			1561 s			847 m		
III ^{b)}		367		230	1637 s	1303 s		757 m	8.10	7.82***
		4.50		4.26	1592 s			844 m		7.97
IV ^{b)}	408	352	~317	232	1649 s	1337 s	1242 s	784 v	8.48	9.68
	3.70	4.42		4.35	1604 s			839 m	8.54	9.07
V ^{b)}		364	~310	230	1629 s	1350 s	1292 s	752 m	8.66	12.07
		4.31		4.17	1593 s			860 m	8.72	
VI ^{b)}	423	357		230	1623 s		1280 s	780 v	8.78	13.56
	2.81	4.34		4.53				832 m		9.56
VII ^{b)}		363		220	1624 s	1342 s	1277 s	756 v	8.88	10.23
		4.40		4.52	1590 s			858 m		

* in CH_3OH ;

** in KBr disk;

*** δNH_2 ;

a) in CDCl_3 ;

b) in $\text{CDCl}_3 + \text{DMSO}$

Table I presents the spectral characteristics, and Fig. 1 shows the u.v. spectra of IV and V. From these results the following conclusions can be drawn.

1. The ultraviolet spectra of methanolic solutions of I, IV and VI show a band with varying intensity between 400 and 430 nm. In III the 2— NH_2 group prevents

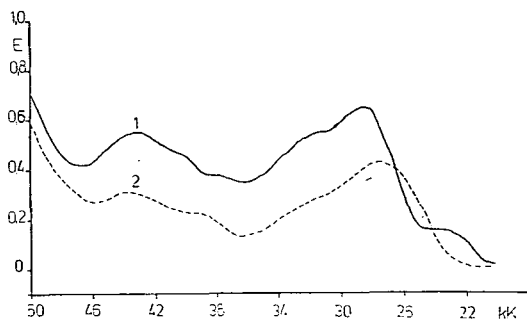


Fig. 1. Spectra of methanolic solutions. 1: IV, $c = 2.48 \cdot 10^{-4}$ M, $d = 0.1$ cm; 2: V, $c = 2.09 \cdot 10^{-4}$ M, $d = 0.1$ cm

the formation of the intramolecular H-bridge and the quinonoid form. In the cases of II, V and VII the strongly electron-withdrawing 4-NO₂ group ($\sigma = +0.778$) decreases the charge-density on the N-atom to such an extent that the keto-amine form cannot exist. It can be observed that, with the increase of the electron-withdrawing power of the aldehyde-substituents and with that of the electron-releasing power of the aniline-substituents, the intensity of the visible band increases. It can be stated that primarily the aniline-substituents play a structure-determining role, but the effect of the aldehyde-substituents cannot be neglected.

2. In the infrared spectra around 1650—1607, 1560—1604 and 1242—1292, and 1300—1350 cm⁻¹ several bands can be found, which correspond to the $\nu\text{C—N}$, $\nu\text{C—O}$ and νNO_2 stretching vibrations, respectively. From the infrared spectra measured with KBr pellets and in solution (CCl₄ or C₂Cl₄) the existence of the keto form is not provable. This corresponds to the experimental fact that the visible spectra of the solid substances show no band in the range mentioned.

3. In the ¹H NMR spectra the δCHN and δOH signals appear at 8.50—8.80 and 13.00—13.80 ppm, respectively. The molecules exist predominantly in the enol-imine form; in the presence of the keto-amine form the splitting of the δCHN signal and a significant change of the aromatic proton signals may be expected. For IV and V the δCHN signals are doublets, due probably to coupling with the 6—H proton. The two δOH signals of IV and VI are well separated.

The fact that the quinoid form cannot be proved by infrared and ¹H NMR methods does not totally exclude its presence, because the solvents used in the above-mentioned methods do not favour the formation of this structure.

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СПЕКТРЫ ШИФ—ОСНОВАНИЙ ТИПА X,Y-БЕНЗИЛИДЕНО-4-Z-АНИЛИНА

И. Часар

Изучены УФ, ИК и ¹H ЯМР спектры ароматических Шиф-оснований типа X,Y-бензил-идено-4-Z-анилина

(X = H, 5-NO₂, 5-Br, Y = 2-OH, 2-NH₂, Z = OH, NO₂).

Сделаны заключения относительно образования keto-аминной таутомерной формы при определяющей роли заместителей в анилине с учетом влияния заместителей в альдегиде на интенсивность полос видимого спектра.