Benzylideneaniline. I. Structure and Ultraviolet Absorption Spectrum of Benzylideneaniline

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(Received July 31, 1959)

Benzylideneaniline has been believed to assume a planar structure without any experimental proof, as it has a similar molecular constitution as stilbene or azobenzene, of which the geometries are proved to be planar by the aid of X-ray diffraction method¹⁾. Benzylideneaniline, however, has many unusual properties which can not be accounted for by the planar structure.

1) Imoto²⁾ measured the pK values of the several carboxyl derivatives of substituted benzylideneanilines and found that the conduction of the effects of the substituents across the central C=N double bond is extraordinarily small. His data show that N-(substituted benzylidene)-p-aminobenzoic acid has the pK value almost equal to that of p-aminobenzoic acid.

2) Hertel and Schinzel³⁾ investigated the reaction of methyl iodide with the lone pair electron of N atom in benzylideneaniline and found that the substituents on the aniline ring exert remarkable effects on reaction velocity, while the effects of the substituents on the other ring are negligibly small.

3) The dipole moment of p,p'-dinitrobenzylideneaniline was reported to have the intermediate value between those expected for *trans* and *cis* forms⁴⁾.

4) Benzylideneaniline seems to show no geometrical isomerism, in contrast to stilbene, azobenzene and azoxybenzene, of which the two isomers can be detected and easily separated. Wyman⁵⁾, by means of the rotating-shutter technique, found that the solution of this substance does not show any spectral change when exposed to light. Gaouck and LeFèvre⁶⁾ investigated the polymorphic crystals of the derivatives of benzylideneaniline by means of

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1) (a) J. M. Robertson and I. Woodward, *Proc. Roy. Soc.*. **162A**, 568 (1937). (b) J. M. Robertson, *J. Chem. Soc.*, 1939, 232.

2) E. Imoto et al., Presented at the 12th Annual Meeting of Chemical Society of Japan, Kyoto, April, 1959.

3) E. Hertel and M. Schinzel, *Z. physik. Chem.*, **B48**, 289 (1941).

4) K. A. Jensen and N. Hofman-Bang, *Ann.*, **548**, 106 (1941).

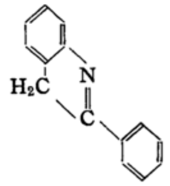
5) G. M. Wyman, *Chem. Revs.*, **55**, 625, (1955).

6) V. De Gaouk and R. J. W. LeFèvre, *J. Chem. Soc.*, **1938**, 741.

the measurements of dipole moments and of absorption spectra, and concluded that these molecules exist exclusively in *trans* forms.

5) It has been shown7) that the phase diagrams of the admixtures of benzylideneaniline with *trans*-stilbene, *trans*-azobenzene, phenanthridine or bibenzyl8) involve discontinuous curves, while those of the admixtures between *trans*-stilbene, *trans*-azobenzene and bibenzyl speak for the perfect miscibility. This fact is likely to show that the structure of benzylideneaniline corresponds to neither *trans* nor *cis* form.

6) The shape of the ultraviolet absorption spectrum of benzylideneaniline is quite different from those of stilbene, azobenzene and azoxybenzene, which resemble each other very closely. Wiegand and Merkel7) found that the spectrum of 2-phenylbenzimidazole (I) exhibits a similarity to stilbene and not to benzylideneaniline, while that of 2-phenylindene (II) is very much similar to that of stilbene, where I and II must have planar *trans* structures. They proposed a linear planar structure for benzylideneaniline, but it seems inadequate, as it has no theoretical basis and is energetically less favorable.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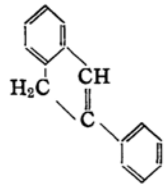

II

7) Benzylideneaniline shows no $n-\pi^*$ transition at the longer wavelength region. Jaffé9) has assumed that this transition is hidden under the long tapering end of the absorption curve of 315 mμ band, but it appears that the strong experimental support is lacking for this assumption.

These experimental facts are not consistent with the generally accepted stilbene-type structure, and yet very few works have been carried out with regard to the very nature of the benzylideneanilinemolecule. Therefore, series of experiments are now undertaken to explain some fundamental problems of benzylideneaniline.

Results and Discussion

Measurements were carried out on the ultraviolet absorption spectra of benzylideneaniline, stilbene, azobenzene and azoxybenzene in *n*-heptane, ethanol and 50% mixture of ethanol and concentrated hydrochloric acid, together with their variations caused by the substituent groups, and for comparison, spectra of some aromatic compounds were also measured. The results are shown in Tables I and II and in Fig. 1.

If benzylideneaniline assumes the stilbene-type planar structure, there must be some substantial similarity in behavior between the spectra of benzylideneaniline and of stilbene, azobenzene or azoxybenzene.

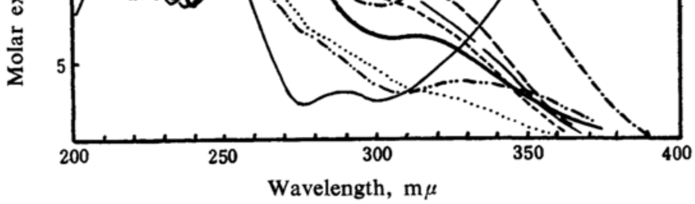
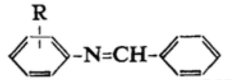


Fig. 1. Spectra of benzylideneanilines :  (in C_2H_5OH)
R= ━━ H ; —— p-NO_3 ; — — m-NO_3 ; -·-·- p-OCH_3 ; -··-··- o-OCH_3 ;
---- p-Cl ; ------ m-Cl ; ······ o-Cl.

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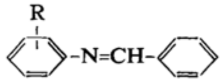
7) C. Wiegand and E. Merkel, *Ann.*, **550**, 175 (1942).

8) Bibenzyl is found to have the planar *trans* conformation (Ref. 1b).

9) H. H. Jaffé, S. Yeh and R. W. Gardner, *J. Molecular Spectroscopy*, **2**, 120 (1958).

TABLE I. WAVELENGTHS AND INTENSITIES OF ULTRAVIOLET ABSORPTION MAXIMA (in C_2H_5OH)



R	Free bases abs. max.		Conjugate acids abs. max.	
	λ, mμ	ε_{max}	λ, mμ	ε_{max}
H	236	10100	250	13900
	263	16400	290	2000
	315	6200	360	—
o-Cl	244	12400	220	7400
	260	11200	250	10300
	290	—	290	2800
	330	2700	360	—
m-Cl	240	10300	220	7200
	264	16900	250	13900
	310	8800	290	3200
			360	—
p-Cl	223	13800	220	8800
	264	16600	250	14600
	314	10400	290	2250
			360	—
o-OCH_3	246	11700	220	10800
	263	—	250	15700
	330	3850	290	—
			373	—
p-OCH_3	229	12900	223	11500
	264	13100	250	15500
	330	13300	290	—
			360	—
m-NO_3	218	19900	252	22900
	267	25900	290	—
	325	6730	355	—
p-NO_3	243	17300	252	22200
	290	3040	290	—
	380	16800	335	—

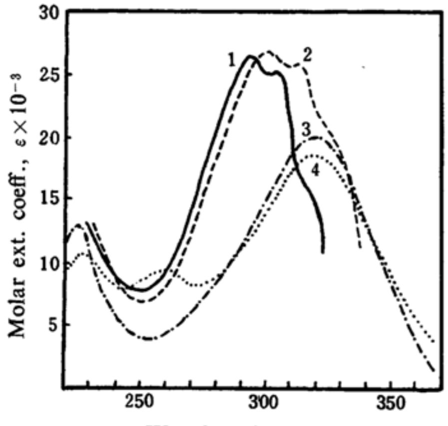
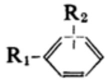


Fig. 2. Spectra of: 1, —— stilbene; 2, ---- *p*-methoxystilbene; 3, -·-· azobenzene; 4, ······ azoxybenzene. (in C_2H_5OH)

TABLE II. WAVELENGTHS AND INTENSITIES OF SOME AROMATIC COMPOUNDS (in C_2H_5OH)



R_1	R_2	λ, mμ	ε_{max}
Cl	H*	209.5	7400
		263.5	190
OCH_3	H	220	7020
		271	1830
NO_3	H*	268.5	7800
NH_2	H	235	8100
		285	1400
	o-Cl	238	8740
		292	2480
	m-Cl	245	9000
		295	2300
	p-Cl	239	11700
		290	1500
	o-OCH_3	235	10000
		285	3700
	p-OCH_3	235	8450
		300	2580
	o-NO_3	230	13100
		278	4220
		406	4250
	m-NO_3	234	14900
		282	3560
		373	1310
	p-NO_3	230	6600
		368	15200
CHO	H*	249.5	11400
		285	—
NH^+_3	H*	203	7500
		254	160
	p-Cl*	215.5	9200
		263	360
	p-NO_3*	208	7800
		258	8700

* L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

Stilbene, as well as azobenzene and azoxybenzene, shows an intense absorption maximum near 300～320 mμ, which has been interpreted to be the $\pi-\pi^*$ transition[9-12]. This band shifts toward longer wavelength when *p*-position is substituted. The spectrum of azobenzene in concentrated sulfuric acid was measured by several authors, and it was suggested that the band at 320 mμ in neutral solvent shifts to 420 mμ in acidic medium, whereby its intensity also increases considerably. This shift has been explained by Jaffé[9] in terms of the LCAO

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10) P. P. Birnbaum, J. H. Linfold and D. W. G. Style, *Trans. Faraday Soc.*, **49**, 735 (1953).

11) H. Suzuki, This Bulletin, **25**, 145 (1952).

12) W. Maier, A. Saupe and A. Englert, *Z. physik. Chem.*, *N. F.*, **10**, 273 (1957).

method by taking into account the increase of Coulombic integral of the nitrogen atom when proton attaches to it.

In the present experiment the activity of proton seems to be insufficient to convert the substance completely into its conjugate acid, and it can be inferred from Fig. 3 that there is an equilibrium between azobenzene and its conjugate acid. In the same condition, azoxybenzene does not undergo any remarkable change in spectrum. This fact may be explained by the consideration that owing to the inductive effect of N→O coordination, basicity of this molecule is greatly reduced compared with that of azobenzene. But the inspection of the shape of the spectrum is likely to tell that also in this case a red shift occurs when conjugate acid is formed.

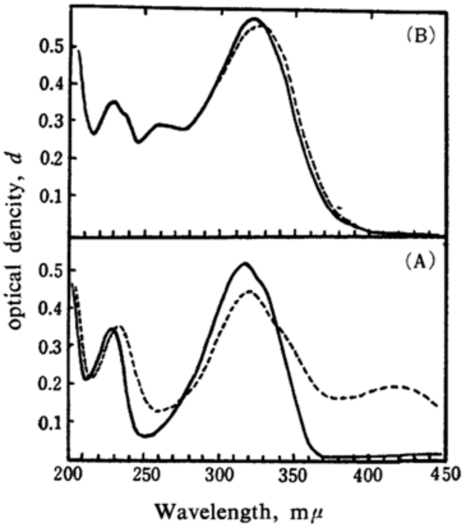

Fig. 3. Spectra of (A) azobenzene and (B) azoxybenzene in —— C_2H_5OH and in ------ C_2H_5OH+conc. HCl

Benzylideneaniline shows an intense band at 263 mμ and a weak band at about 315 mμ, the latter has been assigned as the $\pi-\pi^*$ transition which corresponds to that of stilbene near 300 mμ[9]. But it can hardly be accepted when one compares it with those of azobenzene or azoxybenzene, as the reduction of symmetry in benzylideneaniline would not reduce the intensity more than that of azoxybenzene. Also it is difficult to assume the 263 mμ band as this transition, as its wavelength is too short and the substituents on the ring exert too little effects upon this band as compared with stilbene or azobenzene. In addition to this, these interpretation can not account for the aforementioned spectrum of 2-phenylbenzimidazole (I), for which the planar *trans* structure is to be assumed. Moreover, acidic medium causes large unexpected change on these bands (Fig. 4): these bands become weak and shift toward shorter wavelengths, and the spectrum of free base diminishes completely. Measurements were made with various acid concentrations, but no change occurs unless acid concentration was reduced below $\cdot 10^{-3}$ mol./l. (the base concentration remaining about 10^{-4} mol./l.). In addition to this, these shifted bands are at the same position even when the aniline ring is substituted. As there is no time-dependence in spectrum during the measurements, and the decomposition rate of this molecule is found to be not so large, this spectrum must be attributed to the conjugate acid.

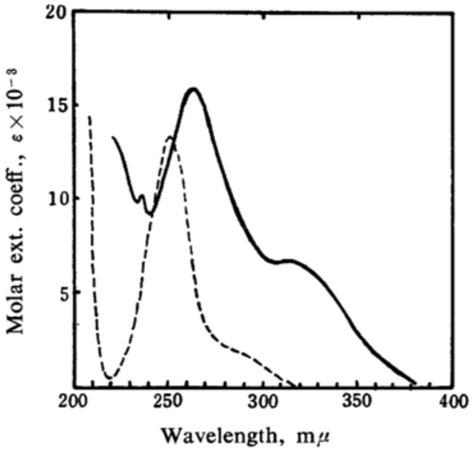

Fig. 4. Spectra of benzylideneaniline —— and its conjugate acid ---- (in C_2H_5OH)

To explain these experimental results, together with the peculiarities cited above, an alternative geometrical structure must be proposed for this molecule. One possible structure may be such that the benzene ring at the N side is nearly perpendicular to the rest of the molecule (which accounts for problem 5 cited above).

When this structure is assumed, there may be a strong aniline-type resonance interaction, and, as a result, the $n-\pi^*$ transition is necessarily missing (problem 7). In addition, the interaction of benzene rings across the C=N double bond would be reduced to a large extent (problem 1), and the ultraviolet absorption spectrum would become close to the superposition of those of its components, aniline-type and styrene-type (problem 6). Then the substituent on the aniline ring would exert a large influence upon the lone-pair electron, whereas that on the other ring would not (problem 2).

The absence of geometrical isomerism can also be explained with this model. The C–N–C bond angle may be 120° with sp^2 hybridization, 180° with sp hybridization or intermediate with higher order hybridization. If it is 180°, there can be no geometrical isomerism at all; if it is

120° or intermediate, there may be bending isomerization through intermediate *sp* structure, where the benzene ring would become absolutely perpendicular so as to reduce the energy of this state by the increase of resonance interaction between nitrogen non-bonding orbital and benzene π orbital, and this would permit the undetectably fast reaction (problem 4). Probably the hybridization and the angle of the twist of the benzene ring would be such as to minimize the energy of the molecule, and when the ring is almost perpendicular, the hybridization will be close to *sp*.

Whether this is the case or not may be inferred also from the examination of the absorption spectra.

The spectra of the conjugate acids must be similar to the superposition of those of substituted anilinium ions and the conjugate acid of *N*-benzylidene-alkylamine, with a slight modification caused by the small interaction between these two. In benzylideneaniline, the former should have the absorption maximum at 254 mμ, of which the intensity is so weak that it should be hidden under the intense band of the latter. The latter is isoelectronic with benzaldehyde and the bands of conjugate acids at 250 and 290 mμ can be compared with 249.5 and 285 mμ bands of benzaldehyde, respectively (247 mμ of benzylidene-methylamine). In the case of the conjugate acids of benzylidene-*m*- and -*p*-nitroaniline, 252 mμ band is very intense, perhaps owing to the overlap of the intense 268.5 mμ band of nitrobenzene component, as its extinction coefficient is just in the same magnitude as the sum of those of two components. For the conjugate acid of benzylidene-*o*- and -*p*-anisidine, there is an additional band at 220 mμ which coincides with 217 mμ band of anisole, intensified by the substituent ($-N^{+}=$). Also the 220 mμ band of chlorine-substituted conjugate acids can be compared with the 210 mμ band of chlorobenzene (216 mμ of *p*-chloranilinium ion).

The assignment of the bands near 360~370 mμ are not certain, but one tentative explanation is that they may be the transitions between orbitals of the two components, as their intensities are of the order of $n-\pi^*$ transition**.

The assignment of the spectra of free bases is more obscure, but the bands near 315 mμ experience considerable perturbation due to the introduction of substituents and can presumably be compared with the 285 mμ band of aniline (296 mμ of dimethylaniline). The latter is found to correspond with $A_{1g}-B_{2u}$ transition of benzene at 260 mμ, allowed by the perturbation of the amino-substituent group, and becomes more intense and shifts toward red by successive substitution, because perturbation becomes larger. In the case of benzylideneanilines, the orbitals will mix to some extent with those of the other benzaldehyde-type part; therefore, one can probably expect that their positions and intensities may be such as these.

The band at 264 mμ is more difficult to interprete, but the absence of the effects of the substituents on this band is likely to show that this band comes from the styrene-type part; i. e. corresponds to the 250 mμ band. It seems at first unlikely that in the conjugate acid the band shifts toward shorter wavelength. However, this can probably be accepted when one assumes that the nitrogen valence orbital is nearly *sp* in free base but becomes sp^2 when conjugate acid is formed, and that the C=N bond length is longer in *sp* than in sp^2. Calculation was carried out for the transition energy of $R-N=CH-C_6H_5$ (R=alkyl) by the simple LCAO method, assuming that for the conjugate acid the Coulombic integral of N atom is $\alpha+\beta$, the exchange integral of C=N bond, which must have strong double bond character, 1.2β, and that of $C-C_{ring}$, which is predominantly single, 0.6β and for the free base, these integrals are $\alpha+\beta/2$, β and 0.6β, respectively; where α and β represent their usual meanings (Fig. 5). The result shows that the effect of the change in C=N bond length offsets the reverse effect of the change in Coulombic integral of the nitrogen atom, and the hypsochromic shift will occur when conjugate acid is formed.

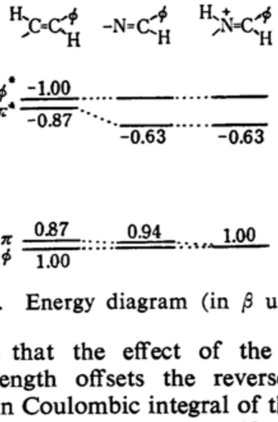

Fig. 5. Energy diagram (in β unit).

Other bands near 230~240 mμ may be attributed to the aniline-type part, as their positions coincide and their intensities are of comparable magnitude.

The spectrum of benzylidene-*p*-nitroaniline exhibits the striking feature that it changes greatly with the solvent, whereas those of chloro-, methoxy- or unsubstituted benzylideneaniline does not. The 380 mμ band in ethanol shifts to 320 mμ in *n*-heptane, and its intensity decreases. This is not the case in *p*-nitrostilbene or -azobenzene, and it is highly likely that this band corresponds to 370 mμ *p*-nitroaniline charge-transfer band, and that the band at 243

** Or it may be that they come from the decomposition products.

mμ is the superposition of 230 mμ of *p*-nitroaniline and 250 mμ of styrene-type part. Their intensities are also consistent with this assumption. In this case, owing to the large charge-transfer resonance interaction between nitro group and nitrogen non-bonding electron, the molecule would assume almost perpendicular conformation with the result that the spectrum of this molecule is much more similar to the superposition of those of components as compared with those of any other benzylideneanilines.

There are some experimental evidences which seem to contradict this assumption. For example, Raman spectra show that the frequencies of C=N stretching vibrations of R–C=N–R′ type compounds decrease in the order R–C=N–R′> R–C=N–Ar> Ar–C=N–Ar, where R and R′ denote alkyl groups—the fact which is parallel to that of the corresponding C=C compounds[13]. This fact is at first likely to show that benzylideneaniline has the planar conformation and the increase of the number of benzene rings causes the increase of resonance interaction, and therefore decreases the force constant of vibration. But in the present model, the resonance interaction will increase though to a smaller extent, and in addition to this, hybridization-change will occur when R′ is replaced by C_6H_5, which would also tend to reduce the force constant.

Another strong objection to this assumption is the evidence of photoisomerism of this substance at low temperature[14]. It is not certain whether this is *cis-trans* isomerism, but if it is so, one explanation is that the bending isomerization is frozen at low temperature.

Some question may arise why benzylideneaniline can assume this structure, while azobenzene can not, and why it does not return to the planar structure when proton attaches to it. In this respect, the author has the impression, though merely speculative at this stage, that azobenzene also behaves in somewhat like manner in solution, and its thermal *cis-trans* isomerization is the mixture of ordinary and bending ones, because it belongs to neither of the two types classified by Eyring[15]. This point will be investigated in future.

Experimental

Benzylideneanilines were prepared by direct condensation of benzaldehyde with corresponding anilines. Stilbene and azobenzene were prepared by recrystallization of commercial substances. *p*-Methoxy-stilbene was kindly supplied by Mr. H. Suzuki. Azoxybenzene was prepared by treating nitrosobenzene with ethanol and sodium hydroxide.

Absorption spectra were measured by Cary self-recording spectrophotometer model 14 M using 1 cm. quartz cell.

Summary

The ultraviolet absorption spectra of benzylideneanilines, as well as of their conjugate acids, have been measured.

These spectra can not be explained with the ever believed stilbene-type planar structures of these molecules.

An alternative structure is proposed for benzylideneaniline with the benzene ring of aniline part nearly perpendicular to the rest of the molecule.

This structure also adequately explains many experimental evidences, which have been investigated previously but are not accounted for by the planar structure.

The author wishes to express his sincere thanks to Professor S. Nagakura for his kind instruction throughout this study. Thanks are also due to Professor K. Shiomi and to the members of his laboratory for their fruitful discussions.

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[13] A. Kirrman and P. Laurent, *Bull. soc. chim. France*, **6**, 1657 (1939).

[14] E. Fischer and Y. Frei, *J. Chem. Phys.*, **27**, 808 (1957).

[15] J. L. Magee, W. S. Shand, Jr., and H. Eyring, *J. Am. Chem. Soc.*, **63**, 677 (1941).