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## Spectroscopic Studies of Substituted Benzalanilines

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### Abstract

Ultraviolet and visible spectra are reported for 28 N-benzylidene-anilines with their molar absorptivities given in absolute ethanol, and in isoctane when feasible. Infrared studies in the 2-15 micron region are reported for these compounds and also for three newly synthesized N-d-benzylideneanilines. With the aid of these deuterated benzalanilines, infrared assignments are given for the frequencies characteristic of the center  $-\text{CH}=\text{N}$ -azomethine group. The ultraviolet and infrared spectra are compared in relation to the reported basicity of their azomethine groups.

### Introduction

The spectral results presented here are part of an analytical study on aromatic azomethines with regard to the

effect of substituents on the resonance interaction of the  $-\text{HC}=\text{N}$ -group. Aside from a preliminary report by Clougherty, Sousa, and Wyman (1), little besides tentative assignments have been reported on the infrared characteristics of aromatic azomethines (2). Ultraviolet spectra have been reported previously for some benzalaniline derivatives, notably the work of Kiss and Pauncz (3) on hydroxy and methoxy derivatives, and data on a few additional benzalanilines by others (4, 5). However, some of the spectra in the literature appear to be actually those of the hydrolyzed products (6). Both ultraviolet and infrared spectra are reported here for several families of substituted benzalanilines in correlation with their relative basicity as measured by Weinstein and McNinch (7).

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TABLE I. PHYSICAL PROPERTIES OF N-BENZYLIDINEANILINES

No.	Compound	M.P. <sup>o</sup> C <sup>a</sup>	M.P. <sup>o</sup> C(Lit)	Elemental Analyses					
				Found			Calcd.		
				C	H	N	C	H	N
I	N-benzylideneaniline	51-52	52 <sup>b</sup>						
Id	N-d-benzylideneaniline	51.5-52	—	86.0		7.63	85.7		7.69
II	N-benzylidene-(p-chloro) aniline	61-61.5	62 <sup>c</sup>						
IIId	N-d-benzylidene-(p-chloro) aniline	61-61.5	—	71.7		6.40	72.1		6.46
III	N-benzylidene-p-anisidine	70-70.5	69 <sup>d</sup>						
IIIId	N-d-benzylidene-p-anisidine	69.5-70	—	79.4		6.74	79.2		6.60
IV	N-benzylidene-(p-bromo) aniline	64.5-65.5	67 <sup>e</sup>						
V	N-benzylidene-(p-amino) aniline	72.0	—	79.1	6.00		79.6	6.16	
VI	N-benzylidene-p-toluidine	53-54	55 <sup>e</sup>						
VII	N-benzylidene-(p-dimethylamino) aniline	104	104 <sup>e</sup>						
VIII	N-benzylidene-(p-nitro) aniline	117-118	117-118 <sup>f</sup>						
IX	N-(p-chloro) benzylideneaniline	64-65	65.5-66 <sup>e</sup>						
X	N-p-anisylideneaniline	63-63.5	63 <sup>e</sup>						
XI	N-(p-bromo) benzylideneaniline	72.5-73	—	59.9	3.76		60.0	3.88	
XII	N-p-tolylideneaniline	45-46	46.5-48 <sup>g</sup>						
XIII	N-(p-dimethylamino) benzylideneaniline	99-99.5	100 <sup>h</sup>						
XIV	N-(p-nitro) benzylideneaniline	91.0-91.5	90-93 <sup>d</sup>						
XV	N-(p-hydroxy) benzylideneaniline	194-195	195 <sup>e</sup>						
XVI	N-(p-acetoamino) benzylideneaniline	139.5-140	—	75.7	5.81		75.6	5.92	
XVII	N-(p-dimethylamino) benzylidene-(p-chloro) aniline	149.5-150.5	—	69.4	5.70		69.6	5.84	
XVIII	N-p-anisylidene-p-anisidine	145-146	146-147 <sup>i</sup>						
XIX	N-(p-chloro) benzylidene-(p-chloro) aniline	110.5-111	111 <sup>e</sup>						
XX	N-(p-nitro) benzylidene-(p-dimethylamino) aniline	220-221	220 <sup>o</sup>						
XXI	N-p-anisylidene-p-toluidine	91.5-92	92-93 <sup>i</sup>						
XXII	N-(p-dimethylamino) benzylidene-(p-dimethylamino) aniline	229-230	229-230 <sup>j</sup>						
XXIII	N-(p-dimethylamino) benzylidene-(o-hydroxy) aniline	118-119	119 <sup>k</sup>						
XXIV	N-p-anisylidene-o-anisidine	59.5-60	—	74.7	6.10		74.7	6.27	
XXV	N-(o-nitro) benzylideneaniline	63-64	—	68.8	4.14		69.0	4.46	
XXVI	N-salicylideneaniline	50-51	51 <sup>f</sup>						
XXVII	N-benzylidene-(o-hydroxy) aniline	94-95	95 <sup>e</sup>						
XXVIII	N-salicylidene-(o-hydroxy) aniline	185	185 <sup>o</sup>						

<sup>a</sup> Uncorrected. <sup>b</sup> L. A. Bigelow and H. Eatnough, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 80. <sup>c</sup> A. Hantsch and O. Schwab, Ber., **34**, 822 (1901). <sup>d</sup> B. A. Porai-Koshits, E. M. Poznankaya, U. S. Shevchenko and L. A. Pavolova, J. Gen. Chem. (U.S.S.R.), **17**, 1774 (1947). <sup>e</sup> G. Smets and A. Delvaux, Bull. soc. chim. Belg., **56**, 106 (1947). <sup>f</sup> W. V. Miller and J. Plöchl, Ber., **25**, 2020 (1892). <sup>g</sup> E. J. Wayne and J. B. Cohen, J. Chem. Soc., 460 (1925). <sup>h</sup> F. Sachs and Wolewin, Ber., **35**, 3569 (1902). <sup>i</sup> A. Senier and R. B. Forster, J. Chem. Soc., 1168 (1915). <sup>j</sup> F. Bender, Ber., **28**, 109 (1895). <sup>k</sup> Möhlau, Adam, Ztschr. für Farbenindustrie, **5**, 410 (1906).

## Experimental and Results

### Preparation of Benzalanilines

Each benzalaniline was prepared from the corresponding amine and aldehyde by refluxing equimolar amounts of purified material for 30 min, cooling to precipitate, and recrystallizing from absolute ethanol to a constant melting point and ultraviolet molar absorptivity. Infrared analyses were used to check for the presence of the azomethine group and the absence of the starting materials. The identity of the product was established by melting point and/or elemental analysis. These are summarized in Table I, which gives the elemental analyses for those compounds where no melting point was found in the literature.

The deuterated benzalanilines (compounds Id, IIId and IIIId) were prepared by condensing the appropriate amine with benzaldehyde-d<sub>1</sub>, which had been prepared with LiAlD<sub>4</sub> using the method of Wiberg (8).

### Ultraviolet-Visible Region

Absorption measurements were made on a Cary model-11 spectrophotometer in 1 cm matched silica cells using absolute ethanol and dry spectral grade iso-octane as solvents. Samples of different concentrations were measured and the molar absorptivities shown in Table II were found to be reproducible within 0.4%.

The benzalaniline spectra shown in Figures 1, 2, and 3 are arranged as families of curves, depending upon which aromatic ring is substituted. The spectra in these figures are arranged in order of decreasing base strength

with the strongest base at the top. Benzalanilines with visible absorption bands, mainly hydroxy compounds, are shown in Figure 4. Their basicities have not been measured, but they are probably all stronger than compound XX, which is a comparatively weak base.

Qualitative observations were made on the effect of acid and base on the spectra of benzalanilines in ethanol. Hydrolysis was found to occur readily in the presence of water, and the rate is particularly rapid in the presence of strong acids (9). In contrast to previous reports (6) only irreversible spectral changes were found upon addition of HCl, even as an anhydrous gas. Some reversible changes were observed using alcoholic potassium hydroxide and glacial acetic acid. For example, N-salicylideneaniline (XXVI) formed the phenoxide type ion (maxima at 385 and 278 m $\mu$ ) in the presence of ethoxide and then reverted to its initial form when acetic acid was added. On the other hand, N-benzylidene-o-anisidine showed virtually no spectral change when ethanolic potassium hydroxide was added.

### Infrared Region

Absorption measurements were made on a Beckman model IR-3 infrared spectrophotometer with sodium chloride optics, and on a Perkin-Elmer model 112 spectrometer with a calcium fluoride prism. The 5,000-2,000 cm<sup>-1</sup> region was scanned with the PE-112 using carbon tetrachloride solutions in 0.1 cm cells, except in cases of low solubility where tetrachlorethylene was used (compounds XIX, XX, XXIII, and XXVI). The 2,000-714 cm<sup>-1</sup> re-

TABLE II. WAVELENGTH (MILLIMICRONS) AND MOLAR ABSORPTIVITIES OF PROMINENT ULTRAVIOLET AND VISIBLE ABSORPTION BANDS

Compound	Ethanol						Isooctane					
	$\lambda_{1max}$	$\epsilon_{1max}$	$\lambda_{2max}$	$\epsilon_{2max}$	$\lambda_{3max}$	$\epsilon_{3max}$	$\lambda_{1max}$	$\epsilon_{1max}$	$\lambda_{2max}$	$\epsilon_{2max}$	$\lambda_{3max}$	$\epsilon_{3max}$
I	262	17,000	310	8,530	—	—	262	17,300	310	6,900	—	—
II	221	14,300	265	17,800	315	10,500	(a)	—	—	—	—	—
III	235	12,400	266	12,600	332	12,400	—	—	235	14,400	269	13,400
IV	220	14,500	265	18,300	315	10,900	—	—	222	14,400	265	19,200
V	247	14,900	355	13,800	—	—	(a)	—	—	—	—	—
VI	264	15,600	318	10,200	—	—	262	15,900	320	8,300	—	—
VII	255	18,400	375	16,300	—	—	250	19,400	370	17,600	—	—
VIII	328	17,100	—	—	—	—	295	17,800	315	15,500	—	—
IX	270	19,000	310	9,650	—	—	269	20,700	310	8,790	—	—
X	223	17,300	290	18,100	314	17,500	—	—	221	19,100	280	20,900
XI	271	20,800	315	10,700	—	—	271	22,000	320	9,000	—	—
XII	220	15,900	268	18,200	310	10,900	—	—	267	19,600	310	8,720
XIII	239	12,400	355	32,400	—	—	234	15,000	340	31,100	—	—
XIV	240	10,700	290	11,900	340	8,410	—	—	230	12,200	288	15,600
XV	226	17,400	295	18,400	315	19,400	417	34.30	(a)	—	—	—
XVI	225	16,700	305	22,500	—	—	(a)	—	—	—	—	—
XVII	240	13,600	360	36,000	—	—	240	15,900	353	33,500	—	—
XVIII	282	18,400	331	19,200	—	—	280	19,400	330	15,100	—	—
XIX	269	19,600	320	11,800	—	—	271	21,200	320	11,200	—	—
XX	275	17,800	442	17,500	—	—	(a)	—	—	—	—	—
XXI	222	15,600	285	18,100	320	17,800	—	—	221	19,200	280	21,500
XXII	239	12,900	325	13,500	378	26,600	—	—	233	11,400	319	14,600
XXIII	242	12,100	346	26,400	—	—	240	11,900	323	24,900	368	18,300
XXIV	280	17,200	325	9,870	—	—	276	22,400	330	9,450	—	—
XXV	260	14,200	325	6,180	—	—	223	18,200	263	14,600	330	6,600
XXVI	225	19,500	270	12,800	339	11,600	435	62.90	225	20,600	268	13,400
XXVII	265	12,900	346	8,970	—	—	273	12,100	355	10,700	—	—
XXVIII	269	10,800	350	12,800	448	1,390	—	—	(a)	—	—	—

(a) Not measured quantitatively due to low solubility.

gion was scanned with the IR-3 using mineral oil mulls between rocksalt plates separated with a lead spacer.

Figures 5 and 6 show solution spectra in the 6 micron region for a more detailed examination of the C=N stretching frequency. They were recorded with the PE-112 using carbon tetrachloride as a solvent except that tetrachloroethylene was used for the nitro-compounds and ethanol was used for the hydroxy compound. These infrared curves are arranged in order of increasing base strength with the strongest base at the bottom of each family of curves.

### Discussion

#### Ultraviolet and Visible Spectra

All of the spectra are presumed to be of the *trans* form of the benzalanilines. Dipole moment studies (10, 11) indicate that the *trans* structure exists at room temperature, and photoisomerization studies (12) add supporting evidence that the sterically hindered *cis*-benzalanilines can be expected to isomerize rapidly to the *trans* form except at low temperatures. If there were no resonance interaction of the aromatic rings through the C=N linkage, the spectrum of benzalaniline (I) would be like that of a composite spectrum obtained by adding together those of *N*-benzylidinemethylamine (4) and *N,N*-dimethylaniline (13). This composite spectrum was calculated to have maxima at 292 millimicrons ( $\epsilon$  ca. 2300) and 248 millimicrons ( $\epsilon$  ca. 30,000), and this probably corresponds roughly to the spectrum of *cis*-benzalaniline in which resonance interaction is limited by the nonplanarity caused by steric hindrance. In comparison, I actually has broad maxima shifted to 310 millimicrons and 262 millimicrons with a more intense  $\epsilon$  of 8530 for the former as a result of the resonance interaction that is possible in the more planar *trans*-configuration.

The spectral effects of *para*-substituents on two families of benzalanilines are shown in Figures 1 and 2 in relation to their decreasing base strength from the top curves down (7). Shifts of the spectral bands and of basicity are greatest for those derivatives in which resonance interaction is involved. The striking effect in these complex spectra is that the apparent result of *para*-substitution on the benzal side is mainly to shift the 262 millimicron benzalaniline band, while *p*-substitution on the aniline side primarily shifts the band initially at 310 millimicrons. According to molecular orbital assignments (14), the spectrum of I consists primarily of the combination a  $\pi_1 \rightarrow \pi_1^*$  band at 310 millimicrons and  $\phi_1 \rightarrow \pi_1^*$  and  $\phi_2 \rightarrow \pi_1^*$  bands at 269 and 255 millimicrons. If this applies, then the electron donating *p*-benzal substituents seem to increase the wavelength position of the  $\phi \rightarrow \pi^*$  bands while the same *p*-aniline substituents increase both the intensity and wavelength of the  $\pi \rightarrow \pi^*$  band.

In general there is an enhancement of the long wavelength absorption band at the expense of the next lower band in changing solvents from isoöctane to ethanol. However, the total integrated absorption for both bands remains approximately constant. The solvent effect, as well as the intensity and the effect of substituents, indicates that the 310 millimicron band of benzalaniline is clearly not an  $n \rightarrow \pi^*$  transition although this has been suggested (15). The *o*- and *p*-hydroxybenzylideneanilines have a weak visible absorption band in ethanol, as shown in Figure 4. The disappearance of this band in isoöctane shows that it also is probably not an  $n \rightarrow \pi^*$  transition. Since the phenoxide form of XXVI in the presence of KOH has a band at 385 millimicrons rather than the 435 millimicron peak shown in curve D, this band does not arise from equilibrium with an ionized form. Kiss and Pauncz (3) have observed similar visible absorption bands in ethanol for a number of hydroxy-substituted

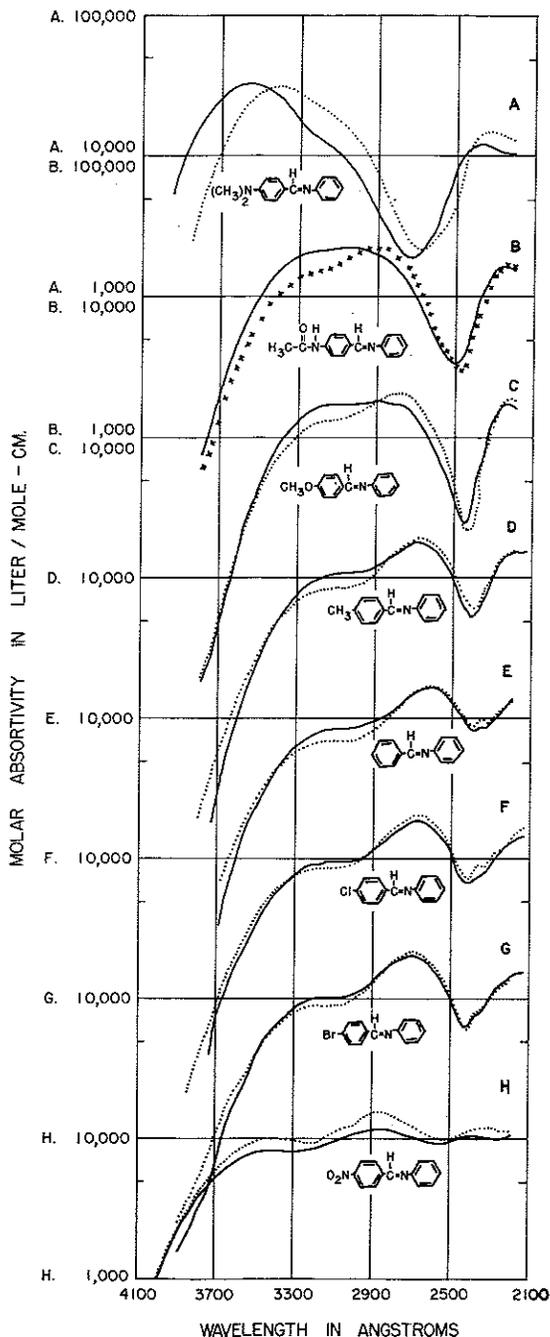


FIG. 1. ULTRAVIOLET SPECTRA OF *N*-(*p*-SUBSTITUTED)-BENZYLIDENEANILINES, COMPOUNDS XIII, XVI, X, XII, I, IX, XI, AND XIV

— absolute ethanol, ..... isoöctane, X X X X X qualitative in isoöctane.

benzalanilines and have interpreted them as due to resonance contributions of a quinone-methine structure. Alternatively, since the hydroxybenzalaniline derivatives have a basic azomethine nitrogen, the visible bands may be due to an equilibrium with a small amount of a keto tautomeric form which has the hydrogen on the nitrogen. Such a red-colored photochromic form of XXVI has been reported by Hirshberg (16) to be stable at  $-80^{\circ}$ .

#### Infrared Spectra

The  $C=N$  stretching frequencies for the solid benzalanilines (Nujol mulls) fall in the  $1616-1631\text{ cm}^{-1}$  range, as indicated by the assignments in Table III. This cor-

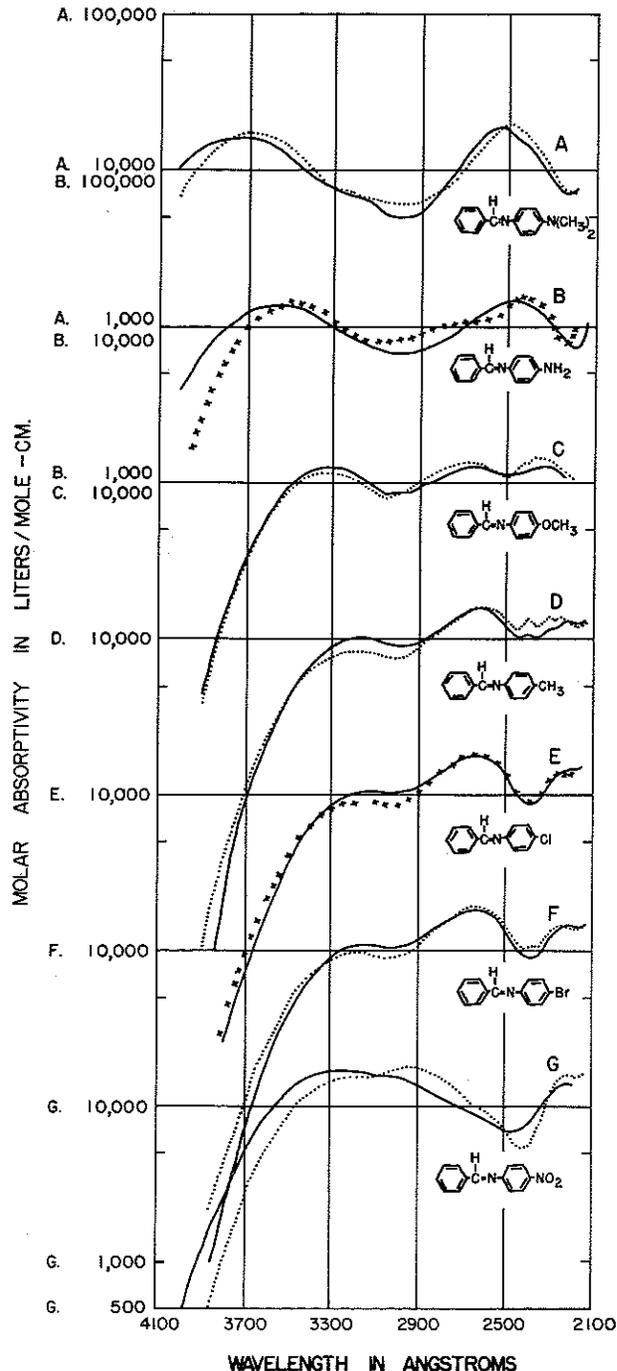


FIG. 2. ULTRAVIOLET SPECTRA OF *N*-BENZYLIDENE-(*p*-SUBSTITUTED)ANILINES, COMPOUNDS VII, V, III, VI, II, IV, AND VIII

— absolute ethanol, ..... isoöctane, X X X X X qualitative in isoöctane.

roborates the preliminary report from this laboratory in which the assignments were checked by hydrogenation of the  $C=N$  (1). Another check on this  $C=N$  assignment is given by the average  $13\text{ cm}^{-1}$  decrease found for this band when deuterium replaces hydrogen in the azomethine group. Further confirmation has been found by the shift of this band in the boron trichloride-azomethine complex of I. In KBr the  $1627\text{ cm}^{-1}$  band of I is decreased to  $1610\text{ cm}^{-1}$  for the  $I \cdot BCl_3$  complex.

The benzalaniline absorption bands in the  $C=N$  region are shown for solution spectra in Figures 5 and 6,

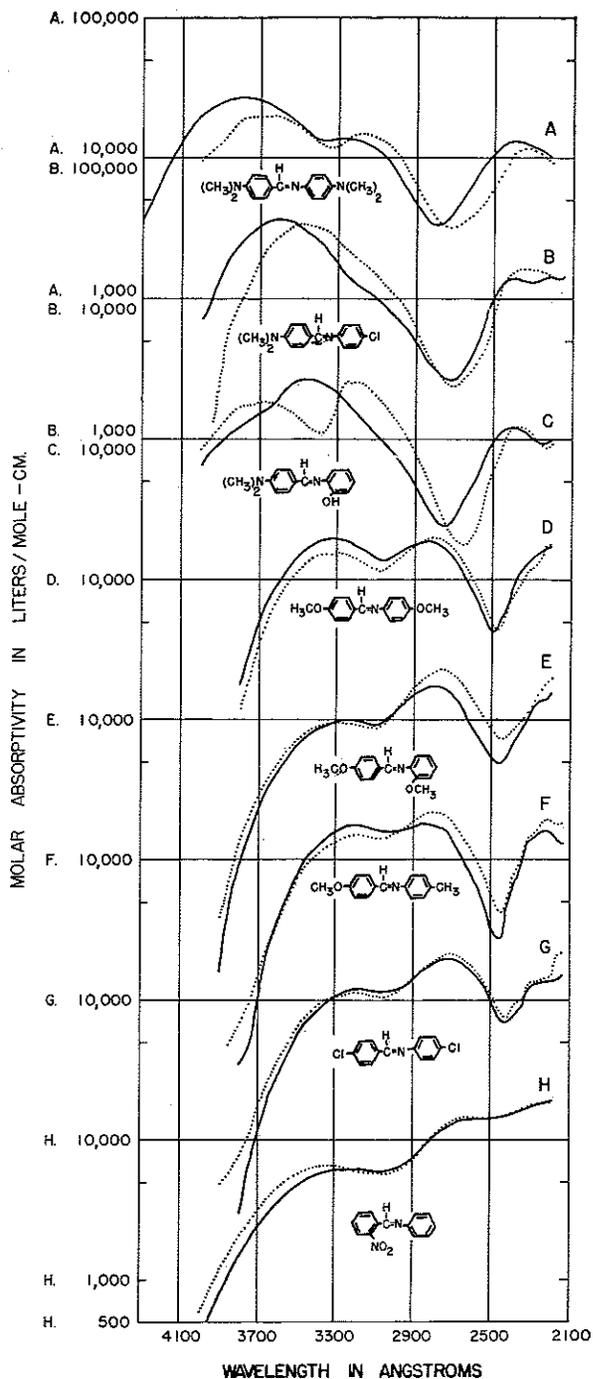


FIG. 3. ULTRAVIOLET SPECTRA OF SUBSTITUTED N-BENZYLIDENEANILINES, COMPOUNDS XXII, XVII, XXIII, XVIII, XXIV, XXI, XIX AND XXV  
 — absolute ethanol, ..... iso-octane.

where the spectra are listed from top to bottom in order of increasing base strength. These 15 compounds all have C=N stretching frequencies in the 1624-1633  $\text{cm}^{-1}$  range, and they show a striking correlation with basicity. The C=N band (near 1629  $\text{cm}^{-1}$ ) of the *p*-benzal derivatives in Figure 5 decreases in relative intensity with increasing basicity. However, another band appears in the 1605-1612  $\text{cm}^{-1}$  region and increases in relative intensity with increasing basicity. The *p*-aniline derivatives in Figure 6 all maintain a strong band near 1629  $\text{cm}^{-1}$ , but also show a new band at 1605  $\text{cm}^{-1}$  with increasing basicity. The possibility that two bands might arise from

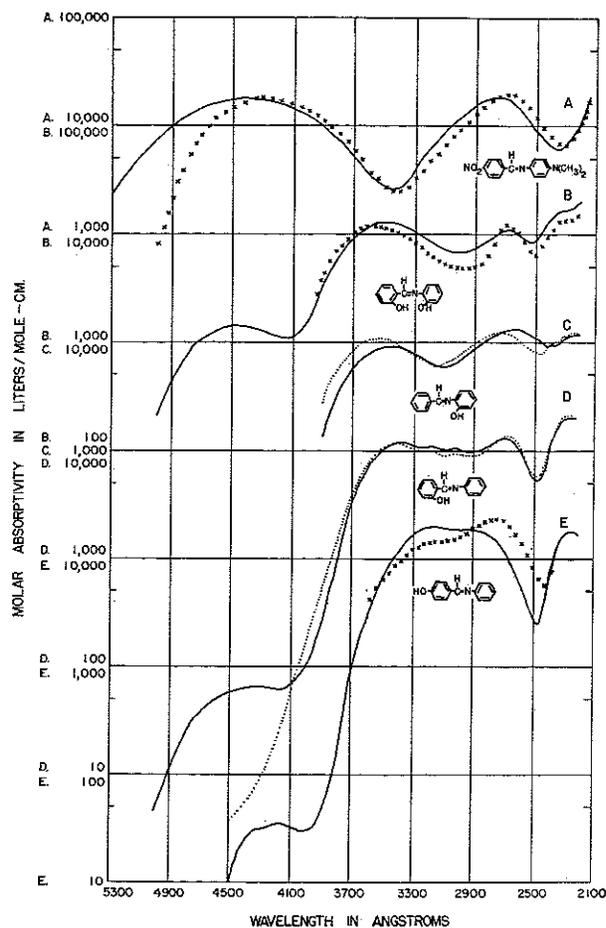


FIG. 4. VISIBLE AND ULTRAVIOLET SPECTRA OF SUBSTITUTED N-BENZYLIDENEANILINES, COMPOUNDS XX, XXVIII, XXVII, XXVI AND XV

— absolute ethanol, ..... iso-octane, x x x x x qualitative in iso-octane.

intermolecular associations due to the increased basicity of the azomethine group was checked by examining compound X in a range of concentrations (0.01 to 0.23 M) and in more polar solvents, including ethanol, dioxane, and tetrachloroethylene containing 8 per cent acetic acid. Compound X has strong bands at both 1628 and 1608  $\text{cm}^{-1}$  which changed only slightly in position and in the ratio of their intensities under these various conditions. Thus, there is no evidence that either of these bands is due to association. It has been concluded that in Figures 5 and 6 the higher frequency band (1624-1633  $\text{cm}^{-1}$ ) is the C=N stretch and the 1605-1612  $\text{cm}^{-1}$  band is an aromatic band that is intensified as the basicity of the nitrogen is increased. This was checked by noting that in the *p*-benzal derivatives the C=N intensity remains about the same while its ratio to the intensity of the first aromatic band below 1600  $\text{cm}^{-1}$  decreases from 1.2 for I, to 0.51 for X, and to 0.23 for XIII. (A similar result was found for the intensity ratios of the C=O to the 1602  $\text{cm}^{-1}$  aromatic band of the corresponding benzaldehydes, where the ratio decreased from 8.6 for benzaldehyde to 0.9 for *p*-methoxybenzaldehyde and down to 0.5 for *p*-dimethylaminobenzaldehyde.)

There are two bands in the C-H stretching region which are directly associated with the central —CH=N— group of the benzaldehydes. One of these is near 2890  $\text{cm}^{-1}$  (in the 2878 to 2907  $\text{cm}^{-1}$  range) and the other is near

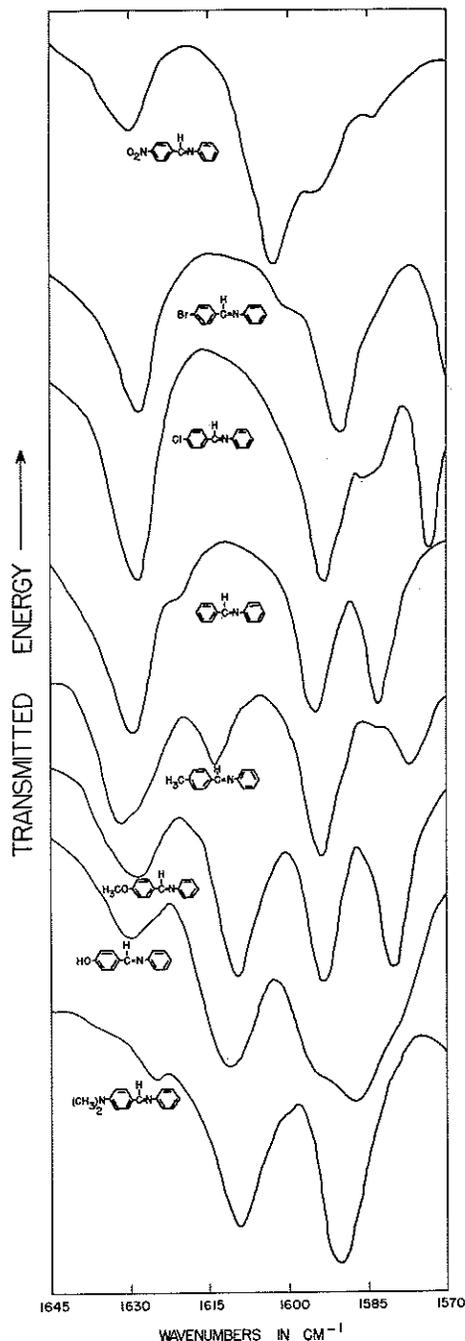


FIG. 5. INFRARED SOLUTION SPECTRA OF N-(*p*-SUBSTITUTED) BENZYLIDENEANILINES IN THE 6.1-6.4 MICRON REGION

2865  $\text{cm}^{-1}$  (in the range 2849 to 2868  $\text{cm}^{-1}$ ). Both disappear on deuteration, and a single C—D stretch shows up at 2151  $\text{cm}^{-1}$ . One of the two bands in the C—H region may be a combination band or an overtone such as Pinchas assigned to one of a similar pair of bands in aromatic aldehydes (17). While the 2890  $\text{cm}^{-1}$  is the more prominent of the two bands in most of the benzalanilines, there is insufficient evidence to rule out either band as the C—H stretching vibration.

Nearly all of the benzalanilines (25 of the 28) have a band in the 872-888  $\text{cm}^{-1}$  region, which is absent in the three deuterated compounds. This is a reasonable position for the C—H out of plane deformation of the —CH=N— group and is assigned as such in Table III.

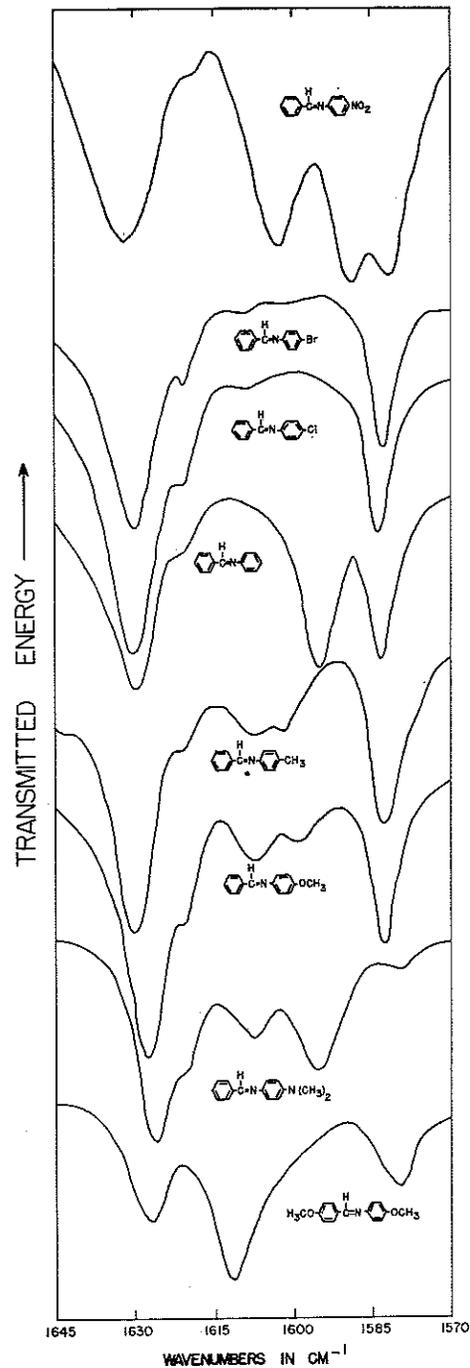


FIG. 6. INFRARED SOLUTION SPECTRA OF N-BENZYLIDENE-(*p*-SUBSTITUTED) ANILINES IN THE 6.1-6.4 MICRON REGION

#### Acknowledgements

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TABLE III. INFRARED ASSIGNMENTS OF THE —CH=N— GROUP FREQUENCY, CM<sup>-1</sup>

Compound	C=N Stretch <sup>a</sup>	C—H Stretch <sup>b</sup>	C—H Deformation <sup>a</sup>
I	1631	2890 (2865)sh	872
II	1631	2884 (2865)sh	886
III	1624	2890 (2865)	879
IV	1631	2885 (2865)	886
V	1623	2885 (2857)sh	882
VI	1631	2890	886
VII	1623	2899 (2858)	877
VIII	1630	2907 (2857)	884
IX	1626	2886 (2857)sh	879
X	1626	2890 (2865)	883
XI	1626	2890 (2868)sh	881
XII	1631	2890 (2865)sh	880
XIII	1624 <sup>w</sup>	2890 (2858)	879
XIV	1623 <sup>w</sup>	2890 (2865)	885
XV	1627	— (2859)	883
XVI	1623	2878 (2860)	885 <sup>w</sup>
XVII	—	2907 (2849)	883 <sup>w</sup>
XVIII	1623	2907 (2857)	885
XIX	1628	2890 (2865)	885
XX	1616	— (2857)	883 <sup>w</sup>
XXI	1621 <sup>sh</sup>	2874 (2865)	—
XXII	— <sup>c</sup>	2884 (2861)	882 <sup>w</sup>
XXIII	— <sup>d</sup>	2890 (2849)	885 <sup>w</sup>
XXIV	1618	— (2857)	886
XXV	1621	2924 (2865)	888
XXVI	1618	2890 (2849)	—
XXVII	1623	2890 (2849)sh	876 <sup>w</sup>
XXVIII	1621	2886	—
Id	1617	2150 <sup>e</sup>	—
IIId	1616	2152 <sup>e</sup>	—
IIIId	1615	2151 <sup>e</sup>	—

<sup>a</sup>Solids in Nujol. <sup>b</sup>Solutions in CCl<sub>4</sub> or C<sub>2</sub>Cl<sub>4</sub>. <sup>c</sup>A band at 1613 cm<sup>-1</sup> is believed to be an intensified aromatic band. <sup>d</sup>A 1656 cm<sup>-1</sup> band indicates that this compound exists in the tautomeric keto-imine form. <sup>e</sup>C-D stretch. w = weak; sh = shoulder.

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