UV AND ¹H NMR SPECTRA AND CONFORMATIONS OF SUBSTITUTED N-BENZYLIDENEANILINES

By

J. Császár

Institute of General and Physical Chemistry, József Attila
University, P.O.B. 105, H-6701 Szeged, Hungary

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The UV and ¹H NMR spectra of forty-three N-benzylidene-
aniline derivatives were compared and the substituent effects
on the molecular conformation were discussed on the basis of
the twisting of the aromatic rings.

Introduction

The results of theoretical [1-7], crystallographic [8-12]
and spectroscopic [7, 13-20] investigations on N-benzylidene-
aniline (BA; I) and its substituted derivatives have been in-
terpreted in terms of the twisting of the aromatic rings. UV
absorption measurements revealed that the spectrum of BA differs
markedly from those of the isoelectronic trans-stilbene and
trans-azobenzene, and it can be concluded that the molecule is
non-planar: the C-phenyl and the N-phenyl rings twist away
from the other part of the molecule by different amounts (8-14°
and 30-90°, respectively; II). One very interesting problem is

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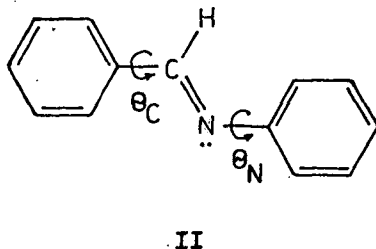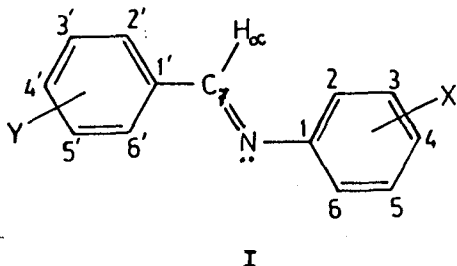
how substituent effects influence the conformation of the BA
molecule and how this phenomenon is reflected in the different
spectral characteristics.

In earlier papers [21-24] we discussed the UV and ^{1}H NMR
spectra of the salicylideneaniline-type Schiff bases and, as a
continuation of this work, we have now studied the spectral
behaviour of the N-benzylideneanilines. In this work we report
UV and ^{1}H NMR data.

Experimental

The Schiff bases were prepared by refluxing for about 15
min equimolar amounts of the appropriate aldehyde and aniline
derivatives in methanol. After the solution was cooled, the
crude crystalline products precipitated out; they were filtered
off, washed with cool ethanol and ether, and recrystallized
from 1:1 methanol-benzene. The analysis data and m.p.s were con-
sistent with the literature data [2, 19, 42].

The UV spectra were recorded on a SPECORD UV-VIS spectro-
photometer in the spectral range 200-500 nm, using spectrosco-
pically pure solvents and 1.0 or 0.1 cm quartz cells. The [1]H
NMR spectra were measured in $CDCl_3$ solution on a JEOL 60 MHz
instrument at room temperature, using TMS as internal standard.

Results and Discussion
UV spectra

The electronic spectra of BA and its derivatives have
already been reported [2-4, 7, 13-15, 18, 19, 25-27]. Several
authors [8-12] have determined the molecular structures of
these compounds by X-ray crystallography. Their absorption
spectra may be characterized by three high-intensity bands, at
around 230 (v_1), 280 (v_2) and 330 nm (v_3). These bands can be
assigned to the $\pi^* \leftarrow \pi$ transitions [2, 4, 7, 17, 18]; however,
in some cases the v_2 and v_3 bands have a $\pi^* \leftarrow n$ character, too
[7].

BA has an electronic structure similar to that of trans-
stilbene, since the -CH=N- and -C=C- groups are isoelectronic
[e.g. 2, 3, 14]. Stilbene gives an intense band at 295 nm and

a less intense one at 229 nm, while the spectrum of BA contains a shoulder at 315 nm and a band at 262 nm (Fig. 1). BROCKLEHURST
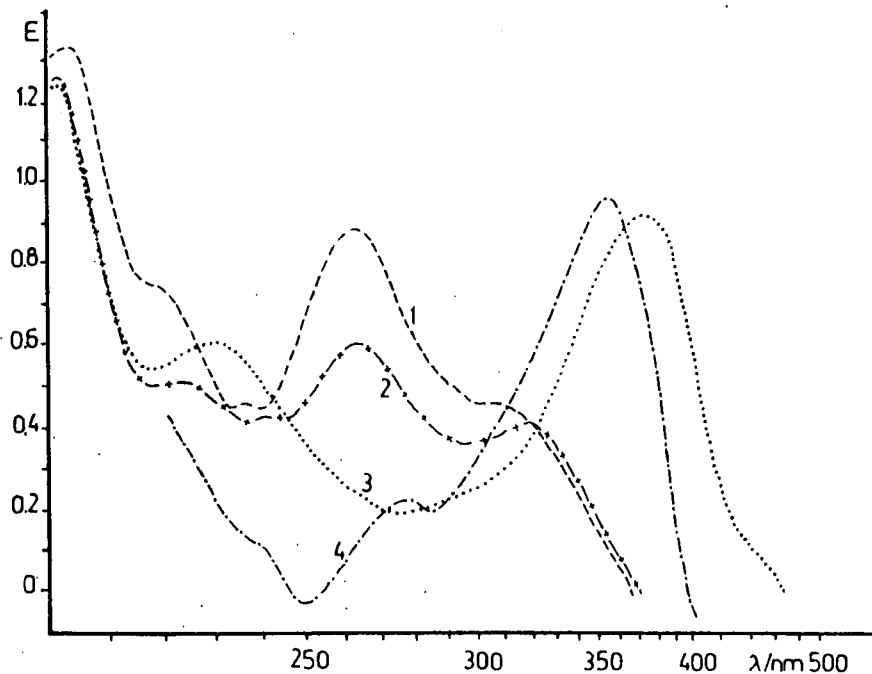
Fig.1. UV spectra of BA (1), c=4.2.10^{-4}; the compound with X= CH_3 (2), c=3.9.10^{-4}; the compound with X=NO_2 (3), c=2.5.10^{-4} mol/dm^3, in methanol; BA in concentrated sulphuric acid (4), c=3.1.10^{-4} mol/dm^3.

[14] suggested that the 315 nm band of BA corresponds to the 295 nm band of stilbene. The intensity of the 315 nm band is reduced compared to that of stilbene; this is due to the non-planarity of BA. The conformations of BA in solution and in the crystals are very similar, as demonstrated by the similarity of the absorption and reflection spectra [see e.g. ref. 30 and references therein].

From a comparison of the spectral data on several 4-X and 4'-Y derivatives (Table 1), it may be stated that the positions of the substitution and the character of the substituents play important roles. A Schiff base having an electron-donating group

Table 1

UV spectral data for BA and its 4- and 4'-derivatives

Y	X	Solvent[*]	nm and ε			θ_N
N(CH$_3$)$_2$	H[a]	CH	238(15100)		356(39100)	
H	N(CH$_3$)$_2$	MA		252(20200)	374(18000)	30[e], 34
OCH$_3$	H[a]	CH	222(18600)	280(19600)	315(12900)	43[f], 38
H	OCH$_3$[b]	EA	229(12900)	264(13100)	330(13300)	33[e], 35
CH$_3$	H[c]	CH	227(14500)	268(18600)	319(8100)	48
H	CH$_3$	MA	224(13200)	265(15050)	321(10050)	52[f], 41
H[d]	H	EA	236(10100)	263(16400)	315(6200)	44[e], 55[f], 54
H	F	MA	228(18500)	263(16600)	312(9550)	36
Cl	H	MA	225(14950)	266(18050)	317(10900)	38
H	Cl	MA	223(13800)	264(16500)	311(10500)	42[e], 55[f], 39
Br	H	MA	233(20050)	269(19050)	318(12500)	42
H	Br	MA	232(19950)	263(18400)	312(10600)	38[e], 40
I	H	MA		266(21900)	324(13550)	
H	I	MA		262(20200)	310(11600)	40
NO$_2$	H[d]	CH	238(16250)	288(15600)	346(10200)	44[f]
H	NO$_2$[b]	EA	243(17300)	290(3040)	380(16800)	~80

a) ref.[18],   b) ref.[16],   c) ref.[2],   d) ref.[28],   e) ref.[32],   f) ref.[3];

[*] CH: cyclohexane,   EA: ethyl alcohol,   MA: methyl alcohol

in position 4 should absorb at longer wavelengths, in contrast to the base with the same substituent in position 4'; for an electron-withdrawing group the reverse tendency may be true.

The data in Table 1 show that for Y=H the ν_3/ν_2 or $\Delta\nu = \nu_3 - \nu_2$ values change regularly with the HAMMETT constant σ_p, but no appreciable tendency is to be observed for the halogen group. The very large bathochromic shift of the 4-NO$_2$ derivative may be interpreted in terms of the conjugation effect of the nitro group (III).
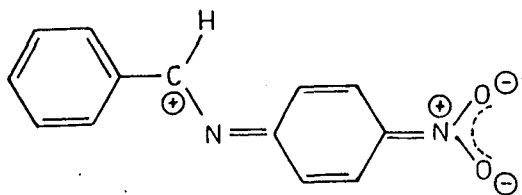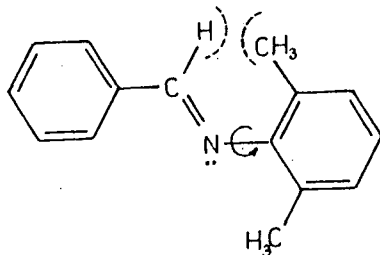
III   IV

.With substituents in positions 2 or/and 2,6 a considerable steric factor exists (IV) and, as may be seen from Table 2, the

Table 2

UV data for some 2-, 2,6- and 2',4',6'-substituted derivatives

X,Y	Solvent[*]	nm and ε		
2-OCH$_3$[a)]	EA	246(11700)	~263	330(3850)
2-CH$_3$[b)]	CH	212(18100)	263(17100)	330(5900)
2-F[c)]	MA	225(17500)	261(17780)	310(8130)
2-Cl	MA	244(12400)	260(11350)	330(2800)
2-Br[c)]	MA	230(20100)	261(19700)	312(5620)
2-I	MA		256(22500)	321(4850)
2,6-(CH$_3$)$_2$[b)]	CH	213(21300)	253(22300)	340(1800)
2',6'-(CH$_3$)$_2$	MA	212(22550)	267(20900)	313(2950)
2,4,6-(CH$_3$)$_3$	MA	213(19750)	258(20300)	322(3700)
2',4',6'-(CH$_3$)$_3$	CH	210(20800)	273(17500)	326(6300)

a) ref.[16],   b) ref.[7],   c) ref.[29],   d) ref.[2];   [*] EA: ethyl alcohol, CH: cyclohexane, MA: methyl alcohol

absorbancy of the ν_3 peak decreases, while that of the ν_2 band increases; the change is due to the steric hindrance of planarity of the Schiff base molecules. The intensity of the ν_2 band decreases in the sequence H $\sim$ 2-CH$_3$ $\sim$ 2,6-(CH$_3$)$_2$. The effects of the substituents in position 2' are not so significant; the $\varepsilon_2/\varepsilon_3$ values for BA and the 2-CH$_3$ and 2,6-(CH$_3$)$_2$ derivatives are 2.65, 2.90 and 12.40, respectively, while for the 2',4',6'-(CH$_3$)$_3$ derivative it is only 2.78.

Interpretation of the spectra of the BA derivatives containing different substituents in positions 4,4' (Table 3) is

Table 3

UV data for Schiff bases containing different substituents in 4 and 4'-positions

| X	Y	Solvent[*]	nm and ε		
CH$_3$	OCH$_3$[a)]	CH	221(18400)	280(20500)	322(14500)
OCH$_3$	OCH$_3$[a)]	CH	221(20300)	280(22300)	330(17900)
CH$_3$	NO$_2$	MA	238(18600)	267(10480)	355(8350)
OCH$_3$	NO$_2$	MA	240(16750)	263(12600)	374(9550)
N(CH$_3$)$_2$	NO$_2$	MA		277(20400)	436(21000)
N(CH$_3$)$_2$	NO$_2$[b)]	CH		272(15200)	447(21300)[c)]
NO$_2$	N(CH$_3$)$_2$	MA	246(10400)	302(7700)	386(29350)
NO$_2$	N(CH$_3$)$_2$[b)]	CH	253(10900)	294(6560)	409(36800)[c)]

a) ref.[18], b) ref.[28], c) the corresponding indole derivatives;
[*] MA: methyl alcohol, CH: cyclohexane

complicated. The compounds with CH$_3$ or/and OCH$_3$ groups give spectra quite similar to those of the compounds listed in Table 1; our calculations indicate that these compounds have a twisted conformation with a twist angle of about 40-45°. A similar conclusion may be drawn for 4-methyl(methoxy)-N-(4-nitrobenzylidene)aniline. However, the spectrum of 4-dimethylamino-N-(4-nitrobenzylidene)-aniline shows a close similarity [11] to those of the corresponding indole (Fig. 2) [28] and stilbene [11] (θ_C = 3.5° and θ_N = 9.1° [11]). 4-Nitro-N-(4-dimethylaminobenzylidene)aniline is not planar and a very highly conjugated system can be formed (V). The conjugation effect of the nitro group also plays an impor-
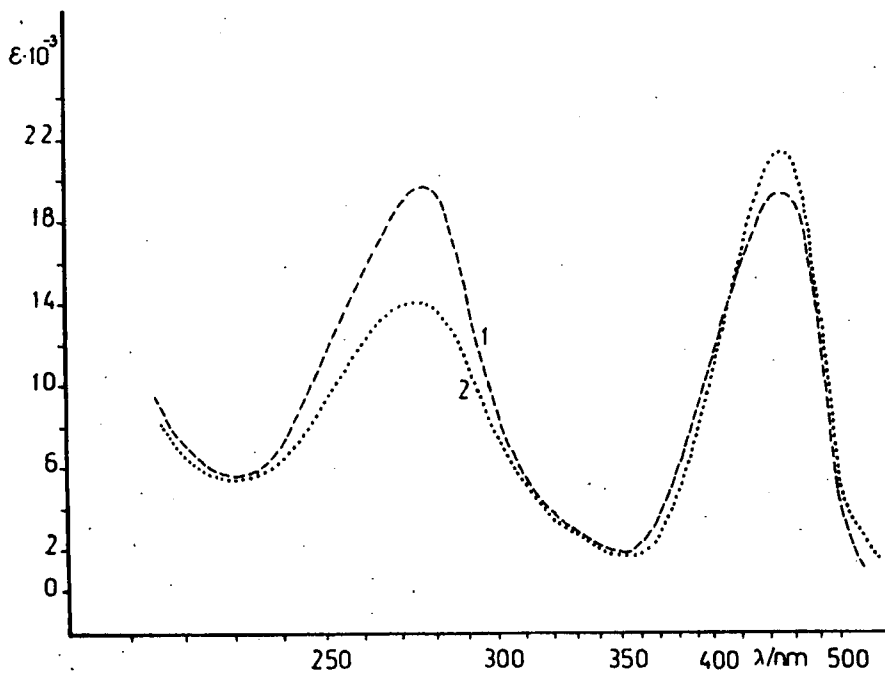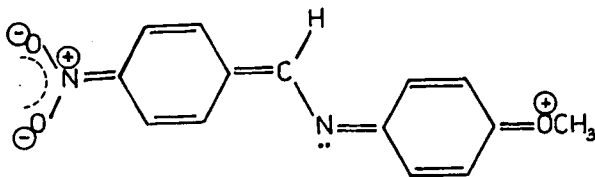
Fig.2. UV spectra of 4-dimethylamino-N-(4-nitrobenzylidene)-aniline (1) and of 5-dimethylamino-3,3-dimethyl-2-(p-nitro-phenyl)-3H-indole (2) in cyclohexane.
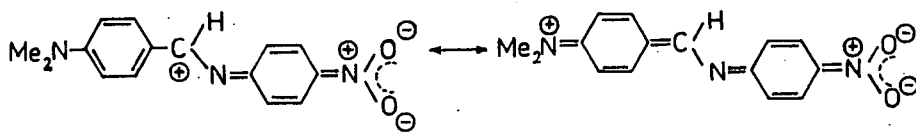

V

tant role in the formation of a quinoidal system (VI) in, for


VI

example, 4-methoxy-N-(4-nitrobenzylidene)aniline, with a consi-
derable bathochromic shift (see Table 3). SKRABAL et al. [28]
concluded that the former compound is planar or nearly planar.
On the other hand, the electron-acceptor CN derivative gives a
spectrum quite similar to that of BA; the ring is rotated around
the =N-C- bond. It seems that, with strong electron-donor and
electron-acceptor groups in positions 4 and 4', the π-electron
system extends to the whole molecule with a planar or nearly
planar conformation.

If the molecule is planar, the π system extends over both
of the phenyl rings and the azomethine group; the spectrum is
similar to that of stilbene. However, if the molecule is non-
planar, the spectrum should be a superposition of the spectra
of two weakly interacting moieties $\underline{A}$ and $\underline{B}$ (VII) [17]. This is
supported by the fact that the ν_3 band shifts to longer wave-
lengths as a result of N-phenyl substitution, while the ν_2 bands
do not change their position. Thus, it is very probable that the
ν_2 bands correspond to the C-phenyl ring, while the ν_3 bands
correspond to the N-phenyl ring in the molecules.
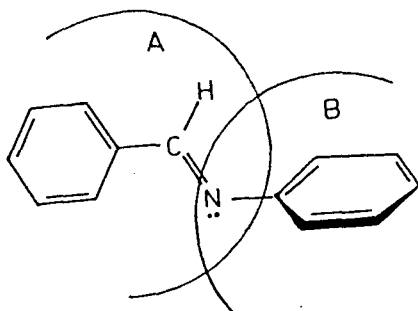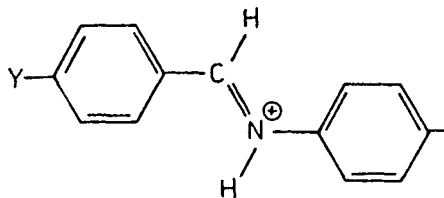
VII   VIII

If the nitrogen lone-pair is localized by protonation [3, 14]
or by nitrone formation [3], the Schiff base favours the planar
structure (VIII). In this case the lone-pair is not available for
conjugation with the N-phenyl ring, and the spectrum of the pro-
tonated Schiff base is expected to be similar to that of _trans_-
stilbene. According to theoretical calculations [28], the non-
planar twisted conformation is favoured by ca. 8.4 kJ/mol; con-
sequently, the -C=N- bond order is a function of the twist angle,

and a combination of the twisting and substituent effects should
be taken into account in the explanation of the observed behaviour.

These Schiff bases show an anomalous solvent effect; the in-
tensities of the ν_3 and ν_2 bands are higher in alcoholic and in
benzene solution, respectively. This observation supports the
conclusions that the molecules have a non-planar conformation
and that the nitrogen lone-pair plays an important role in the
spectra [14]. If hydrogen-bonding occurs between the lone-pair
and the solvent molecule, the partial localization of the nitro-
gen doublet should favour a resonance contribution from the whole
molecule.

If the spectra of the N-benzylideneanilines are measured in
concentrated sulphuric acid, protonation takes place and the
absorbancy of the ν_3 band ($\varepsilon = 21000$; Fig. 3) increases conside-
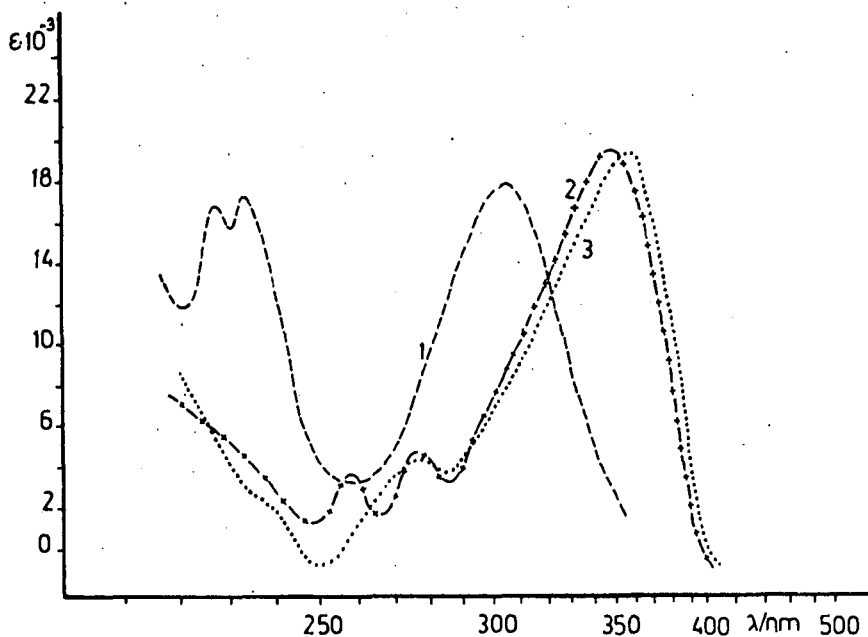
Fig.3. UV spectra of 3,3-dimethyl-2-phenylindolenine in hexane
(1) and in concentrated sulphuric acid (2); BA in concentrated
sulphuric acid (3).

rably. These spectra are similar to that of stilbene [28, 30].
In organic solvents the N-phenyl ring is twisted out of the plane

of the conjugate system consisting of the C-phenyl ring and the azomethine group, and the nitrogen lone-pair takes part in the π conjugation with the N-phenyl ring. In the protonated planar form the π conjugation extends over the whole molecule, but the nitrogen lone-pair does not take part in the π conjugation.

The degree of twisting of the N-phenyl ring around the =N-C-bond may be given in terms of the twist angle, θ_N, which can be estimated through the approximate formula $\cos^2\theta_N = \varepsilon/\varepsilon_O$ [31]; ε and ε_O are the molar extinctions of the base with non-planar (measured, e.g., in benzene) and planar (measured, e.g. in concentrated sulphuric acid) structures, respectively.

The θ_N values determined by different methods show considerable difference; e.g. for BA $\theta_N = 36^O$ [from UV data [32]), 46° (from HMO calculations [20]), 52° (from electron diffraction studies [5]), 55.2^O (according to X-ray structural determination [10]), 65° (from NDDO calculation [6]). The different values make it necessary to calculate the twisting angles from data obtained by the same method under the same experimental conditions. It is interesting that the calculated θ_N values do not differ appreciably for the 4-X derivatives, except for the $4-NO_2$ compound, and the substituents in the C-phenyl ring influence the twisting of the N-phenyl ring only slightly. The $2-CH_3$ and $2,6-(CH_3)_2$ compounds give twist angle $\theta_N = 48-55^O$ and $> 77^O$, respectively [34], corresponding to the high steric hindrance.

The twisted conformation of the N-benzylideneanilines is supported by several other experimental facts and theoretical considerations [35-39], as discussed, for instance, in [3].

Unfortunately, from UV spectral data alone it is not possibl to conclude anything about the twisting of the C-phenyl ring.

^{1}H NMR spectra

Several studies have been reported [e.g. 40-49] on the effects of substituents on the NMR spectra of N-benzylideneanilines. In this work we discuss only the shift of the azomethine proton, H_α; the data are given in Tables 4-6.

The 4- or 4'-substituted compounds show an anomalous substituent effect on the H_α chemical shift. With an electron-withdra-

Table 4

Chemical shifts for H_α atom of the 4- or 4'-substituted
N-benzylideneanilines

Substituents	δH_α (ppm)	
	X = H	Y = H
$N(CH_3)_2$	8.27[a], 8.35[b], 8.31	8.54[b], 8.47
OCH_3	8.35[a], 8.40[b], 8.38	8.45[a], 8.50[b], 8.51
CH_3	8.34[a], 8.50[b], 8.46	8.39[a], 8.48[b], 8.45
H	8.49[b], 8.47	
F	8.43	8.40[c], 8.48
Cl	8.36[a], 8.50[b], 8.45	8.39[a], 8.51[b], 8.48
Br	8.36[a], 8.44	8.40[a], 8.44
I	8.45	8.36[a], 8.37
NO_2	8.54[a], 8.56[b], 8.52	8.46[b], 8.44

a) ref[35],   b) ref.[38],   c) ref.[40]

wing substituent in position 4, H_α exhibits an upfield shift
with a positive ρ [from the plot of δH_α vs. $\dot\sigma_p$) value, whereas
with the same substituent in position 4', H_α exhibits a normal
downfield shift with a negative ρ value. The H_α shifts for the
4'-derivatives correlate with the HAMMETT constants σ_p [40, 41,
45], while for the 4-derivatives there is no similar correlation
[42]. In general, it may be said that the 4-X substituents have
only weak effects on the H_α chemical shift [43] (Table 4).

The directions and magnitudes of the observed changes may
be interpreted through the change in the twist angle Θ_N [44],
which is sensitive to the positions of substitution and to the
properties of the substituents. With the strong electron-with-
drawing NO_2 and the strong electron-donating $N(CH_3)_2$ groups,
the picture is more complicated. The 4-NO_2 group generally results
in an upfield shift, and the 4-$N(CH_3)_2$ group in a downfield shift.
The 4-NO_2 group enhances the delocalization of the nitrogen lone-
pair into the N-phenyl ring, while the $\pi \longleftarrow n$ conjugation is
accompanied by an increase in Θ_N [7, 50]. This effect reduces the
paramagnetic deshielding of the N-phenyl ring on the H_α, resul-
ting in an upfield shift. The electron-donating $N(CH_3)_2$ group
exerts a reverse effect [51].

AL-TAI et al. [43] suggested that the substitution effect of the 4-N(CH$_3$)$_2$ group could be ascribed to the predominance of the inductive effect over the resonance effect, because the N-benzylideneanilines generally assume a twisted conformation in solution, regardless of the substituents on them. However, AKABA et al. [45] proposed that the inverse substituent effect may arise primarily from the contribution of the paramagnetic deshielding effect of the N-phenyl ring on the H$_\alpha$ proton.

Alkyl substituents in position 4' or 4 do not influence the H$_\alpha$ chemical shift considerably (Table 4), but for the 2-CH$_3$, 2,6-(CH$_3$)$_2$ or 2'-CH$_3$ derivatives they give rise to up- or downfield shifts. The effects of methyl groups are not additive, which suggests that the upfield shift caused by the second or third methyl substitution might be due to the further distortion of the C-phenyl ring, but the inductive effect is also important. The increase in θ_N on successive methyl substitution in the N-phenyl ring [44] will reduce the paramagnetic deshielding effect of the ring on H$_\alpha$, resulting in an upfield shift; for the substitution on the C-phenyl ring the reverse effect may be observed. Table 5 shows that for 2-CH$_3$, 2,6-(CH$_3$)$_2$, 2,4,6-(CH$_3$)$_3$,

Table 5

Chemical shifts for H$_\alpha$ atom of N-benzylideneanilines substituted in 2-, 2,4-, 2,4,6-, 2',6'- or 2',4',6' positions

X	Y	δH_α(ppm)	X	Y	δH_α(ppm)
2-OCH$_3$	H	8.45	2,4,6-(CH$_3$)$_3$	H	8.16[a]
2-CH$_3$	H	8.27[a] 8.40[b]			8.14
			2,6-(CH$_3$)$_2$	4-NO$_2$	8.48
2-F	H	8.44	2,4,6-(CH$_3$)$_3$	4-NO$_2$	8.28
2-Cl	H	8.47	H	2',6'-(CH$_3$)$_2$	8.25[b]
2-Br	H	8.38			8.23
2-I	H	8.31	H	2',4',6'-(CH$_3$)$_3$	8.72[a] 8.77
2-NO$_2$	H	8.26	4-OCH$_3$	2',4',6'-(CH$_3$)$_3$	8.75[c]
2,6-(CH$_3$)$_2$	H	8.20	2,4,6-(CH$_3$)$_3$	4'-OCH$_3$	8.09

a) ref.[41],   b) ref.[37],   c) ref.[36]

2',6'-(CH$_3$)$_2$ and 2',4',6'-(CH$_3$)$_3$ δH_α is 8.27, 8.20, 8.17, 8.25 and 8.72 ppm, respectively. In our calculations based on the UV

spectral data, θ_N varies approximately in the same sequence. The $^{13}C_7$-H coupling constant of BA (157.3 Hz) is increased to 158.5 and 159.6 Hz by methyl groups in positions 2 or 2,6, respectively, which indicates that methyl substitution on BA leads to an increase in the $\underline{s}$ character of the C_7-H_α bond, possibly through a decrease in the π electron density on C_7 [44].

If substituents are present on both the C-phenyl and N-phenyl rings, the interpretation of the observed H_α chemical shift (see Table 6) is ambiguous. 4-Dimethylamino-N-(4-nitrobenzylidene)aniline has a nearly planar conformation in solution [11, 28], with $\delta H_\alpha = 8.64$, while 4-nitro-N-(4-dimethylaminobenzylidene)aniline (according to our spectral studies) has a non-planar structure, with $\delta H_\alpha = 8.31$ [45] (Table 6). In

Table 6

Chemical shifts for H_α atom of 4,4'-substituted derivatives

X	Y	δH_α(ppm)	X	Y	δH_α(ppm)
Cl	Cl	8.25[a]	CH$_3$	NO$_2$	8.43[c]
OCH$_3$	OCH$_3$	8.37[b] 8.42	Cl	OCH$_3$	8.26[b] 8.31
N(CH$_3$)$_2$	N(CH$_3$)$_2$	8.40[c] 8.38	OCH$_3$	Cl	8.25[b] 8.28
NO$_2$	NO$_2$	8.55[c] 8.59	CH$_3$	NO$_2$	8.53[b]
CH$_3$	Cl	8.28[a] 8.26	OCH$_3$	NO$_2$	8.55[b]
			N(CH$_3$)$_2$	NO$_2$	8.64[c]
Cl	NO$_2$	8.39[a]	NO$_2$	N(CH$_3$)$_2$	8.31[c]

a) ref.[42], b) ref.[36], c) ref.[38]

general, θ_N decreases from 4-NO$_2$ to 4-N(CH$_3$)$_2$, while the H_α chemical shift increases in this sequence. It is interesting that a NO$_2$ or N(CH$_3$)$_2$ group in position 4 results in an anomalous shift, regardless of the character of Y on the C-phenyl ring [45].

PAVLIK and PUTTEN [48] have published chemical shift data for BA and its methylated derivatives in concentrated sulphuric acid. The spectra are consistent with an ion in which the N-phenyl ring is twisted out of the molecular plane, and a limited positive charge delocalization into the C-phenyl ring is detectable.

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УФ и ^{1}Н ЯМР СПЕКТРЫ И КОНФОРМАЦИИ ЗАМЕЩЕННЫХ N-БЕНЗИЛИДЕНАНИЛИНОВ

Й. Часар

Изучены спектры протонного ядерного магнитного резонанса и в ультрафиолетовой области сорока трех N-бензилиденанилиновых производных. Обсуждено влияние заместителей на конформации молекул на основании представлений о вращении ароматических колец.