COMPARISON OF UV SPECTRA OF AROMATIC SCHIFF BASES AND THEIR REDUCTION PRODUCTS; POSSIBILITY OF ASSIGNMENT OF π* ← n TRANSITION OF AZOMETHINE GROUP

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The UV spectra of Schiff bases of 4-X-N(2-hydroxybenzylidene)aniline type (X = C_2H_5, OC_2H_5, CH_3, OCH_3, H, Cl, Br) and their reduction products obtained via $NaBH_4$ reduction were studied, primarily with regard to the appearance of the π* ← n transition characteristic of the azomethine group.

The spectra of Schiff bases prepared from salicylaldehyde with aliphatic mono- and diamines [1], aniline [2-5] and pyridine [6] derivatives, and their molecular conformations [7] were discussed previously, the absorption spectra of the secondary amines obtained from the above Schiff bases via $NaBH_4$ reduction have also been described [8].

The present paper compares the spectra of the Schiff bases (I) and those of their reduction products (II), containing -CH=N- and -CH_2-NH- linkages, respectively, and dis-

cusses the possibility of assignment of the $\pi^* \leftarrow n$ transition involving the lone-pair electrons of the azomethine group.

Experimental

The Schiff bases and the secondary amines were prepared as described previously [1, 2, 7, 8]. The spectra of n-hexane solutions were measured on a SPECORD UV-VIS spectrophotometer. The compounds studied show a reasonable solubility in this solvent, and the enol/keto tautomeric equilibrium [9-12] need not be reckoned with. The spectral data are presented in Table I.

Results and Discussion

The secondary amines are characterized by two high--intensity bands (210 and 230-240 nm, $\log\varepsilon > 4$) and a medium--intensity one (270-280 nm, $\log\varepsilon < 4$). If these spectra are compared with those of 1:1 mixtures of o-cresol and the corresponding aniline derivatives, the analogy is obvious (Fig. 1). Therefore, it seems that the spectra of the amine studied comprise the slightly perturbed absorptions of the two aromatic parts of the molecule, as more or less independent chromophores.

Table I

Spectral data of several Schiff bases and the corresponding secondary amine

X	Typ	Solv*		λ/nm and logε			
C$_2$H$_5$	SB	Hex.	211(4.28)	232(4.33)	269(4.11)	344(4.13)	
		MeOH		228(4.28)	270(4.03)	342(4.10)	430(2.48)
	SA	Hex.	210(4.39)	238(4.37)	278(3.78)	~295	
		MeOH	203(4.86)	246(4.36)	~280	~310	
OC$_2$H$_5$	SB	Hex.	212(4.24)	233(4.28)	269(4.01)	350(4.22)	
		MeOH		230(4.22)	268(3.96)	346(4.21)	430(2.46)
	SA	Hex.	207(4.32)	236(4.19)	279(3.56)	~300	
		MeOH	203(4.58)	243(4.18)	~275	310(3.43)	
CH$_3$	SB	Hex.	210(4.30)	231(4.35)	269(4.12)	346(4.16)	
		MeOH		228(4.32)	269(4.02)	340(4.10)	430(2.40)
	SA	Hex.	209(4.39)	235(4.35)	279(3.71)	~295	
		MeOH	203(4.67)	244(4.14)	~277	~300	
OCH$_3$	SB	Hex.	212(4.36)	230(4.37)	269(4.10)	350(4.28)	
		MeOH		224(4.19)	274(3.95)	347(4.18)	430(2.43)
	SA	Hex.	207(4.26)	234(4.13)	279(3.47)	~305	
		MeOH	203(4.28)	241(4.15)	~275	304(3.22)	
H	SB	Hex.	209(4.37)	229(4.42)	268(4.23)	344(4.15)	
		MeOH		224(4.27)	269(3.98)	340(3.93)	435(2.26)
	SA	Hex.	208(4.23)	233(4.18)	279(3.60)	?	
		MeOH	205(4.50)	246(4.16)	276(3.53)	~310	
Cl	SB	Hex.	213(4.43)	233(4.47)	272(4.31)	347(4.27)	
		MeOH		230(4.34)	272(4.16)	342(4.14)	436(4.04)
	SA	Hex.	207(4.32)	243(4.31)	278(3.60)	~300	
		MeOH	206(4.19)	255(3.98)	~280	307(4.21)	
Br	SB	Hex.	212(4.33)	232(4.39)	270(4.24)	344(4.21)	
		MeOH		228(4.42)	274(4.07)	344(4.10)	434(2.02)
	SA	Hex.	208(4.41)	244(4.32)	278(3.67)	~305	
		MeOH	205(4.56)	256(4.35)	~280	307(3.23)	

* SB: Schiff base, SA: secondary amine,
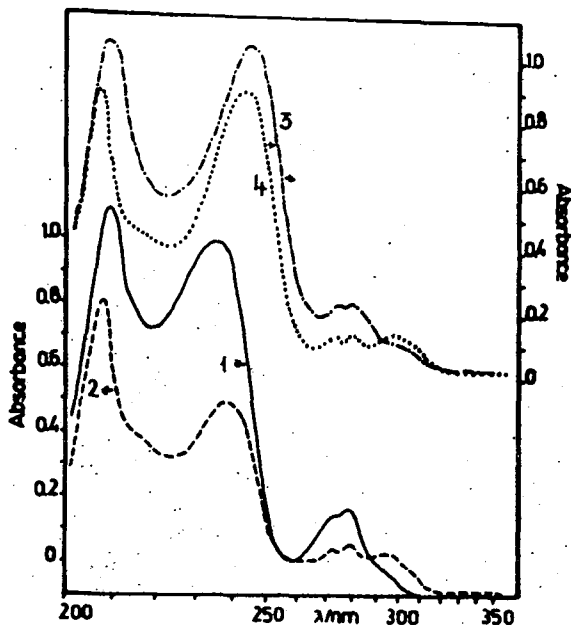Hex: n-hexane, MeOH: methanol

Figure 1.: UV spectra of 1: salicylidene-p-toluidine;
2: o-cresol + p-toluidine;
3: salicylidene-p-Cl-aniline;
4: o-cresol + p-Cl-aniline. $c = 5 \cdot 10^{-4}$ mol/dm^3,
d = 0.1 cm.

The three bands mentioned correspond to perturbed benzene bands (E_{1u}, B_{1u}, $B_{2u} \leftarrow A_{1g}$). This assignment is supported by the high intensities of the bands, the splitting of the long-wavelength band, and the fact that the λ_3/λ_2 values lie in the interval 1.15-1.20, which differs only slightly from that obtained for the monosubstituted benzene derivatives [13]. The bands shift bathochromically on going from n-hexane to methanol. Of course, a detailed assignment is difficult, because the $\pi^* \leftarrow \pi$ bands of the aldehyde and

aniline parts overlap.

The spectra of the Schiff bases are more complicated, since these three chromophores and their interactions must be taken into account. The spectra of the Schiff bases differ markedly from those of the corresponding secondary amines (Fig. 2). The difference is understandable for, with the transmission of the azomethine group, a uniform conjugated system involving the whole molecule is present (III)
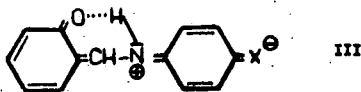
and the lone-pair of the nitrogen atom also takes part in the conjugation, to an extent depending on the dihedral angle [7].

Since the Schiff bases and the secondary amines studied differ only in the connecting bridge between the two aromatic systems, a comparison of their spectra is important. Characteristic features in the spectra are the high-intensity bands of the $\pi^* \leftarrow \pi$ transitions. The band due to the $\pi^* \leftarrow n$ transition of the non-bonding lone-pair electrons of the azomethine group is not readily observable, because this is relatively weak in intensity as compared to the $\pi^* \leftarrow \pi$ type transitions. The $\pi^* \leftarrow n$ transitions within the aromatic nucleus are also important, but this problem will not be dealt with now.

The unconjugated azomethine group gives a weak band in the range 230-250 nm, with $\log\varepsilon \sim 1.8-2.5$ [14, 15]. The band disappears on acidification of the solution, supporting the postulate that the lone-pair electrons are involved in the transition [15, 16]. Platt [17] and Sindman [18] estimated that the $\pi^* \leftarrow n$ transition lies at ~210 nm if the azomethine

group carries aliphatic substituents, and at ~250 nm or at ~290 nm if it is conjugated with a vinyl group or with a benzene ring. Because of the difficulty of assignment, the interpretation of the long-wavelength absorption of the Schiff bases and the assignment of the $\pi^* \leftarrow n$ transition have been the subjects of several conflicting reports [e.g. 24].

We have prepared several Schiff bases containing an n-butyl group on the carbon or on the nitrogen and of the azomethine group. The spectrum of butylidene-n-butylamine (Fig. 2) exhibits only a single band (236 nm, $\log\varepsilon = 2.30$),
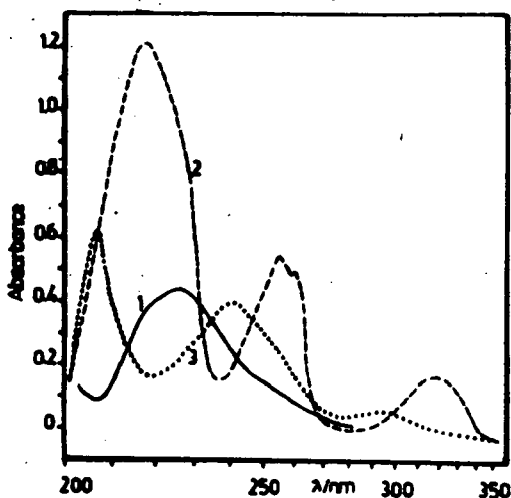

Figure 2.: UV spectra of 1: butylidene-n-butylamine; 2: salicylidene-n-butylamine; 3: n-butylidene-p-toluidine. $c = 5 \cdot 10^{-4}$ mol/dm^3, d=1.0 (1), 0.1 cm (2,3)

which can be assigned, in all likelihood, to the $\pi^* \leftarrow n$
transition. The maximum moves to higher frequencies on
change from non-polar to hydroxylic solvents with high per-
mittivity, which is characteristic of the $\pi^* \leftarrow n$ transition
[19-21]. The spectra of benzylidene-n-butylamine (246 and
280 nm, $\log\varepsilon$ = 4.16 and 3.13) and butylidene-aniline (235
and 287 nm, $\log\varepsilon$ = 4.03 and 3.42) differ only slightly from
those of benzaldehyde and aniline, respectively, but the
curves are flattened towards longer wavelengths, showing
the presence of a low-intensity band, which may be located
at around 300 and 320 nm, respectively. This band is pre-
sumably a $\pi^* \leftarrow n$ band which, as a consequence of the conjuga-
tion, displays a bathochromic shift. The spectrum of benzy-
lidene-aniline has a long tapering end at long wavelengths,
analysis of which suggests the presence of a weak band
($\log\varepsilon$ ~2.0) near 360 nm, due to a $\pi^* \leftarrow n$ transition [22,
23].

The conjugation of an aromatic system with the azo-
methine chromophore (having lone-pair electrons) generally
shifts the $\pi^* \leftarrow n$ band to longer wavelengths and produces a
large increase in intensity. Bonnett [24] suggested that an
aryl group appears to conjugate effectively when substi-
tuted on the carbon atom of the azomethine group, but it may
not do so when substituted on the nitrogen atom. Thus, the
spectrum of benzylidene-aniline differs in detail from that
of stilbene [25], because the N-phenyl group is twisted out
from the plane of the rest of the chromophore [24, 26].

A similar conclusion can be drawn in the case of salicy-
lidene derivatives. It is noteworthy that, in the spectrum
of salicylidene-n-butylamine (218, 256, 262 and 320 nm,
$\log\varepsilon$ = 4.38, 4.03, 3.90 and 3.51) (see Fig. 2), the intensi-
ty relation of the two maxima of the middle band is reversed

and the halfband width increases. Analysis of the curve gives
a weak band at 270 nm (logε ~ 2.50).

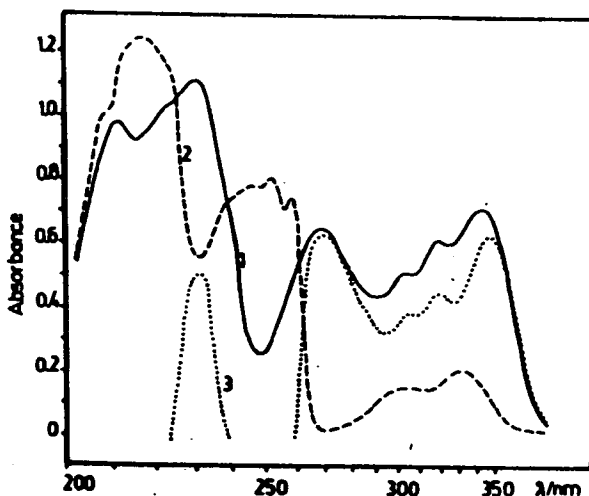The spectra of the salicylidene-anilines (Fig 3.) dif-

Figure 3.: Spectra of n-hexane solutions. 1: salicylidene-
-p-toluidine; 2: salicylaldehyde + p-toluidine;
3: (salicylidene-p-toluidine) - (salicylaldehyde+
+ p-toluidine), differential spectrum.
$c = 5 \cdot 10^{-4}$ mol/dm^3, d = 0.1 cm

fer completely from those of the components, and also from
the sum of the spectra of the components (Fig. 3). The
greatest difference can be observed in the range 280-360 nm,
resolution of which into gaussian curves results in several
bands, and we presume that the weak band (f ~ 10^{-4}) in the
interval 270-280 nm (logε ~ 2.60-2.80) is assignable to the

π^* ← n transition.

It is known [19] that, in general, absorption involving lone-pair electrons moves to higher frequencies if, for example, a hydrogen-bond stabilizes the lone-pair in the ground state. In the case of the salicylidene derivatives, an intramolecular hydrogen-bond is formed (IV) in which the
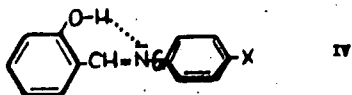
lone-pair also takes part; consequently, the promotion energy will be increased. The Schiff bases of salicylal-dehyde and 2-aminopyridines also display a weak band between 300 and 400 nm, which is probably a π^* ← n band [27].

It seems that the N-phenyl group does not appreciably influence the energy of the π^* ← n transition. This is understandable, because the N-phenyl ring is twisted out from the plane of the rest of the molecule; consequently, the conjugation between the aromatic ring and the azomethine linkage is limited and the 4-X substituents studied do not essentially influence the dihedral angle [7]. The probable data on the π^* ← n bands of the Schiff bases studied are given in Table II.

Table II

Characteristics on the π* ← n bands

Compound	λ/nm	logε
butylidene-n-butylamine	230	~2.30
benzylidene-n-butylamine	300	~2.45
n-butylidene-aniline	320	~2.40
benzylidene-aniline	360	~2.00
salicylidene-n-butylamine	270	~2.60
salicylidene-4-X-aniline	270-290	~2.60-2.80

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СРАВНЕНИЕ УФ СПЕКТРОВ АРОМАТИЧЕСКИХ ШИФФОВЫХ ОСНОВАНИЙ И ПРО-
ДУКТОВ ИХ ВОССТАНОВЛЕНИЯ: ВОЗМОЖНОСТЬ ОТНЕСЕНИЯ $\pi^* \leftarrow n$ ПЕРЕХОДА
В АЗОМЕТИНОВОЙ ГРУППЕ

Й. Часар

. Изучены УФ спектры Шиффовых оснований 4-x-N(2-гидрокси-
бензилидено) анилинового типа (x=C_2H_5, OC_2H_5, CH_3, OCH_3, H,
Cl, Br) и их продуктов восстановления, после действия $NaBH_4$.
Основное внимание было обращено на явление $\pi^* \leftarrow n$ перехода харак-
терного для азометиновой группы.