

# SPECTRA AND MOLECULAR CONFORMATIONS OF AROMATIC SCHIFF BASES

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The torsion angles  $\theta_N$  of the aniline ring in benzylideneaniline and oxybenzylideneaniline Schiff bases were calculated and discussed in connection with the molecular conformation.

The u.v. spectrum of benzylideneaniline differs markedly from those of stilbene and *trans*-azobenzene [1], although the azomethine and vinyl groups are isoelectronic [e.g. 2—4]. Stilbene has an intense band at 295 nm ( $\pi \rightarrow \pi^*$ ;  $\epsilon = 24\,000$ ) and a less intense band at 229 nm ( $\epsilon = 21\,300$ ), while the spectrum of benzylideneaniline exhibits a shoulder at 315 nm ( $\epsilon = 8800$ ) and a maximum at 262 nm ( $\epsilon = 21\,300$ ) [5]. The intensity of the first absorption band of benzylideneaniline is considerably lower than that of stilbene; this difference must be due to the different electronic structures and molecular conformations (see Fig. 1).

BROCKLEHURST [6] suggested that the 315 nm band of benzylideneaniline corresponds to the intense band at 295 nm of stilbene, and that the decrease in the intensity is due to the non-coplanarity of the molecule. If the molecule is planar, its  $\pi$  system would extend over both phenyl rings and the azomethine group, and the spectrum would be expected to be similar to that of stilbene. However, if the molecule is non-coplanar, the spectrum should be more or less a superposition of the spectra of the two weakly interacting moieties of the molecule. ISMAILSKII and SMIRNOV [7] postulated that the nitrogen lone pair can conjugate with the N—Ph ring. This implies a non-coplanar molecular structure, since the N—Ph ring can only conjugate with the nitrogen lone pair if it is rotated out of the plane of the conjugate system consisting of the C—Ph and the azomethine groups. The non-planar structure is energetically less favourable than the planar configuration; in the

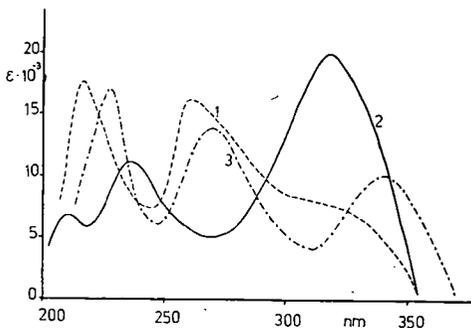
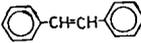
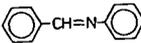
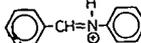
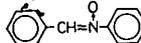


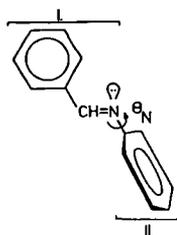
Fig. 1. Spectra of methanolic solutions of benzylideneaniline (1), benzylideneaniline nitrone (2) and 2-OH-benzylideneaniline (3)

latter the  $\pi$  conjugation extends over the whole molecule. On the basis of theoretical calculations, SMITH [8] has shown that an increase in the steric requirement for planarity of the base results in a marked decrease in the extinction of the 315 nm band, with a corresponding increase in the intensity of the 262 nm band. If the nitrogen lone pair is localized by protonation or by nitrone formation, a planar structure is energetically favoured for the benzylidene-aniline molecule, since the nitrogen lone pair is not available for conjugation with the N—Ph ring; the spectrum is expected to be similar to that of stilbene (Table I). The conjugation increases the N—Ar bond order, as indicated by a shift of the infrared absorption band to higher frequency [9].

Table I  
Long-wave band data on stilbene and benzylideneanilines

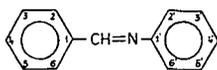
Compound	nm	$\epsilon$	Lit.
	295 298	24 000 27 500	[5] [6]
	315 310	8 800 8 200	[5] [6]
	335 335	24 000 19 500	[5] [6]
	322 316	19 900 20 000	[15] [6]

In benzylideneanilines, benzaldehyde type (I) and aniline type (II) molecular halves are distinguishable. EBARA ET AL. [10] assumed that the absorption bands at 262 and 315 nm are due to I and II, respectively (Structure 1). It was found that sub-



stitution on II had little effect on the 262 nm band, whereas marked shifts were experienced in the 315 nm band. EL-BAYOUMI ET AL. [5] assigned the bands of benzylideneanilines as follows. The  $\sim 310$  nm band is sensitive to N—Ph substitution and corresponds to a transition to a benzene  ${}^1B_{2u}$  state in the aniline part. The 262 nm band is interpreted as a transition to a CT state, in which the azomethine group acts as an electron acceptor and the aldehyde ring as an electron donor. The 238 nm band corresponds to the CT band of the aniline part. The 218 nm band is sensitive to C—Ph substitution and is assigned as a perturbed  ${}^1B_{1u}$  band of the benzal part.

The effect of twisting of the aniline ring of benzylideneaniline and of similar molecules (Structure 2) is to decrease the resonance throughout the length of the



molecule, but at the same time it increases the interaction of one of the nitrogen lone pairs with the twisted phenyl ring. Thus, for benzylideneaniline the decrease in the resonance integral of the C—N  $\pi$ -bond as a result of the twist will be compensated for to some extent by an increase in the resonance integral as a result of conjugation of the nitrogen lone pair with the N—Ph ring. The resonance integral of a bond may be taken as proportional to the cosine of the angle of twist,  $\theta_N$  [11]. The value of this twist angle,  $\theta_N$ , can be estimated from the approximate formula [12]  $\cos^2 \theta_N = \epsilon_x / \epsilon_0$ , where  $\epsilon_x$  and  $\epsilon_0$  are the molar extinctions of the compounds with non-planar and planar structure, respectively.

Similar phenomena can be found for the oxybenzylideneanilines, too; the aniline part in these molecules is rotated out of the plane of the molecule.

The nitrones are suitable reference structures. In these molecules the N-electrons are occupied in the bond with oxygen, which excludes the effect of competitive conjugation and results in almost complete planarity [13]. KRASZOVICKIJ ET AL. [14] have proposed reference molecules in which the aniline ring is perpendicular to the plane of the molecule.

The  $\theta_N$  values published in this work were calculated on the basis of extinctions measured in apolar solvents (benzene, cyclohexane, n-heptane). The reference benzylideneaniline nitron has a band at 316 nm, with  $\epsilon = 19\,900$ . MINKIN ET AL. [15] have prepared and measured the extinctions of the corresponding nitrones of all the Schiff bases studied, and with these  $\epsilon$ -values have calculated the twist angles. We have used only benzylideneaniline nitron as reference molecule for all the compounds studied, hoping to obtain better information about the substitution effects, too.

In Table II are summarized the spectral data and the calculated angles for several benzylideneaniline derivatives. It is an observation of importance that the reflectance spectra are similar to the solution spectra, so it seems that the stable configurations of the molecules do not change upon dissolution. X-ray analysis [16] indicates that the angle of twist is near  $55.2^\circ$  for benzylideneaniline. By means of photoelectron spectroscopy, BALLY ET AL. [17] estimate  $\theta_N = 36^\circ$ , and by means of gas-phase electron diffraction TRAUETBURG ET AL. [18] have determined  $\theta_N = 52^\circ$ . AKABA ET AL. [19] estimate a solution-phase  $\theta_N = 30\text{--}35^\circ$  and a gas-phase  $\theta_N = 48\text{--}55^\circ$ . Our calculated  $\theta_N = 54^\circ$  for the parent benzylideneaniline is in good agreement with the literature data [14, 16, 18]. Considerable changes can be observed for the substituted aniline derivatives. From Table II it can be seen that the twist angles are increased for the 2'- and 2', 6'- dimethyl substituents:  $\theta_N = 62^\circ$  and  $73^\circ$ , respectively. However, in the case of the 3'-, 3', 5'- or 4'-methyl derivatives, no significant differences can be observed. A Schiff base with an electron-donating or electron-withdrawing group in the 4' position should absorb bathochromically or hypsochromically, respectively, relative to the isomeric Schiff base with the same group in the 4 position of the aldehyde ring. Independently of the character of the 4'-X substituents, the  $\theta_N$  values show only small changes and no correlation can

Table II  
Spectral data and twist angles for benzylideneanilines

X	Y	nm	$\epsilon$	$\theta_N$	Lit.
H	H	314	6 740 <sup>8</sup>	54	55 <sup>15</sup>
H	2'-F	314	6 480	55	
H	2'-CH <sub>3</sub>	325	4 230 <sup>8</sup>	63	64 <sup>15</sup>
H	3'-CH <sub>3</sub>	319	6 150 <sup>8</sup>	56	56 <sup>15</sup>
H	4'-F	313	8 470	49	
H	4'-Cl	317	5 410	59	55 <sup>15</sup>
H	4'-Br	317	8 110	50	
H	4'-OH	284	11 510	40	
H	4'-CH <sub>3</sub>	321	8 070	50	52 <sup>15</sup>
H	4'-OCH <sub>3</sub>	287	9 330	47	
H	3', 5'-(CH <sub>3</sub> ) <sub>2</sub>	320	7 200 <sup>8</sup>	53	
H	3', 6'-(CH <sub>3</sub> ) <sub>2</sub>	331	1 740 <sup>8</sup>	73	
H	2', 4'-Cl <sub>2</sub>	321	7 300	53	
H	2', 6'-Cl <sub>2</sub>	321	2 720	68	
4-CH <sub>3</sub>	H	319	8 100 <sup>8</sup>	50	
2,4,6-(CH <sub>3</sub> ) <sub>3</sub>	H	326	6 300 <sup>8</sup>	56	
2,6-(CH <sub>3</sub> ) <sub>2</sub>	H	322	6 450	55	
4-OH	H	315	12 020 <sup>10</sup>	39	
4-OCH <sub>3</sub>	H	315	10 950 <sup>10</sup>	42	
4-Cl	H	318	9 950 <sup>10</sup>	45	

be found between this effect and the  $\theta_N$  angle. AKABA ET AL. [19] present evidence that the twist angle  $\theta_N$  is significantly changed by the introduction of a 4'-NO<sub>2</sub> group. Electron-donor and/or electron-acceptor substituents in the aldehyde ring do not have a drastic influence on the  $\theta_N$  values [15]. According to several authors [19—21], the benzylidene rings are also twisted, but in the opposite sense and by smaller amounts ( $\theta_N \approx 8$ —15°).

The spectral data and twist angles of oxybenzylideneanilines are listed in Table III. It is seen that 2-OH-benzylideneaniline has the highest twist angle ( $\theta_N = 57^\circ$ ), in agreement with the literature data ( $\theta_N = 55^\circ$ ) calculated from spectroscopic [22] and X-ray measurements [20]. All the 2-OH-benzylideneaniline derivatives studied have lower angle values, varying in the range 30—50°. No clear-cut correlation can be found between the twist angles and the electron-donor or electron-acceptor properties of the N—Ph substituents. The general tendency is for  $\theta_N$  to change in the sequence ortho  $\gg$  meta  $>$  para. Except for 2-OH-benzylideneaniline, our data agree well with the values published by KRASZOVICKIJ ET AL. [14].

A similar tendency may be observed for the 2-OH-3-OCH<sub>3</sub>-benzylidene and 4-OH-benzylidene derivatives, while in the case of 4-OH-3-OCH<sub>3</sub>-benzylidene derivatives the molecule containing no substituent on the N—Ph ring gives the smallest twist angle,  $\theta_N = 37^\circ$ .

In any case, our calculated  $\theta_N$  values differ markedly from the literature data. This is understandable, as other authors have calculated with other reference molecules or used the extinction of alcoholic solutions for their calculations. It is well known that in polar, H-bonding solvents the geometry and electronic structures of Schiff bases change considerably; a tautomeric equilibrium is present. For 2-OH-benzylideneaniline, for example,  $\epsilon = 10\,000$  is measured in methanol, leading to a

Table III

Spectral data and twist angles for oxybenzylideneanilines

X	Y	nm	$\epsilon$	$\theta_N$	Lit.
2-OH	H	342	5 750	57	44 <sup>14</sup> , 55 <sup>22</sup>
2-OH	2'-OH	357	10 715	43	
2-OH	3'-OH	342	11 750	40	43 <sup>14</sup>
2-OH	4'-OH	350	13 800	34	31 <sup>14</sup>
2-OH	2'-OCH <sub>3</sub>	347	11 750	40	
2-OH	3'-OCH <sub>3</sub>	343	9 330	47	43 <sup>14</sup>
2-OH	4'-OCH <sub>3</sub>	351	12 300	38	33 <sup>14</sup>
2-OH	2'-CH <sub>3</sub>	362	10 000	45	
2-OH	3'-CH <sub>3</sub>	342	10 000	45	42 <sup>14</sup> , 56 <sup>22</sup>
2-OH	4'-CH <sub>3</sub>	345	11 480	41	37 <sup>14</sup> , 52 <sup>22</sup>
2-OH	2'-F	343	9 120	47	
2-OH	3'-F	344	9 120	47	
2-OH	4'-F	342	10 960	42	
2-OH	2'-Cl	347	10 230	44	
2-OH	3'-Cl	343	10 720	43	46 <sup>14</sup>
2-OH	4'-Cl	345	11 750	40	42 <sup>14</sup> , 55 <sup>22</sup>
4-OH	H	320	10 000	45	
4-OH	2'-OCH <sub>3</sub>	333	6 920	54	
4-OH	3'-OCH <sub>3</sub>	344	9 330	47	
2-OH-3-OCH <sub>3</sub>	H	318	9 550	46	
2-OH-3-OCH <sub>3</sub>	3'-OCH <sub>3</sub>	323	12 020	39	
2-OH-3-OCH <sub>3</sub>	4'-OCH <sub>3</sub>	338	14 120	33	
3-OCH <sub>3</sub> -4-OH	H	322	12 600	37	
3-OCH <sub>3</sub> -4-OH	2'-OCH <sub>3</sub>	322	6 310	56	
3-OCH <sub>3</sub> -4-OH	3'-OCH <sub>3</sub>	322	8 910	48	
3-OCH <sub>3</sub> -4-OH	4'-OCH <sub>3</sub>	339	14 120	33	
2-OH-5-CH <sub>3</sub>	H	320	9 120	47	
2-OH-5-CH <sub>3</sub>	4'-CH <sub>3</sub>	323	12 590	37	
2-OH-5-CH <sub>3</sub>	2'-Cl	329	8 710	49	
2-OH-5-CH <sub>3</sub>	3'-Cl	322	8 910	48	

calculated  $\theta_N=45^\circ$ , in contrast to the  $\theta_N=57^\circ$  obtained from the extinction of the benzene solution. The enol imine/keto amine equilibrium in alcoholic solution and the partial quinoidal rearrangement of the molecules influence the bond orders and bond distances, and at same time decrease the possibility of  $n\pi$ -conjugation.

In the case of multiple substitution, no appreciable change in  $\theta_N$  can be observed; *e.g.* for 2-OH-3-OCH<sub>3</sub>-benzylidene-3', 4'-dimethoxyaniline, 3-OCH<sub>3</sub>-4-OH-benzylidene-3', 4'-dimethoxyaniline and 2-OH-benzylidene-3', 4'-dimethoxyaniline,  $\theta_N=35^\circ$ ,  $33^\circ$  and  $35^\circ$ , respectively.

It is important to note that the twist angles  $\theta_N$  calculated in this way give the degree of torsion of the N—Ph ring only approximately. The observed decrease in the extinction is not only due to the non-coplanarity of the N—Ph ring; the inductive and mesomeric effects of the substituents also play an important role. To distinguish these effects on the basis of spectroscopic investigations alone is not possible.

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КОНФОРМАЦИИ МОЛЕКУЛ И СПЕКТРЫ АРОМАТИЧЕСКИХ  
ОСНОВАНИЙ ШИФФА

Й. Часар

Рассчитаны углы поворота анилиновых колец в основаниях Шиффа бензилиденанилинового и оксibenзилиденанилинового типов и обсуждены возникающие конформации молекул.