an increasing contribution of positive spin, possibly due to torsional displacement about the C–N bond.

Addendum

After this work was completed, we received a preprint from Professor H. Fischer describing a similar study by himself and Dr. H. Paul of radicals derived from amino acids and amides. There is excellent agreement between our experimental results, and they offer the same interpretation of the spectra as we do.[33]

[33] H. Paul and H. Fischer, *Ber. Bunsenges. Phys. Chem.*, **73**, 972 (1969).

Electronic Spectra and Structures of Schiff's Bases. I. Benzanils[1]

M. Ashraf El-Bayoumi,[*2] **M. El-Aasser,**[3] **and F. Abdel-Halim**

Contribution from the Faculty of Science, Alexandria University,
Alexandria, Egypt. *Received September 17, 1969*

Abstract: Electronic absorption spectra of various benzanils have been measured at room temperature in different media. Spectral changes due to substitution, change of solvent, and protonation support a noncoplanar structure for benzanils in which the nitrogen lone pair is conjugated to the phenyl group of the aniline part of the molecule. The spectra have been adequately interpreted in terms of two weakly interacting moieties of the molecule, namely the benzal and aniline parts. States have been identified as either locally excited or predominantly charge-transfer states. This classification has been useful in the assignment of the various electronic transitions.

A clear understanding of the electronic structure and spectral properties of Schiff's bases[4] is required for the explanation of their photochemical properties, phototropism, and photoisomerism. In particular, one needs to determine the nature of their lower electronic excited states, *e.g.*, the extent of charge-transfer character and the role of the solvent, protonation, and substitution in altering the energies of these states.

Schiff's bases contain the azomethine group $-\mathrm{CH}{=}\ddot{\mathrm{N}}-$, the same group that occurs in rhodopsin, the visual pigment extracted from rod cells. Rhodopsin consists of a retinal molecule (vitamin A aldehyde) and a large protein, opsin, linked together *via* the azomethine group. Moreover, Schiff's bases bear structural resemblance to stilbenes, azobenzenes, and several heterocyclic molecules; thus, a correlation of the electronic spectra of these compounds is useful in the assignment of their electronic transitions.

One aim of our study is to identify absorption bands as being due to intramolecular charge-transfer (CT) transitions involving the azomethine group or due to locally excited (LE) transitions. We also seek a confirmation of earlier evidence,[5-9] both experimental and theoretical, that benzylideneaniline is not coplanar and that π conjugation is interrupted at the nitrogen atom. If the molecule is planar, its π system would extend over both phenyl rings and the azomethine group, and the spectrum is expected to be similar to that of stilbene. However, if the molecule is noncoplanar, the spectrum should be more or less a superposition of the spectra of the two weakly interacting moieties of the molecule, namely the benzal and aniline parts.

The methods which we have used in our studies include substitution effects (both in the phenyl ring of the aniline part, $\mathrm{Ph_N}$, and in the phenyl ring of the benzal part, $\mathrm{Ph_C}$), solvent effects, and protonation effects on the spectra.

Experimental Section

Solvents were extensively purified to remove impurities that may interact with the solute molecules and to be spectrally transparent in the region down to 2000 Å.

Benzylideneaniline, benzylidene-*p*-hydroxyaniline, benzylidene-*p*-anisidene, *p*-hydroxybenzylideneaniline, *p*-hydroxybenzylidene-*p*-toluidine, *p*-hydroxybenzylidene-*p*-anisidene, *p*-methoxybenzylideneaniline, *p*-methoxybenzylidene-*p*-toluidine, *p*-methoxybenzylidene-*p*-anisidine, and *p*-*N*,*N*-dimethylaminobenzylideneaniline were prepared by warming (or refluxing, if required) equimolar amounts of the appropriate amine and aldehyde in alcohol. The products were recrystallized several times from alcohol.

Ultraviolet absorption spectra were measured at room temperature with a Zeiss PMQ II manual spectrophotometer using matched 1.00-cm fused-silica cells. All the spectra are plotted in terms of molar extinction coefficient ϵ *vs.* wavelength in Å.

Substituent Effects

Benzylideneaniline may be considered to have an electronic structure similar to that of stilbene, since the azomethine and vinyl groups are isoelectronic. One may therefore predict, at first consideration, similar absorption spectra for both molecules. Such expectations are not realized, however. Stilbene has an intense absorption band at 2950 Å (ϵ 24,000) and a less intense band at 2290 Å (ϵ 14,200), while the spec-

---

[1] Part of this work was carried out at the Biophysics Department, Michigan State University, under Contract No. AT(11-1)-2039, Division of Biology and Medicine, U. S. Atomic Energy Commission.

[2] Biophysics Department, Michigan State University, East Lansing, Mich. 48823.

[3] The major portion of this work is from the M.S. thesis of M. El-Aasser, Alexandria University, Sept 1966.

[4] Compounds containing the azomethine group $-\mathrm{CH}{=}\ddot{\mathrm{N}}-$ are given several names, *i.e.*, Schiff's bases, anils, azomethines, and benzylideneamines.

[5] V. A. Ismailskii and E. A. Smirnov, *J. Gen. Chem. USSR*, **26**, 3389 (1956).

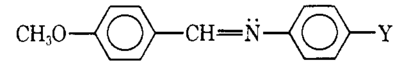
[6] P. Brocklehurst, *Tetrahedron*, **18**, 299 (1962).

[7] W. F. Smith, *ibid.*, **19**, 445 (1963).

[8] N. Ebara, *Bull. Chem. Soc. Jap.*, **34**, 1151 (1961).

[9] V. I. Minken, Yu A. Zhandanov, E. A. Medyantzeva, and Yu A. Ostroumov, *Tetrahedron*, **33**, 365 (1967).

Table I. Absorption Maxima[a] (Å) and ε Values of Ph_N-Substituted Schiff's Bases in Cyclohexane Solutions



	Band I			Band II			Band III		Band IV		
Substituent Y	λ_{max}	$\epsilon_{max} \times 10^{-3}$	$\Delta\bar{\nu}$	λ_{max}	$\epsilon_{max} \times 10^{-3}$	$\Delta\bar{\nu}$	λ	$\Delta\bar{\nu}$	λ_{max}	$\epsilon_{max} \times 10^{-3}$	$\Delta\bar{\nu}$
H	3150	12.9	0	2800	19.6	0	(2370)	0	2215	18.6	0
CH_3	3225	14.5	−740	2800	20.5	0	(2400)	−527	2215	18.4	0
OCH_3	3300	17.9	−1440	2800	22.3	0	(2440)	−1210	2215	20.3	0

[a] Wavelengths enclosed in parentheses indicate a shoulder rather than a band maximum.

trum of benzylideneaniline (shown in Figure 1) exhibits a shoulder at 3150 Å (ε 8800) and a maximum at 2625 Å (ε 21,300). The intensity of the first absorption band is considerably reduced compared to that of stilbene; such differences must reflect differences in their electronic structures.

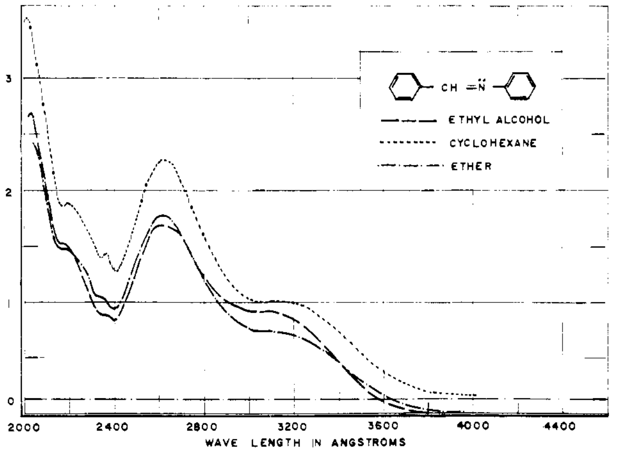


Figure 1. Room-temperature ultraviolet absorption spectra of benzylideneaniline in different solvents (concentration = 4.97 × 10^{-5} *M*).

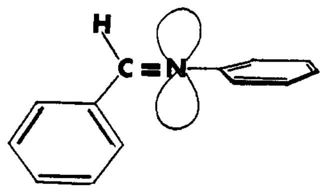


Figure 2. Nonplanar structure of benzylideneaniline.

Ismailskii and Smirnov[5] recognized that while π conjugation extends over the whole molecule in the case of stilbene, it is reduced in benzylideneaniline. They postulated that the unshared pair of electrons on the nitrogen atom can conjugate with the N-phenyl ring, Ph_N. This implies a noncoplanar molecular structure, since Ph_N can only conjugate with the nitrogen lone pair if the Ph_N ring is rotated out of the plane of the conjugated system consisting of the C-phenyl group, Ph_C, and the azomethine group. Thus, the nonplanar structure shown in Figure 2 is energetically more favorable than the planar configuration. In the latter the π conjugation extends over the whole molecule but the nitrogen lone-pair electrons do not take part in π conjugation and exhibit repulsion with neighboring hydrogen atoms.

Brocklehurst[6] suggested that the 3150-Å band of benzylideneaniline corresponds to the intense 2900-Å band of stilbene and that the reduction of its intensity is due to the noncoplanarity of the molecule. He explained the appearance of the 3150-Å band in terms of a solution equilibrium between planar and nonplanar forms.

To throw more light on the subject, we have prepared a number of azomethines with substituents on the phenyl ring of the aniline part, Ph_N, and others with substituents on the phenyl ring of the benzal part, Ph_C. Figure 3 shows the ultraviolet absorption spectra of Ph_N-substituted *p*-methoxybenzylideneanilines. Their absorption maxima (λ_{max}), corresponding extinction coefficient (ϵ_{max}), and spectral shifts $\Delta\bar{\nu}$ (cm^{-1}) due to Ph_N substitution are summarized in Table I. Shifts are measured relative to the unsubstituted compound.

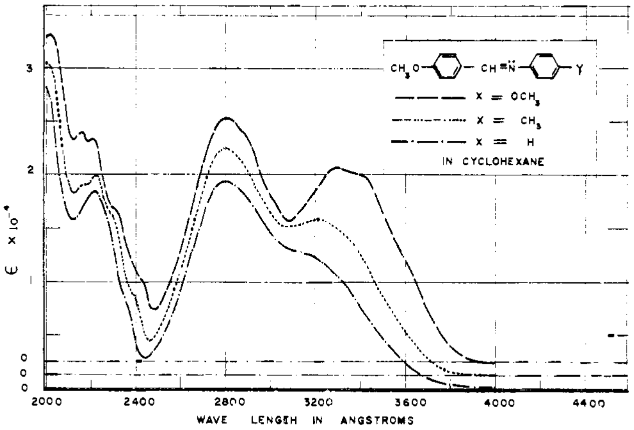
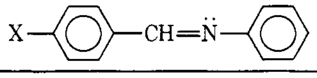


Figure 3. Room-temperature ultraviolet absorption spectra in cyclohexane of *p*-methoxybenzylideneaniline with different substituents in the aniline part (Ph_N).

From Table I and Figure 3, it is clear that some absorption bands (band I at 3150 Å and band III at 2370 Å) shift to longer wavelengths as a result of Ph_N substitution, while other bands (band II at 2800 Å and band IV at 2215 Å) do not change their energies. A shoulder appears at 2340 Å as a result of substitution. These observations probably indicate that bands sensitive to substitution correspond to electronic transitions involving the phenyl ring of the aniline part, and bands which remain unchanged correspond to transitions involving the benzal part of the molecule. Such results are in favor of the noncoplanar structure of benzylideneanilines and indicate that the Ph_N ring is nearly perpendicular to the benzal part of the molecule; *i.e.*, the two phenyl rings are weakly interacting with each other.

Table II. Absorption Maxima[a] (Å) and ϵ Values of Ph_C-Substituted Schiff's Bases in Alcohol Solutions



	Band I			Band II			Band III		Band IV		
Substituent X	λ_{max}	$\epsilon_{max} \times 10^{-3}$	$\Delta\bar{\nu}$	λ_{max}	$\epsilon_{max} \times 10^{-3}$	$\Delta\bar{\nu}$	λ	$\Delta\bar{\nu}$	λ_{max}	$\epsilon_{max} \times 10^{-3}$	$\Delta\bar{\nu}$
H	3110	9.0	0	2620	16.7	0	(2380)	0	2180	15.0	0
OCH_3	3110	18.1	0	2900	18.6	−3690	(2380)	0	2230	17.3	−1030
$N(CH_3)_2$	(3130)		−206	3560	39.1	−10080			2380	15.1	−3850

[a] Wavelengths enclosed in parentheses indicate a shoulder rather than a band maximum.

Further evidence of the noncoplanarity is provided by the effect of Ph_C substitution on the spectra of the benzylideneanilines; this is shown in Figure 4. The absorption data are summarized in Table II. As a result of Ph_C substitution, the energies of the first and third absorption bands do not change, while the second and fourth bands change their energies, the reverse situation occurring as a result of Ph_N substitution. The second band exhibits a large red shift due to the substitution of a dimethylamino group in the Ph_C ring, such that it becomes the longest wavelength band; *i.e.*, the order of the energies of the first and the second band is reversed in the spectrum of *p-N,N*-dimethylaminobenzylideneaniline.

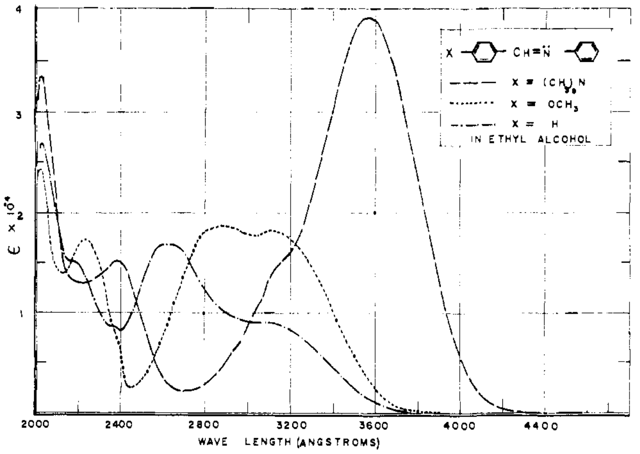


Figure 4. Room-temperature ultraviolet absorption in alcohol of benzylideneaniline with different substituents in the benzal part (Ph_C).

On the basis of substitution effects, the spectrum of benzylideneaniline shown in Figure 1 is interpreted in terms of aniline and benzal noninteracting moieties.

Band I (3110 Å) is sensitive to Ph_N substitution and corresponds to a transition to a benzene $^1B_{2u}$-type state in the aniline part of the molecule. A transition to a benzene $^1B_{2u}$-type state in the benzal part of the molecule is hidden under more intense transitions since it is expected to be of lower intensity and to absorb at around 2900 Å.

Band II (2620 Å) is sensitive to Ph_N substitution and is interpreted as a transition to a charge-transfer state in which the azomethine group acts as an electron acceptor and the Ph_C ring as an electron donor. This is supported by the fact that the energy of this band depends on the ionization potential of the donating moiety.

Band II (2380 Å) appears to be sensitive to Ph_N substitution and may correspond to the CT band of the aniline part. This band of aniline has appreciable local-excited-state character corresponding to a benzene $^1B_{1u}$-type state. One must emphasize here that a distinction between locally excited and charge-transfer states is not valid when configuration interaction is significant. This appears to be the case for the second excited state of aniline.[10] A shoulder that appears at 2340 Å in some substituted benzanils (*e.g.*, *p*-methoxybenzylidene-*p*-anisidine) probably corresponds to the third electronic transition of aniline. The latter involves an electronic state which has also mixed CT and LE characteristics.

Band IV (2180 Å) is sensitive to Ph_C substitution and is interpreted as the perturbed $^1B_{1u}$ band of the benzal part.

One should point out here that bands I and III, which correspond to electronic transitions involving the Ph_N ring, do not appear in *N*-benzylimines where the Ph_N ring is replaced with an aliphatic group.

Solvent Effects

Intramolecular CT bands are solvent sensitive, while LE bands are relatively insensitive to change of solvent. Benzylideneaniline spectra in different solvents are shown in Figure 1. Practically no shift occurs due to change of solvent from cyclohexane to ether. In alcohol the 3150-Å band blue shifts (+408 cm^{-1}). This blue shift is analogous to the observed blue shift of the first absorption band of aniline (2900 Å) due to a change of medium from cyclohexane to alcohol and is due to hydrogen bonding with the nitrogen lone-pair electrons.

Solvent effects on *p*-methoxybenzylideneaniline are shown in Figure 5. The 3150-Å band shifts to the blue (+408 cm^{-1}). In alcohol, the 2800-Å band (CT) shifts to the red (−1231 cm^{-1}), while the 2210-Å band undergoes a slight shift to the red (−406 cm^{-1}).

Solvent effects on *p-N,N*-dimethylbenzylidineaniline are shown in Figure 6. In cyclohexane the longest wavelength absorption band has a maximum at 3400 Å and appears to have a shoulder in the neighborhood of 3100 Å. In alcohol the maximum undergoes a red shift (−1150 cm^{-1}) while the shoulder does not shift appreciably. Thus, although alcohol usually causes a blurring effect on spectra, the shoulder at 3100 Å appears more resolved in that solvent. This supports our earlier conclusion that the absorption band in cyclohexane between 2800 and 4200 Å consists mainly of two $\pi \rightarrow \pi^*$ electronic transitions, namely a solvent-

---

(10) M. Godfrey and J. M. Murrell, *Proc. Roy. Soc., Ser. A*, **278**, 71 (1964).

Table III. Study of the Effect of Substitution on the Spectra of Azomethines and Their Conjugate Acids

Comparison pair	Solvent	λ_{max} (Å)	ϵ_{max}	$\Delta\bar{\nu}$, cm^{-1}
$Ph{-}CH{=}CH_2$	Cyclohexane	2480	15,000	−6424
$Ph{-}CH{=}CH{-}Ph$	Cyclohexane	2950	24,000	
$Ph{-}CH{=}\overset{H^+}{N}{-}CH_3$	Concentrated H_2SO_4	2830		−5924
$Ph{-}CH{=}\overset{H^+}{N}{-}Ph$	Concentrated H_2SO_4	3350	24,000	
$Ph{-}CH{=}\ddot{N}{-}CH_3$	Cyclohexane	2440	13,000	−2892
$Ph{-}CH{=}\ddot{N}{-}Ph$	Cyclohexane	2625	21,300	
$Ph{-}CH{=}\ddot{N}{=}CH_3$	Alcohol	2450		−4180
$Ph{-}CH{=}\overset{H^+}{N}{-}CH_3$	Alcohol + HCl	2730		

sensitive charge-transfer band (λ_{max} 3420 Å) and a solvent-insensitive band (λ ~3100 Å) corresponding to a transition to a locally excited state ($^1B_{2u}$-type state of the aniline part of the molecule). This selective solvent effect reflects the difference in the nature of the two excited states and is a nice example of a resolution of a band by changing the solvent from cyclohexane to alcohol.

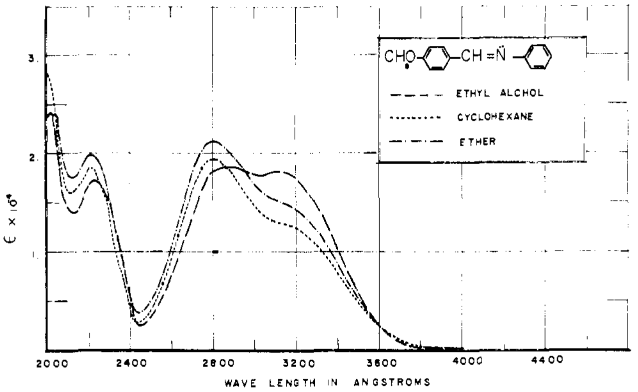


Figure 5. Room-temperature ultraviolet absorption spectra of *p*-methoxybenzylideneaniline in different solvents.

Protonation Effects

As mentioned before, the unshared pair of electrons on the nitrogen interrupts π conjugation across the whole benzylideneaniline molecule. The benzylideneaniline molecule energetically favors a noncoplanar structure in which the Ph_N ring is at an angle to the plane of the Ph_C ring and the nitrogen lone pair is conjugated with the π-electronic system. We have interpreted the 3150- and 2625-Å bands to correspond respectively to transitions involving the aniline part and the benzal part of the benzylideneaniline molecule.

If the nitrogen lone pair is localized by protonation, the benzylideneaniline molecule energetically favors a planar structure since the nitrogen lone pair is not available then to conjugate with the Ph_N ring. Thus, the spectrum of protonated benzylideneaniline is expected to be similar to that of stilbene.

Ebara[11] attributed the spectral changes of benzylidineaniline in acidic medium as being due to protonation, such changes occurring only at acid concentrations below 10^{-3} *M*. At such acid concentrations fast hydrolysis occurred and the resulting spectrum is not due to the conjugate acid but rather due to the hydrolyzed products. However, Kubota[12] realized that azomethines are unstable in dilute acid media. He measured the spectrum of *N*-benzylimine conjugate acid by recording the spectra immediately after dissolving *N*-benzylimine in sulfuric acid or in anhydrous alcohol containing HCl. In the latter medium the first band has an absorption maximum at 2730 Å.

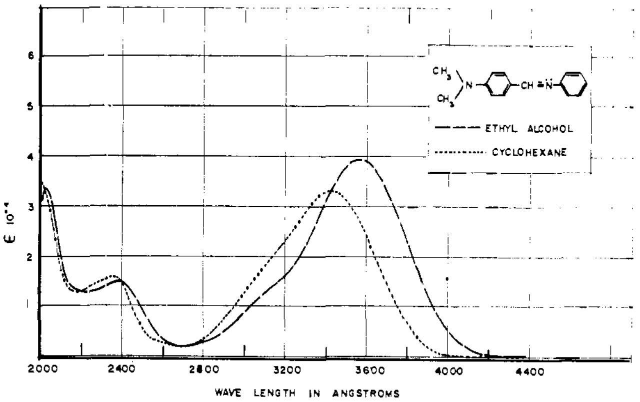


Figure 6. Room-temperature ultraviolet absorption spectra of *p*-*N*,*N*-dimethylaminobenzylideneaniline in ethyl alcohol and in cyclohexane (concentration = 2.45×10^{-5} *M*).

To slow down and minimize hydrolysis we have used concentrated sulfuric acid as our medium and measured the spectra immediately after making the solution. Our data are similar to those of Brocklehurst,[6] yet our interpretation is different because he compared the longest wavelength absorption band of the benzylideneaniline conjugate acid with the 3150-Å band of benzylideneaniline instead of comparing it with the 2625-Å CT band of benzylidineaniline. Our data are summarized in Table III.

Comparing the CT band maxima of *N*-benzylimine and benzylideneaniline in cyclohexane, a red shift of 2892 cm^{-1} is observed due to a substitution of the methyl by a phenyl group. The first absorption bands of the corresponding conjugate acids in concentrated sulfuric acid show a shift of 5924 cm^{-1}. This indicates that the Ph_N ring in benzylideneaniline conjugate acid

---

(11) N. Ebara, *Bull. Chem. Soc. Jap.*, **33**, 534 (1960).

(12) T. Kubota and M. Yamakawa, *ibid.*, **36**, 1564 (1963).

is in plane with the rest of the molecule and its π molecular orbitals extend over the whole molecule. However, in benzylideneaniline itself, the Ph_N ring is out of plane and therefore the shift caused by substituting the methyl group in *N*-benzylimine by a phenyl group is small compared to the shift caused by a similar substitution in *N*-benzylimine conjugate acid.

Comparing the spectrum of styrene and *trans*-stilbene, it is clear that phenyl group substitution in styrene shifts the absorption band by 6424 cm^{-1} to the red, which is comparable to the red shift (5924 cm^{-1}) observed when the methyl group in the *N*-benzylimine conjugate acid is replaced by a phenyl group which presumably assumes a planar configuration.

A large (about 7000 cm^{-1}) red shift of the CT band of benzylideneaniline is observed due to protonation. The value of this shift is obtained by comparing the CT band maxima of benzylideneaniline in alcohol and in concentrated sulfuric acid and by taking into consideration medium effects. The latter are estimated by comparing the CT band maxima of *N*-benzylimine in alcohol + HCl and in concentrated sulfuric acid. This shift is due in part to the positive charge on the nitrogen atom and also to having the phenyl group of the aniline part assume a coplanar configuration in the conjugate acid. Similar red shifts have been observed[13] as a result of protonation of carbon tetrachloride solutions containing retinal (vitamin A aldehyde) and a secondary amine, *e.g.*, diphenylamine, indole, carbazole, and piperidine. These results were interpreted in terms of the formation of enamine salts of retinal with secondary amines.

Energy calculation[14] of CT and LE states of Schiff's bases using a localized orbital model provides further support for our assignments of the electronic transitions of benzanils. Also, the study of the absorption spectra of *N*-benzylimines[15] and their interaction with iodine gives more evidence that in benzanils the lone-pair electron on the nitrogen atom is conjugated to the phenyl group.

(13) J. Toth and B. Rosenberg, *Vision Res.*, **8**, 1471 (1968).

(14) M. A. El-Bayoumi, M. El-Aasser, and F. Abdel-Halim, manuscript in preparation.

(15) M. El-Aasser, F. Abdel-Halim, and M. A. El-Bayoumi, *J. Amer. Chem. Soc.*, **93**, 590 (1971).

Electronic Spectra and Structures of Schiff's Bases. II. *N*-Benzylimines[1]

M. El-Aasser,[2] F. Abdel-Halim, and M. Ashraf El-Bayoumi*[3]

Contribution from the Faculty of Science, Alexandria University, Alexandria, Egypt. *Received September 17, 1969*

Abstract: Electronic absorption spectra of substituted *N*-benzylimines have been measured at room temperature in different media. The spectra support our interpretation of the spectra of benzanils as being essentially a superposition of the spectra of the corresponding benzal and aniline parts of the molecule. It is shown that the azomethine group acts as an electron acceptor when linked to a phenyl group at its carbon end and as an electron donor when linked to a phenyl group at its nitrogen end. Iodine interaction with *N*-benzylimine in carbon tetrachloride indicates that the lone pair of electrons on the nitrogen are more available to interact with iodine than in benzylideneaniline.

Electronic absorption spectra of benzanils have been interpreted in terms of two weakly interacting moieties of the molecule, namely the benzal and aniline parts. The various absorption bands were assigned[4] to transitions involving locally excited states (LE) or to intramolecular charge-transfer states (CT) of the benzal and aniline parts. We have measured the absorption spectra of substituted benzylimines in different media. In benzylimines, the phenyl group is substituted with an aliphatic group. This will help in distinguishing electronic transitions involving the aniline part, which should be absent in the spectra of *N*-benzylimines, from those transitions involving the benzal part.

Experimental Section

Ultraviolet absorption spectra were measured at room temperature with a Zeiss PMQ II manual spectrophotometer. All solvents were extensively purified by standard procedures. *N*-Methylbenzylimine (bp 183–185°) and *p*-methoxy-*N*-methylbenzylimine [bp 112° (2 mm)] were prepared using the following procedure.[5] The corresponding aldehyde was treated slowly with excess aqueous solution of methylamine and allowed to stand overnight. The oily condensation product was then extracted with ether, sodium chloride was added, and the ether extract was dried over anhydrous calcium sulfate. Ether was evaporated, the residual oil was fractionally distilled under vacuum, and the boiling point of the oil was determined.

p-Hydroxy-*N*-methylbenzylimine (mp 178°) was prepared[6] by dissolving *p*-hydroxybenzaldehyde in hot alcohol; excess 33% aqueous methylamine at about 40° was added rapidly and the resulting solution was cooled in an ice bath for 2 hr. The crystalline product was filtered and washed with cold 40% alcohol and water, and its melting point was determined.

---

[1] Part of this work was carried out at the Biophysics Department, Michigan State University, under Contract No. AT(11-1)-2039, Division of Biology and Medicine, U. S. Atomic Energy Commission.

[2] The major portion of this work is from the M.S. thesis of M. El-Aasser, Alexandria University, Sept 1966.

[3] Biophysics Department, Michigan State University, East Lansing, Mich. 48823.

(4) M. A. El-Bayoumi, M. El-Aasser, and F. Abdel-Halim, *J. Amer. Chem. Soc.*, **93**, 586 (1971).

(5) N. H. Cromwell, R. S. Babson, and C. E. Harris, *J. Chem. Soc.*, **65**, 313 (1943).

(6) N. H. Cromwell and H. Hoeksma, *J. Amer. Chem. Soc.*, **67**, 1658 (1945).