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APPLICATION OF MOLECULAR ORBITAL THEORY TO THE ELECTRONIC ABSORPTION SPECTRA OF SCHIFF BASES*

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Abstract—The linear combination of atomic orbitals-molecular orbital (LCAO-MO) method with inclusion of overlap has been applied to benzylideneaniline. The energy levels, electron densities and bond orders were calculated and the results applied to an interpretation of the electronic absorption spectra of benzylideneaniline and some of its derivatives. It is concluded that the anomalous spectrum of benzylideneaniline can be explained on the basis of twisting of the aniline ring out of the plane of the molecule.

INTRODUCTION

ALTHOUGH the linear combination of atomic orbitals-molecular orbital (LCAO-MO) method has been applied in some detail to the stilbene[1–3] and azobenzene[4–6] molecules, the isoconjugate benzylideneaniline molecule (I) has received relatively little attention. Jaffé *et al*[6]., neglecting overlap, have calculated the energy levels of benzylideneaniline and have used these results to interpret some of the electronic transitions of this molecule in the near U.V. region. Ban[7] has calculated the absorption maxima for two of the long-wavelength bands of benzylideneaniline from the stilbene spectrum by a perturbation method.

In the present investigation of Schiff bases we have calculated, in addition to the energy levels, the bond orders and electron densities of benzylideneaniline. We have also investigated steric effects on the U.V. absorption spectra of Schiff bases. This paper presents the results of these calculations and their interpretation in the light of the experimental results.

In the course of this work, a paper appeared by Brocklehurst[8] on the U.V. spectra of azomethine compounds. He found that in Schiff bases in which either (i) the nitrogen lone-pair electrons are localized by protonation or nitrone formation, or (ii) the molecule is constrained to a more planar form by ring formation, the intensity of the long wavelength absorption maximum is increased two to three times. He concluded that benzylideneaniline is not entirely planar, the nitrogen lone-pair interfering with π-conjugation throughout the molecule. Our work substantiates Brocklehurst's regarding the non-planarity of benzylideneaniline.

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* Communication No. 2265 from the Kodak Research Laboratories

[1] W. Drenth, *Rec. Trav. Chim.* **73**, 249 (1954).

[2] C. A. Coulson and J. Jacobs, *J. Chem. Soc.* 1983 (1949).

[3] G. Berthier and B. Pullman, *C.R. Acad. Sci., Paris* **228**, 397 (1949).

[4] P. P. Birnbaum, J. H. Linford and D. W. G. Style, *Trans. Faraday Soc.* **49**, 735 (1953).

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

[6] H. H. Jaffé, S. Yeh and R. W. Gardner, *J. Mol. Spectrosc.* **2**, 120 (1958).

[7] M. I. Ban, *Acta Univ. Szegediensis, Acta Phys. et Chim.* (N.S.) **3**, 49 (1957); *Chem. Abstr.* **52**, 19424 (1958).

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

METHOD

The molecular orbital parameters are defined in the usual manner:

$$\alpha_i = \int \chi_i H \chi_i d\tau, \quad \gamma_{ij} = \int \chi_i H \chi_j d\tau, \quad S_{ij} = \int \chi_i \chi_j d\tau \quad \text{and} \quad \beta = \gamma - S\alpha,$$

where α and S are the Coulomb and non-orthogonality integrals, respectively, γ and β are the resonance integrals neglecting and including overlap,[9] χ_i is the $2p\pi$ atomic orbital on the *i*th atom, H is the one-electron Hamiltonian operator, and $d\tau$ is the volume element of the electron in the configuration space. A subscript zero (β_0, γ_0) indicates the particular parameter in a benzene molecule.

The inclusion of overlap between adjacent atomic orbitals was carried out using Wheland's "ζ-technique"[10] in which the overlap integral of a bond, S_{ij}, is assumed to be proportional to its resonance integral, γ_{ij}. The eigenvectors were normalized according to equation (11) of reference (11). The eigenvalues were converted into units of β_0 in all cases. The parameters used in the calculations are

$$\alpha_C = \alpha; \quad \alpha_N = \alpha + 0{\cdot}2\beta_0; \quad S_0 = 0{\cdot}25;$$

$$\gamma_{CC} = \gamma_0; \quad \gamma_{C-C} = 0{\cdot}9\gamma_0; \quad \gamma_{C=N} = \gamma_0; \quad \gamma_{C-N} = 0{\cdot}8\gamma_0.$$

(for subscript notation, see Streitwieser).[12]

The inductive effect of heteroatoms was neglected. The parameters were chosen to give reasonable agreement with the experimental dipole moment of benzylideneaniline[13](v.i.). Although a set of parameters is already available[14] which gives good agreement with dipole-moment data, the use of these parameters depends upon the neglect of all overlap integrals.

Benzylideneaniline was assumed to have C_s symmetry, thus permitting the secular determinant to be factored into a 4 × 4 determinant (group theoretical representation A″) and a 10 × 10 determinant (group theoretical representation A′). Following customary nomenclature for compounds of this type,[5] A′ molecular orbitals are designated π orbitals and A″ molecular orbitals, ϕ orbitals.

RESULTS

Dipole moments

For benzylideneaniline, the following bond lengths were used:

C—C(Ar)	1·39 Å	C=N	1·30 Å
C_{sp^2}—C_{sp^2}	1·44 Å	C—N	1·40 Å.

Slight deviations of these values from the true ones will not affect the calculated dipole moment significantly. The bond angles at the bridge atoms were assumed to be 120°, and the molecule was considered all *trans*. It is entirely possible that the bond angles

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[9] G. W. Wheland, *J. Amer. Chem. Soc.* **63**, 2025 (1941).

[10] G. W. Wheland, *J. Amer. Chem. Soc.* **64**, 900 (1942).

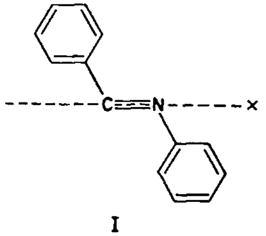
[11] B. H. Chirgwin and C. A. Coulson, *Proc. Roy. Soc.* **A201**, 196 (1950).

[12] A. Streitwieser, *Molecular Orbital Theory for Organic Chemists*, John Wiley, New York, N.Y. (1961).

[13] V. DeGaouck and R. J. W. LeFevre, *J. Chem. Soc.* 741 (1938).

[14] L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.* **47**, 113 (1951).

at the bridge atoms may be greater than 120° since the work of Robertson *et al.*[15,16] has shown that, in the crystal, this angle exceeds 120° for both azobenzene and stilbene. The calculated π-moment was vectorially added to the σ-moments (values of Orgel *et al.*[14]) to obtain the total moment, 1·35D. This was assumed to agree sufficiently well with the experimental value (1·57D[13]) to justify the use of $\alpha_N = \alpha + 0{\cdot}2\beta_0$ as the Coulomb integral for azomethine nitrogen. The angle which the dipole-moment vector makes with a horizontal x-axis (I) is 14°, measured counterclockwise.

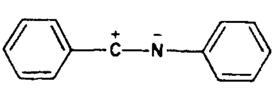


I

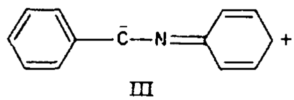
Electron densities and bond orders

Since the overlap integral between adjacent atomic orbitals is included in the calculations, the method of Chirgwin and Coulson[11] was used for calculating bond orders and electron densities. The results (Tables 2 and 3) are self-explanatory. The data for the V_2 state, considered to arise from a $\phi_1 \rightarrow \pi_1{}^*$ transition, are the least reliable, since (i) the state is two-fold degenerate and (ii) the charge separations are larger in this state than in either the N or the V_1 states. Resolution of these difficulties would require in the former case a configuration-interaction treatment and, in the latter case, a self-consistent field calculation. In view of this and the fact that, in azobenzene the $\phi_1 \rightarrow \pi_1{}^*$ transition has not even been assigned with certainty,[5,6] we hesitate to draw any conclusions regarding the structure of benzylideneaniline from the 262-mμ peak, although this is the most reasonable assignment for the $\phi_1 \rightarrow \pi_1{}^*$ transition.

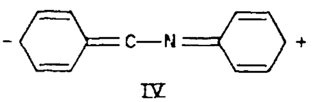
The results indicate that in the ground state of benzylideneaniline, structure II contributes to the resonance hybrid. Upon $\pi_1 \rightarrow \pi_1{}^*$ excitation, structures III and IV



II



III



IV

become important contributors, as shown by the net electron migration out of the aniline ring and into the benzylidene ring and by the large contribution of quinonoid structures. The consequences of this are discussed in more detail in the section on the spectra of Schiff bases.

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[15] J. M. Robertson and I. Woodward, *Proc. Roy. Soc.* **A162,** 568 (1937).

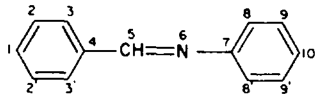
[16] J. J. de Lange, J. M. Robertson and I. Woodward, *Proc. Roy. Soc.* **A171,** 398 (1939).

TABLE 1. ENERGY LEVELS OF BENZYLIDENEANILINE

Ψ	E^a
π_5^*	−4·609
π_4^*	−4·174
π_3^*	−2·224
π_2^*	−1·534
ϕ_1^*, ϕ_2^*	−1·333
π_1^*	−0·607
π_1	0·532
ϕ_1, ϕ_2	0·800
π_2	0·876
π_3	1·094
π_4	1·354
π_5	1·407

[a] In units of the benzene resonance integral, β_0.

TABLE 2. ELECTRON DENSITIES IN BENZYLIDENEANILINE[a]



Atom	N	V_1	V_2
1	+0·010	+0·002	−0·094
2, 2′	0·000	+0·002	+0·118
3, 3′	+0·011	−0·002	+0·059
4	−0·004	+0·005	−0·057
5	+0·077	−0·004	−0·155
6	−0·102	−0·101	−0·305
7	+0·006	+0·037	−0·033
8, 8′	−0·003	+0·011	+0·065
9, 9′	0·000	+0·005	+0·119
10	−0·002	+0·030	−0·078

[a] Figures given are the net charges on the atoms in units of e.

Electronic absorption spectra

The U.V. absorption spectrum of benzylideneaniline is shown in Fig. 1. It is similar to that reported by other workers[6,17–22] except that under higher resolution or at lower temperatures the 262 mμ peak is resolved into two peaks with $\lambda_{\max}$ 251 mμ and 261 mμ and an intensity ratio of $\epsilon_{251\,m\mu}/\epsilon_{261\,m\mu} = 0{\cdot}95$.[22] By equating the

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[17] P. Ramart-Lucas and M. J. Hoch, *Bull. Soc. Chim. France* (5) **3**, 918 (1936).

[18] A. V. Kiss and G. Auer, *Z. Physik. Chem.* **A189**, 344 (1941).

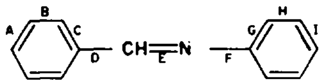
[19] E. Fischer and Y. Frei, *J. Chem. Phys.* **27**, 808 (1957).

[20] V. A. Izmailsky and E. A. Smirnov, *J. Gen. Chem. U.S.S.R.* **25**, 1347 (1955); **26**, 3389 (1956).

[21] J. Schulze, F. Gerson, J. N. Murrell and E. Heilbronner, *Helv. Chim. Acta* **44**, 428 (1961).

[22] E. Fischer. Personal communication.

TABLE 3. MOBILE BOND ORDERS IN BENZYLIDENEANILINE



Bond	N	V_1	V_2
A	0·759	0·702	0·706
B	0·678	0·726	0·577
C	0·715	0·588	0·625
D	0·385	0·594	0·497
E	0·860	0·467	0·643
F	0·356	0·565	0·445
G	0·723	0·606	0·651
H	0·676	0·720	0·569
I	0·760	0·707	0·716

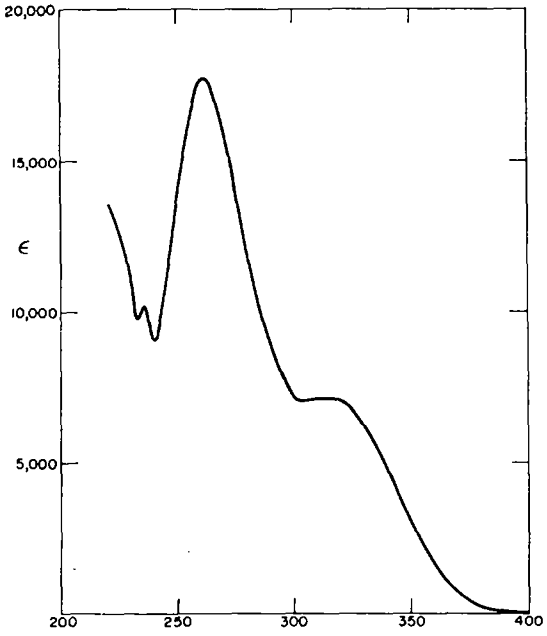
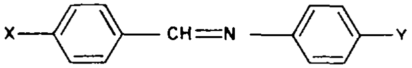


FIG. 1. U.V. absorption spectrum of benzylideneaniline in cyclohexane.

theoretical $\pi_1 \rightarrow \pi_1^*$ transition energy, $-1{\cdot}14\beta_0$, to the experimentally observed energy for the longest wavelength absorption, 91 kcal/mole, a spectroscopic β_0 of −80 kcal/mole is obtained. Similar values have been obtained by Drenth[1] for the ω, ω-diphenylpolyenes.

The result that structures III and IV are contributors to the excited state of benzylideneaniline suggests that a Schiff base with an electron-donating group in the p-position of the aniline ring should absorb bathochromically relative to the isomeric Schiff base with the same group in the p-position of the aldehyde ring. The reverse order would be true for an electron-withdrawing substituent. Table 4 has been compiled[20] on the assumption that the longest-wavelength peak of each of these compounds corresponds to the $\pi_1 \rightarrow \pi_1^*$ transition. The data verify the conclusion reached above regarding the direction of electron flow upon $\pi_1 \rightarrow \pi_1^*$ excitation.

TABLE 4. $\pi_1 \rightarrow \pi_{21}^*$ ABSORPTION MAXIMUM FOR *p*-SUBSTITUTED SCHIFF BASES



X	Y	λ_{max}	Solvent
H	$(CH_3)_2N$	375	C_2H_5OH
$(CH_3)_2N$	H	355	C_2H_5OH
NO_2	H	339[20]	C_2H_5OH
H	NO_2	336[20]	C_2H_5OH
NO_2	$(CH_3)_2N$	452[20]	C_2H_5OH
$(CH_3)_2N$	NO_2	405[20]	C_2H_5OH
NO_2	OH	380[20]	C_2H_5OH
OH	NO_2	348[20]	C_2H_5OH
$(CH_3)_3\overset{+}{N}$	OH	335[a]	H_2O
OH	$(CH_3)_3\overset{+}{N}$	330[a]	H_2O
$(CH_3)_3\overset{+}{N}$	O^-	380[a]	H_2O
O^-	$(CH_3)_3\overset{+}{N}$	345[a]	H_2O

[a] R. L. Reeves, unpublished results.

The most striking difference between the spectra of azobenzene, stilbene and benzylideneaniline is the relative extinctions of the long-wavelength peaks. In the case of azobenzene and stilbene, the longest-wavelength peak is the most intense one in the near-U.V. region, a fact which agrees with theoretical calculations of dipole strengths and f-numbers.[5] This peak occurs with markedly reduced intensity in the spectrum of benzylideneaniline (Fig. 1), appearing as a shoulder (λ_{max} 314 mμ) on a much more intense peak at 262 mμ. Jaffé[6] *et al.*, have attributed this to the reduced symmetry of the benzylideneaniline molecule (C_s) relative to the azobenzene and stilbene molecules (C_{2h}).

Theoretical dipole strengths[23] were calculated for the first two transitions of benzylideneaniline, a *trans* configuration and 120° bond angles at the bridge atoms being assumed. Overlap between adjacent atomic orbitals was also included in these calculations.[24] It was found (Table 5) that the $\pi_1 \rightarrow \pi_1^*$ transition should occur with reduced intensity relative to azobenzene ($Q^2 = 4{\cdot}88$[5]) and stilbene ($Q^2 = 5{\cdot}26$[5]). If one assumes the 314-mμ peak to be the $\pi_1 \rightarrow \pi_1^*$ transition, then the semitheoretical oscillator strength (f_{th}) is 1·36. The experimental oscillator strength (calculated from the equation $f_{exp} = 4{\cdot}32 \times 10^{-9}\epsilon\Delta\nu_{1/2}$, where ν is in wavenumbers) is $\sim$0·26, and therefore $f_{exp}/f_{th} \simeq 0{\cdot}19$. The f_{exp}/f_{th} ratios reported for stilbene and azobenzene are

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[23] R. S. Mulliken, *J. Chem. Phys.* 7, 121 (1939).

[24] R. Daudel, R. Lefebvre and C. Moser, *Quantum Chemistry* pp. 215-221. Interscience, New York, N.Y. (1959).

0·40 and 0·27, respectively.[5] There is thus a progressive decrease in this ratio as one proceeds along the series from stilbene to azobenzene to benzylideneaniline. Although ring-chain compounds generally give f_{exp}/f_{th} ratios of the order of 0·30,[25] low ratios have been reported for other compounds.[26]

TABLE 5. THEORETICAL DIPOLE STRENGTHS FOR TRANSITIONS IN TRANS-BENZYLIDENEANILINE

Transition	θ^2	θ^a
$\pi_1 \rightarrow \pi_1^*$	3·94	−43°
$\phi_1 \rightarrow \pi_1^*$	0·94	+30°

[a] Measured counterclockwise to the x-axis (structure I).

In an attempt to shed further light upon the nature of the bands in the benzylidenaniline spectrum, we have drawn upon steric effects on the electronic transitions of Schiff bases. In Table 6 are recorded the absorption maxima and extinction coefficients of a series of increasingly sterically hindered Schiff bases (1–6), along with four model compounds (7–10). It may be seen from the table that an increase in the steric requirement for planarity of the Schiff base results in a marked decrease in the extinction of the 314 mμ peak, with a corresponding increase in the extinction of the 262 mμ peak.

The relative integrated intensities of the $\pi_1 \rightarrow \pi_1^*$ transition for compounds 1–6 are approximately: 1·0: 0·9: 0·8: 0·4: 0·4: 0·2. Since this series does not follow the vibrational sum rule,[27] the progressive decrease in extinction cannot be explained as a Franck-Condon effect involving merely a redistribution of a constant integrated intensity. The results require that the electronic transition moment decrease in the series. For such cases Jaffé and Orchin[28] have suggested that the steric hindrance is at least "moderate."

These data suggest an explanation for the anomalous spectrum of benzylideneaniline. The results clearly indicate that increasing steric hindrance to planarity decreases the extinction of the 314 mμ peak and enhances the extinction of the 262 mμ peak. If benzylidenaniline itself were not completely planar, then a situation could exist in which $f_{314\,m\mu}$ has been reduced below $f_{262\,m\mu}$, thus reversing the theoretical intensity ratio calculated from Table 5. A similar conclusion has been reached by other workers[8,20] on the basis of other evidence. The data (cf. spectra of compounds 2, 4 and 5) show that rotation about bond F is more important for relief of slight steric crowding than is rotation about bond D. This is reasonable when one considers that the distance a (structure V) is ~2·5 Å, whereas the distance b is ~1·7 Å.

This would explain why an *o*-methyl substituent in stilbene and its derivatives has a greater effect on the absorption spectrum[29] of the parent compound than the

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[25] R. S. Mulliken and C. A. Rieke, *Reports Prog. Phys.* **8**, 23 (1941).

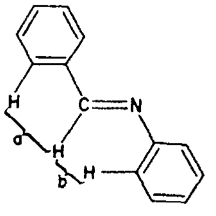
[26] B. Pullman and A. Pullman, *Les Théories Electroniques de la Chimie Organique* p. 526. Masson et Cie., Paris (1952).

[27] G. Herzberg, *Spectra of Diatomic Molecules* p. 203. Van Nostrand, New York, N.Y. (1950).

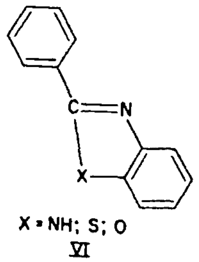
[28] H. H. Jaffé and M. Orchin, *J. Chem. Soc.* 1078 (1960).

[29] W. H. Laarhoven, R. J. F. Nivard and E. Havinga, *Rec. Trav. Chim.* **79**, 1153 (1960) and references cited therein.

methyl group in 2-methylbenzylideneaniline. The short-range steric interactions of type b are important in stilbene derivatives, no matter which ring carries the *o*-substituent (s), whereas, in benzylideneaniline, the $C_6H_5CH{=}N{-}$ portion of the molecule involves no such interactions. In the $-CH{=}NC_6H_5$ portion of the molecule, however, type b steric interferences will be greater than in stilbene since the carbon-nitrogen single and double bonds in benzylideneaniline will be shorter than the corresponding



V



VI

carbon-carbon single and double bonds in stilbene. It is interesting that, in compounds of type VI,[8] the extinction coefficient of the $\pi_1 \rightarrow \pi_1^*$ transition is 2·5 times as great as that of benzylideneaniline, in good agreement with the theoretical calculations of intensity for planar, all *trans*, benzylideneaniline.

The decrease in the f_{exp}/f_{th} ratio as one proceeds along the series, stilbene to azobenzene to benzylideneaniline, suggests that even in azobenzene the phenyl rings may be slightly twisted out of the plane of the molecule. The effect of twisting a phenyl ring in azobenzene will be to decrease resonance throughout the length of the molecule, but at the same time to increase the interaction of one of the nitrogen lone pairs with the twisted phenyl ring. Thus for both azobenzene and benzylideneaniline the decrease in the resonance integral of the carbon-nitrogen π-bond as a result of twist will be compensated for to some extent by an *increase* in the resonance integral as a result of conjugation of the nitrogen lone pair with the phenyl ring. The resonance integral of a bond may be taken proportional to the cosine of the angle of twist, θ.[30] For small angles of twist, the decrease in the resonance integral of the carbon-nitrogen π-bond will be small since $\cos\theta$ is a slowly changing function of θ near $\theta = 0°$, whereas the increase in the resonance integral due to conjugation of the nitrogen lone pair will be relatively large since $\cos(90 - \theta)$ is a more rapidly changing function of θ near $\theta = 0°$. The nitrogen lone pair is of course not pure p in character, but more likely sp^2, so that the intrinsic resonance integral involving the nitrogen lone pair is less than that involving the pπ-electron. Nevertheless, a minimum in the potential energy may occur at a value of $\theta > 0°$, θ being the angle of twist about the carbon-nitrogen single bond(s). This angle should be greater for benzylideneaniline than for azobenzene since the former has the additional steric effect of the α-hydrogen atom.

EXPERIMENTAL

The UV spectra were determined on a Cary Model 11MS Recording Spectrophotometer. M.p.'s and b.p.'s are uncorrected. The Schiff bases were prepared by refluxing equimolar amounts of the amine and aldehyde in benzene or xylene containing a trace of *p*-toluenesulfonic acid until the theoretical amount of water was collected in a Dean-Stark trap. The sterically hindered Schiff bases required extended reflux periods (2–3 days) in xylene. Although several of the Schiff bases were solids, it was

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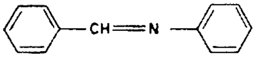
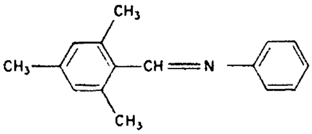
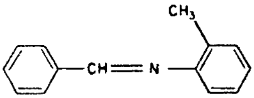
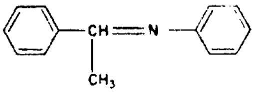
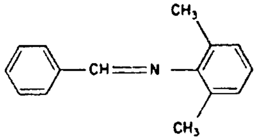
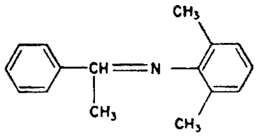
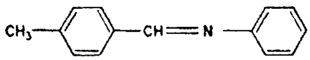
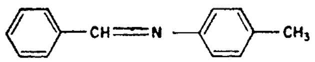
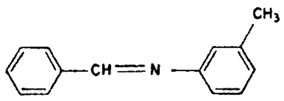
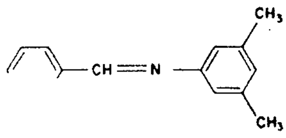
[30] M. J. S. Dewar, *J. Amer. Chem. Soc.* **74**, 3345 (1952).

TABLE 6. U.V. LIGHT ABSORPTION OF SCHIFF BASES[a]

		λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}
(1)		227 236	12,000 9,900	262	17,300	314	6,940
(2)				273	17,500	326	6,300
(3)		226 235	7,800 8,300	244 261	9,700 12,400	325	4,230
(4)				242	20,650	320	1,840
(5)				251	22,100	331	1,740
(6)				244	25,100	323	730
(7)				268	18,600	319	8,100
(8)		225 232	12,100 12,300	240 262	12,000 15,100	321	8,070
(9)		225 233	12,100 12,800	241·5 251 262	14,200 14,000 15,000	319	6,150
(10)		237	13.600	244 262	16,100 16,600	320	7,200

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[a] Solvent. C_6H_{12} in all cases.

found that distillation *in vacuo* was the best means of purification. Crystallization generally does not eliminate the odor of starting aldehyde, whereas one vacuum distillation is usually sufficient.

Benzylideneaniline[31] (1). M.p. 51–52° (n-heptane); b.p. 100–106°/0·15 mm. (Found: C, 86·6; H, 6·2; N, 7·7. Calc. for $C_{15}H_{11}N$: C, 86·2; H, 6·1; N, 7·7%).

2,4,6-*Trimethylbenzylideneaniline*[32] (2). M.p. 50–52°; b.p. 120–122°/0·15 mm. (Found: C, 85·6; H, 7·5; N, 6·3. Calc. for $C_{16}H_{17}N$: C, 86·1; H, 7·7; N, 6·3%).

Benzylidene-O-Toluidine[33] (3). B.p. 124–126°/0·45 mm. (Found: C, 86·3; H, 6·6; N, 7·2. Calc. for $C_{14}H_{13}N$: C, 86·1; H, 6·7; N, 7·2%).

α-*Methylbenzylideneaniline*[34] (4). B.p. 117–118°/0·12 mm. (Found: C, 85·9; H, 6·8; N, 7·8. Calc. for $C_{14}H_{13}N$: C, 86·1; H, 6·7; N, 7·2%).

Benzylidene-2,6-dimethylaniline[35] (5). B.p. 107–110°/0·12 mm. (Found: C, 86·9; H, 7·3; N, 6·4. Calc. for $C_{15}H_{15}N$: C, 86·1; H, 7·2; N, 6·7%).

α-*Methylbenzylidene-2,6-dimethylaniline* (6). M.p. 59–60°; b.p. 114–120°/0·12 mm. (Found: C, 85·8; H, 7·6; N, 6·3. $C_{16}H_{17}N$ requires: C, 86·1; H, 7·7; N, 6·3%).

p-*Methylbenzylideneaniline*[33] (7). B.p. 110–120°/0·10 mm. (Found: C, 86·3; H, 7·1; N, 7·0. Calc. for $C_{14}H_{18}N$: C, 86·1; H, 6·7; N, 7·2%).

Benzylidene-p-*toluidine*[33] (8). B.p. 122–125°/0·20 mm. (Found: C, 86·3; H, 7·0; N, 7·4. Calc. for $C_{14}H_{13}N$: C, 86·1; H, 6·7; N, 7·2%).

Benzylidene-m-*toluidine*[33] (9). B.p. 130–132°/1·0 mm. (Found: C, 86·2; H, 6·3; N, 7·1. Calc. for $C_{14}H_{18}N$: C, 86·1; H, 6·7; N, 7·2%).

Benzylidene-3,5-dimethylaniline (10). B.p. 139–140°/0·85 mm. (Found: C, 86·2; H, 7·1; N, 6·5. $C_{15}H_{15}N$ requires: C, 86·1; H, 7·2; N, 6·7%).

p-*Dimethylaminobenzylideneaniline*[36]. M.p. 98–99° (ethanol). (Found: C, 80·0; H, 6·9; N, 12·4. Calc. for $C_{15}H_{16}N_2$: C, 80·3; H, 7·2; N, 12·5%).

Benzylidene-p-*dimethylaminoaniline*[37]. M.p. 97·5–98·5° (ligroin). (Found: C, 80·3; H, 7·3; N, 12·8. Calc. for $C_{15}H_{16}N_2$: C, 80·3; H, 7·2; N, 12·5%).

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