Benzylideneaniline. III. Anils of Substituted Benzaldehydes

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In the first paper of this series¹⁾ a non-planar structure was proposed for benzylideneaniline, where the benzene ring of aniline part is almost perpendicular to the rest of the molecule (Fig. 1). In such a case the ultraviolet absorption spectrum of this molecule would be closely allied to those of benzaldehyde type I and aniline type II molecular halves, and it was assumed that the absorption maxima at 263 mμ (A) and at 315 mμ (B) is due to I and II respectively. The effects of substituents upon these bands were examined and it was found that the substituents on II had little to do with band A, whereas marked shifts were experienced by band B.

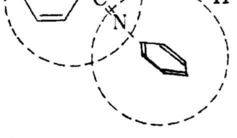

Fig. 1. Assumed structure of benzylideneaniline.

In the present paper, derivatives of benzylideneaniline of which the substituents are on aldehyde ring I, together with anils bearing aliphatic halves, were synthesized and their spectral features as well as other properties were examined.

Ultraviolet Absorption Spectra.—Ultraviolet absorption spectra of anils were measured in *n*-heptane, ethyl alcohol and 50% mixture of hydrochloric acid and ethyl alcohol. The spectra in *n*-heptane are illustrated in Fig. 2 and pertinent data are listed in Table I.

Bands A.—Bands A shift markedly as substituents vary, in contrast to the case where the substituents are on II. Moreover, they shift furthermore towards longer wavelengths when alcohol is used as solvent. In acidic

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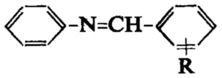
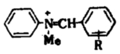
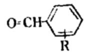
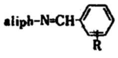
1) N. Ebara, This Bulletin, 33, 534 (1960).

TABLE I. WAVELENGTHS OF UV ABSORPTION MAXIMA (in Å)

							
R	Solvent			Crystal state	in	in	in
	C_7H_{16}	C_2H_5OH	HCl+ C_2H_5OH		C_2H_5OH (above 3000 Å)	C_2H_5OH	C_7H_{16}
p-OH	2750 3150	(2950) 3140			—	2815	
p-OCH_3	2790 3150	(2790) 3030		2800 3250	—	2765	2680
o-OH	2680 3010 3180 3415	2700 2990 3160 3360	2570 3240	3100~3500	3280	2540 3244	2540 2590 3170
o-OCH_3	2650 3220	2660 3280			3200?	2528 3210	
p-NO_2	2860 3130 3420	2910 3180	2340 (3500)		—		
p-NMe_2	3000 3100 3200 3270	3430	2430 2815 (3500)		—	3420	3390
p-Cl	2680 3180	2685 3150	2590 2900 (3480)		—		
m-NO_2	2550 3220	2580 3180	2340 (3480)		—		
m,*m*'-$(NO_2)_2$	2550 3160	2590 3200	2640 3180 (3670)				

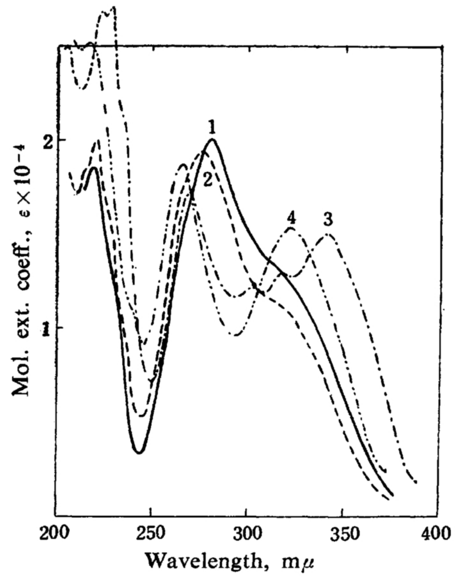


Fig. 2(A). Spectra of anils in *n*-heptane.

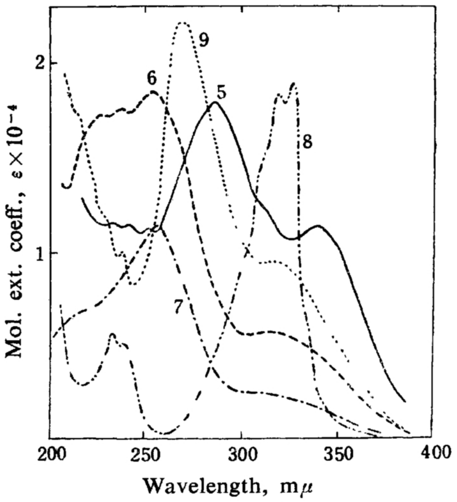
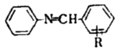


Fig. 2(B). Spectra of anils in *n*-heptane:



R= 1) *p*-OH; 2) *p*-OCH_3; 3) *o*-OH; 4) *o*-OCH_3; 5) *p*-NO_2; 6) *m*-NO_2; 7) *m*, *m*'-diNO_2; 8) *p*-$N(CH_3)_2$; 9) *p*-Cl; (Intensities of 3 and 7 are in arbitrary unit and that of 8 in half scale).

medium, the blue shift is again observed with these bands as in the former case¹⁾, but their maxima are by no means at the same position, but vary in a manner similar to those of corresponding anils and aldehydes. These facts are in good accordance with the above proposal that band A is largely of the nature of CT band of I.

Bands B.—Unfortunately the behavior of bands B is not quite obvious as anils bearing the electron-donating groups at the ortho position of I exhibit the expected maxima of enhanced intensities at the longer wavelength region (presumably the second CT bands²⁾ from I) and the positions of bands B become obscure. But in cases where they are observable, they are in general almost at the same position. It is perplexing, however, that substitution at the para position of I by NO_2 group also gives rise to a new band at the longer wavelength region, of which the explanation is not yet deduced.

There remains another discrepancy as to the intensities of bands B, which are too much enhanced to be largely of the nature of A_1-B_2 transition of II.

Comparison with the Anils Bearing Aliphatic Halves. — Benzylidene-*n*-butylamine, anisylideneisopropylamine, *p*-dimethylaminobenzylideneisopropylamine, salicylideneisopropylamine and *n*-butylideneaniline were synthesized and their spectra were measured (Fig. 3).

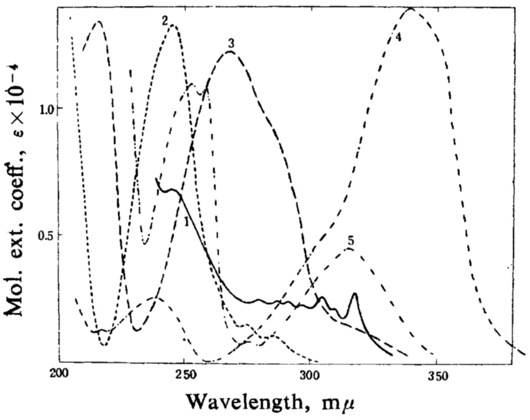
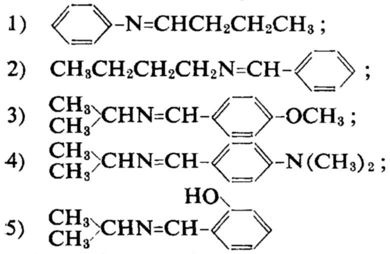


Fig. 3. Spectra of aliphatic anils in *n*-heptane:



(Intensity of 4 is in half scale).

Anils of aliphatic amines and aromatic aldehydes exhibit intense bands in the proximity of those of aldehydes, which may therefore be correlated to bands A of aromatic anils. Bands B vanish completely in these anils.

n-Butylideneaniline shows an intense band at 2470 Å and a weak one with a structure between 2820 and 3200 Å, which should correspond to those of aniline. The position of the latter band coincides almost exactly with band B of benzylideneaniline, although their intensities differ considerably. It is not certain whether *n*-butylideneaniline assumes benzaldehyde type or aniline type structure (presumably, the former), but apart from this, it may be concluded that $A_{1g}-B_{2u}$ transition of benzene at 2600 Å rises to this position in the presence of the perturbation of R–CH=N– and that this band shifts no more towards longer wavelengths when R turns from aliphatic to aromatic groups.

Therefore, no substantial difference seems to exist between the spectra of aliphatic and aromatic anils.

Spectra of *N*-Methylated and Protonated Anils.—Similar spectra are observed with *N*-methylated anils and with *N*-protonated anils. Bands B vanish completely, whereas bands A shift towards shorter wavelengths: the explanation of the latter phenomenon was given tentatively in terms of hybridization change in the previous paper¹⁾.

No anils giving rise to second CT bands of I miss these bands when they are methylated or protonated.

***p*-Hydroxybenzylidene- and Anisylideneaniline.** —Striking are the features of the spectra of

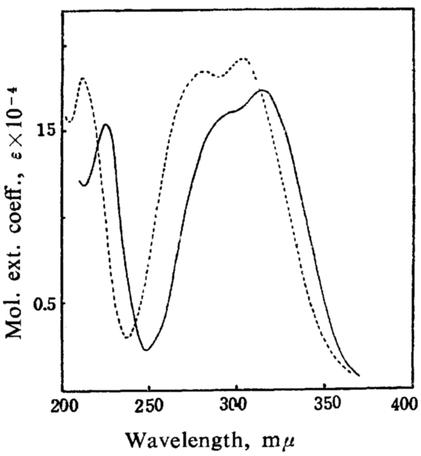
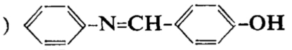
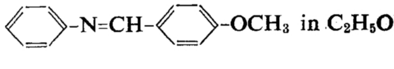


Fig. 4. Spectra of 1)  and 2)  in C_2H_5OH.

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2) J. Tanaka and S. Nagakura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 78, 1200 (1957).

p-hydroxybenzylidene- and anisylideneaniline, where the spectra are very greatly different in alcohol as compared with those in *n*-heptane, the latter exhibiting the ordinary shape of anils (Fig. 4). In contrast to this, the spectra of anils bearing these substituents on II are free from any remarkable solvent effect. It seems plausible to assume that the bands A at 2750 Å and at 2790 Å of these compounds in *n*-heptane, presumably the CT band of I, shift to 3140 and 3030 Å in alcohol, respectively, owing to the pronounced stabilization of the solvated excited states where there are large resonance polarizations due to strongly electron-donating substituents at the para positions. These molecules decompose very quickly in alcohol, as will be described in a following section, and the bands near 2800∼2900 Å may be attributed to the inevitably present decomposition products.

Salicylidene- and *o*-Methoxybenzylideneaniline. —Another peculiar feature is that of salicylideneaniline, where three bands are observed above 3010 Å, which are too conspicuous to be the vibrational structure. It had been reported that strong hydrogen bonding exists between hydroxyl hydrogen and azomethine nitrogen atoms[3], and that this would be responsible for the unusual spectrum of this molecule[4]. But it is highly improbable that a hydrogen bonding would cause such a large variation in the spectrum as the appearance of new bands.

In phenylazonaphthol a tautomerism is known to exist between azo and hydrazone forms[5], whereas *o*-hydroxyazobenzene does not exhibit this tautomerism[6]. To see whether this is the case or not with salicylideneaniline, and to examine whether or not some of these bands correspond to the tautomeric enamine form, the temperature dependence of the ultraviolet absorption spectrum was examined. The spectrum was measured at several temperatures between −60 and 47°C, but no remarkable change was observed except for the ordinary sharpening and broadening of the peaks accompanying the temperature change. The infrared spectrum was also examined in carbon tetrachloride solution and in solid state, but there was observed no band attributable to C=O stretching vibrational mode. Moreover the spectra in the solution and in the solid state resemble each other very closely, indicating that the molecular structure is not so greatly different in these two states, and that there seemes to exist no tautomeric equilibrium between the above two structures. The shift of C=N stretching vibration from that of unsubstituted benzylideneaniline is considerably great as compared with other anils where the shifts are at most within a few cm^{-1} (Table II). OH stretching vibration is hidden under the lower frequency side of CH stretching vibration. Deuterated salicylideneaniline was synthesized. This gives rise to a very broad band between 2020∼2180 cm^{-1}, doubtless attributable to OD stretching vibration, from which the position of the original OH band is calculated to lie between 2800∼3000 cm^{-1}, showing an unusual shift towards lower frequencies.

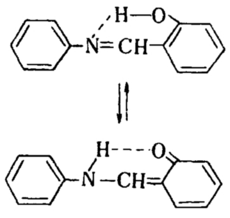
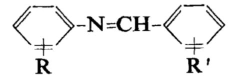


TABLE II. WAVE NUMBERS OF C=N STRETCHING VIBRATIONS



in CCl_4

R	R'	Wave number, cm^{-1}
H	H	1629
p-OCH_3	H	1626
o-Cl	H	1630
m-Cl	H	1631
p-Cl	H	1628
m-NO_2	H	1631
H	*p*-OCH_3	1624
H	*o*-OCH_3	1620
H	*m*-NO_2	1629
H	*p*-NO_2	1629
H	*o*-OH	1616

Presumably a large resonance coupling would exist between azomethine and enamine forms, the former still being predominant. The molecule may safely be referred to as existing almost exclusively in azomethine form rather than in enamine form in the solution as well as in the solid state, and the new ultraviolet absorption bands might not be ascribed to the tautomerism.

Ionization equilibrium might exist in this molecule between phenolic and phenolate structures, and some of the bands might be attributed to anion form. But this seems also not to be the case, as the change of solvent, as well as of temperature, proves no evidence of the noticeable variation in the ionization constant. Moreover, in alkaline solution, the

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3) e. g., L. Kahovec and K. W. Kohlrausch, *Zeitschr. phys. Chem.*, (B) **38**, 119 (1938).

4) A. von Kiss and G. Auer, ibid., (A) **189**, 344 (1941).

5) e. g., A. Burawoy and I. Markowitsch, *Ann.*, **503**, 180 (1933).

6) e. g., D. Hadži, *J. Chem. Soc.*, **1956**, 2143.

bands above 3010 Å disappear and a new band comes out at 3800 Å, which is raised too much to be led back to any of the bands of salicylideneaniline.

It turns out that an intense band exists at 3220 Å in the spectrum of *o*-methoxybenzylideneaniline. This is all but congruent with that at 3210 Å of *o*-methoxybenzaldehyde and is presumably the second CT band of I. Salicylaldehyde, salicylaldoxime⁷⁾, salicylaldimine⁷⁾ and bis-salicylidene-ethylenediamine⁸⁾ as well as *N*-methyl-salicylideneanilinium ion exhibit similar bands. All of these bands may demand their replica in the spectrum of salicylideneaniline: the band at 3415 Å is the most adequate for this, though it is conflicting that this band experiences the blue shift when alcohol is used as solvent.

One of the other two bands at 3010 and 3180 Å, preferably the latter, may be assigned as band B, which comes from I of the molecule.

Hydrolyzation Reaction of *p*-Hydroxybenzylidene-, Anisylidene- and *o*-Methoxybenzylideneaniline.—These three compounds decompose very quickly in alcoholic solutions. The reaction rates were found to depend upon the water content of alcohol, and would conceivably be hydrolyzation reactions. The rates of these reactions were measured at several temperatures by tracking their spectral changes, and it was found that the reactions are first-order as to the concentrations of anils in the presence of excess water. The results are shown in Table III and in Figs. 5, 6 and 7.

TABLE III. HYDROLYZATION REACTION RATES IN $C_2H_5OH(2)+H_2O(1)$

Temp., °C	$k\times10^2$	E, kcal./mol.	A
o-Methoxybenzylideneaniline			
31.6	9.90	7.72	1.6×10^4
26.0	7.92		
20.6	6.40		
12.0	4.40		
p-Hydroxybenzylideneaniline			
45.6	5.87	6.56	2.5×10^3
40.1	4.95		
25.85	2.97		
13.95	1.89		
Anisylideneaniline			
45.5	5.16	6.11	1.0×10^3
39.7	4.28		
24.5	2.62		
13.85	1.77		

It is probable that owing to the strongly electron-donating properties of the substituents, the addition of proton at the nitrogen atom, or conceivably the heterolytic fission of OH bond of hydrogen-bonded water at the nitrogen atom, accompanied by the addition of OH^- to the azomethine carbon atom, would proceed easily.

The activation energies are almost equal in these three cases, whereas the frequency factor is the largest in *o*-methoxybenzylideneaniline. One tentative explanation is that owing to the closely standing hydrogen-bonded *o*-methoxyl group, the chance of the reaction in which water participates is greater in this case.

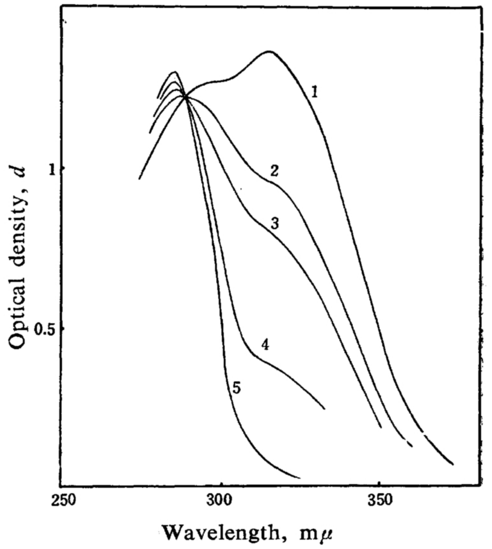
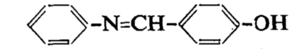


Fig. 5. Time-dependence of the spectrum of



1) Immediately after dissolution;
2) After 7 min.; 3) After 10 min.;
4) After 24 min.; 5) After 4 hr.

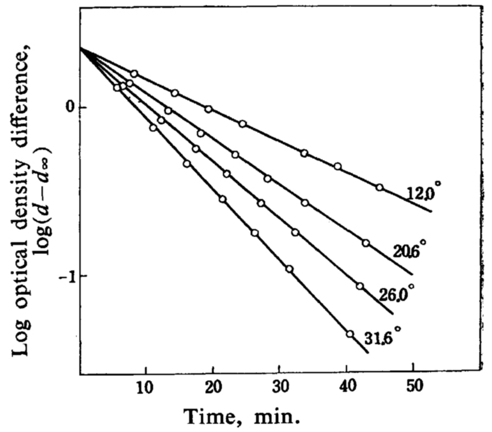
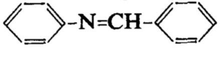


Fig. 6. Hydrolyzation reaction of



in $C_2H_5OH(2)+H_2O(1)$.

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7) K. Sone, *J. Am. Chem. Soc.*, **75**, 5207 (1953).
8) L. N. Ferguson and I. Kelly, ibid., **73**, 3707 (1951).

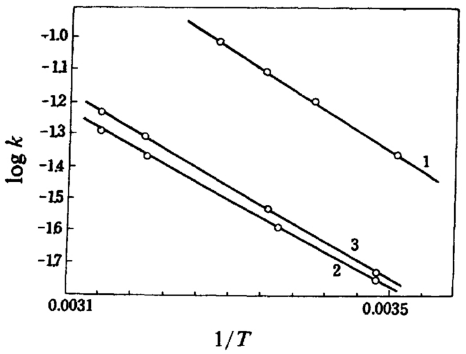
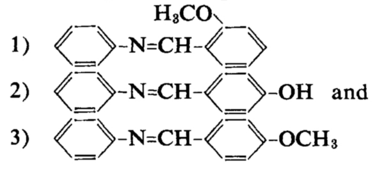


Fig. 7. Temperature dependences of



When the substituents are on II, hydrolyzation reaction does not take place, presumably because the substituents would only affect the C=N bond through the participation in the migration aptitude of nitrogen non-bonding electrons.

Spectra in the Solid States.—The spectra of benzylideneaniline, anisylideneaniline, salicylideneaniline, salicylidene-*p*-chloraniline and salicylidene-*p*-bromoaniline were measured in the solid states by means of either the potassium chloride disk method or the film method (Fig. 8). In the former three cases the spectra are very similar to those in *n*-heptane solutions, indicating that the molecular shapes are not greatly different in these two states, provided that the ignorance of the effect due to the orientation of the crystal axis may be permitted in the latter method. In the latter two cases, single peaks are always observed above 3000 Å instead of three, though their spectra in the solution are very similar to that of salicylideneaniline. It is not certain whether this is due to the variation in molecular shapes or due to the difference in crystal structures, or in turn due to the preferred orientation of crystal axis against the plates, which tends to favor the absorption band whose transition moment is perpendicular to it.

Trial Interpretation of UV Spectrum on the Basis of Planar Model. — Because of some discrepancies arising in the above consideration, the interpretation of the ultraviolet spectrum of benzylideneaniline is intended tentatively to be regarded on the basis of the planar model.

The symmetry C_{2v} may be assigned to the molecule, so far as the π electrons are concerned. In this approximation, the allowed electronic transitions are A_1-A_1 and A_1-B_2 (A_1-B_1 may be excluded, because the π electronic levels are always constructed with atomic 2p orbitals).

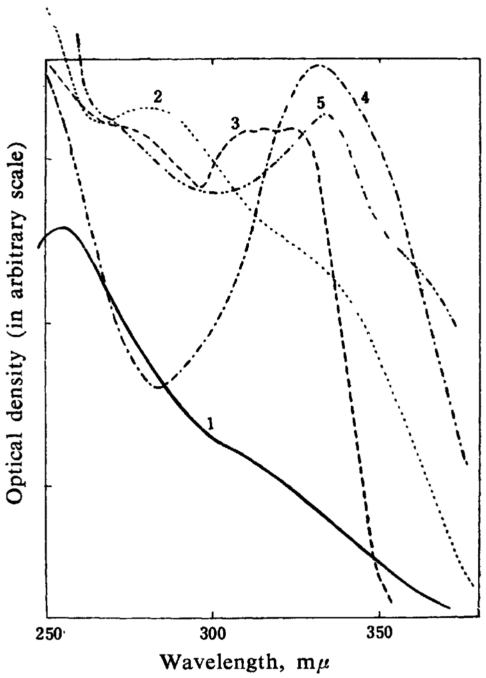
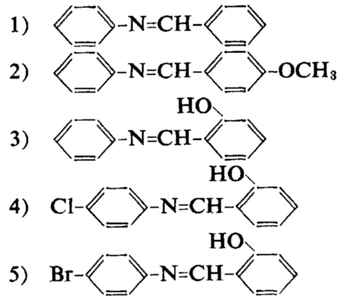


Fig. 8. Spectra in solid states,



Following the method of Nagakura and Tanaka[9], the perturbation diagram of this molecule is drawn, where the ionization potential and electron affinity of C=N group are assumed to lie between those of C=O and C=C, largely approaching the former (Fig. 9). Although the coefficients of atomic orbitals at N and C atoms in the MO of C=N group differ from each other, the resulting molecular energy level diagram might not be so far from those of stilbene and azobenzene at least in the lower region, and the lower excitations should be $\pi-\pi^*$ (or A_1-A_1) and $\pi-\phi^*$ (or A_1-B_2)[10]. The former should involve the charge transfer from two benzene rings to the

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[9] S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954).

[10] The energy diagram is drawn by taking account of Jaffé's calculations (see Ref. 11).

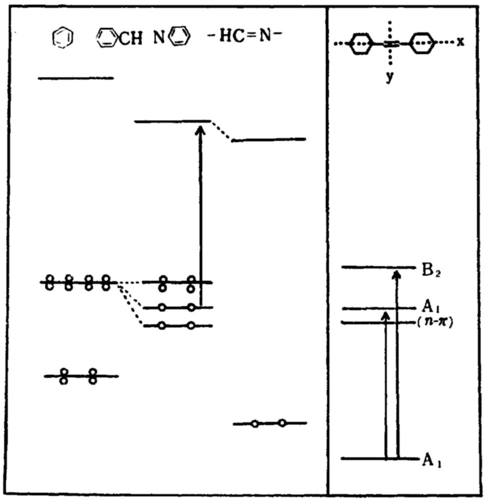

Fig. 9. Energy level diagrams of planar benzylideneaniline molecule.

central C=N part, although the mixing with other configurations would in part reduce it. The latter has much in common with benzene $A_{1g}-B_{2u}$ transition except that it becomes allowed by the perturbation. The intensity of the former should be reduced by the unsymmetrically situated central N atom and that of the latter would be much lower.

Two bands, A and B, arising in the spectrum of benzylideneaniline must be interpreted from the above standpoint. Jaffé[11] had assumed that they are $\pi-\phi^*$ and $\pi-\pi^*$, respectively.

In the present experiment, however, it was found that band A has the character of CT band, whereas band B does not, and that the nitrogen non-bonding electrons are responsible for the appearance of band B. Moreover this band is too intense to be A_1-B_2 transition. These findings go behind with Jaffé's interpretation.

An alternative interpretation in which band A is assigned as $\pi-\pi^*$ does not hold, as the energy of this transition might not be so great.

Thus, the planar model presents more discrepancies with regard to the ultraviolet spectrum of the molecule.

Conclusion

The results obtained here can be explained adequately by the non-planar model proposed in the previous paper. In particular, the coincidence in the ultraviolet spectrum seems to be excellent. But the explanation is not unique and leaves many discrepancies. It remains in doubt whether or not the failure of explaining the spectrum of this molecule with the hitherto believed planar model might be ascribed to the misestimation or ignorance of some quantities which will arise in the calculation of molecular energies.

The molecule seems to assume the same conformation in the solid state as in the solution. The X-ray crystal analysis is now in progress. This will provide indisputable information with regard to the precise conformation of benzylideneaniline molecule.

Experimental

Materials.—Benzylidene-, *p*-hydroxybenzylidene-, *p*-chlorobenzylidene-, *p*-nitrobenzylidene, *m*-nitrobenzylidene-, anisylidene-, *p*-dimethylaminobenzylidene- and salicylideneaniline were prepared by the direct condensation of aniline with corresponding aldehydes, without any dehydrating agent and were recrystallized from ethyl or isopropyl alcohol. M. p. 63, 193~194, 61~62, 90~90.5, 64.5~65, 51.5~52, 67~68 and 50~50.5°C, respectively.

o-Methoxybenzaldehyde was prepared from salicylaldehyde by methylating it with dimethyl sulfate. The distilled and crystallized aldehyde was readily submitted to condensation reaction with aniline, affording *o*-methoxybenzylideneaniline. The product was dehydrated and distilled and then recrystallized from isopropyl alcohol. M. p. 39~40°C.

Salicylidene-*p*-chloraniline and -*p*-bromaniline were synthesized by the condensation of salicylaldehyde with corresponding anilines and recrystallized from ethyl alcohol. M. p. 100 and 107°C, respectively.

n-Butylideneaniline, benzylidene-*n*-butylamine and anisylidene-, salicylidene- and *p*-dimethylaminobenzylideneisopropylamine were prepared by the following procedure. Equimolecular amounts of corresponding amines and aldehydes were put into a round-bottomed flask equipped with a good condenser. Vigorous reaction took place and water was separated out. The mixture was heated on a water bath for about one hour, then shaken with ether, dried over calcium chloride and distilled under reduced pressure. B. p. 118°C/13 mmHg, 111°C/17 mmHg, 119~120°C/14 mmHg., 155°C/25 mmHg, respectively.

Deuterated Salicylideneaniline. — Deuterated ethyl alcohol was prepared from sodium ethoxide and deuterium oxide, and this alcohol was again used for the preparation of sodium ethoxide. The procedure was repeated so as to reduce the hydrogen content of the resulting alcohol. Salicylideneaniline was dissolved in this alcohol and the solvent was evaporated at room temperature under reduced pressure. The moisture was carefully excluded throughout the whole process.

***N*-Methylated Anils.**—Excess amounts of methyl iodide were added in the solutions of anils and they were kept standing for several hours. The absorption spectra were measured at times in order to check the degree of completion of the reaction. The intense absorbancy due to methyl iodide was compensated for, but the spectra below 3000 Å could not be measured. Another method is

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[11] H. H. Jaffé, Si-Jung Yeh and R. W. Gardner, *J. Molecular Spectroscopy*, **2**, 120 (1958).

employed as well, in which anils were dissolved in pure methyl iodide, kept standing for a night, desiccated to dryness, dissolved in alcohol and subjected to the measurements of absorption spectra.

Measurements.—Ultraviolet spectra were measured by means of a Cary 14-type self-recording spectrophotometer using 1 cm. quartz cell. To follow the reaction rate, the spectra were measured by the use of Hitachi EPU 2-type spectrophotometer.

Hydrolyzation Reactions.—The anils were dissolved in alcohol containing one-third the amount of water, and immersed in a thermostat. The absorbances of the solutions were measured at times in the vanishing band region. The final absorbances were also measured from which a rate equation could be derived. The plotted points fell on straight lines in very good coincidence.

Infrared spectra were measured by means of Nihon-bunko self-recording spectrophotometer model 301, using sodium chloride prism and sodium chloride cells of 0.1 mm. in thickness. Solid samples were prepared by allowing the melt to cool between sodium chloride plates pressed together.

Solid samples for the ultraviolet measurements were prepared either by allowing the melt to cool between quartz plates or by pressing the mixtures of finely powdered materials with specially prepared potassium chloride crystals(12).

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