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Electronic Structures and Conformations of *N*-Benzylideneanilines. I. Electronic Absorption Spectral Study Combined with CNDO/S CI Calculations

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The electronic structures and molecular conformations of *N*-benzylideneaniline and its several derivatives bearing 2-methyl, 2,6-dimethyl, and/or 4-nitro groups on the anilino benzene ring (ring A) have been investigated by electronic absorption spectroscopy combined with CNDO/S CI calculations. The lower energy bands are assigned and the molecular conformations are estimated. The results show that the 4-nitro derivatives as well as the 2,6-dimethyl derivatives take considerably twisted conformations.

It is well known that the UV absorption spectral pattern of *N*-benzylideneaniline is remarkably different from those of π-isoelectronic *trans*-stilbene and *trans*-azobenzene,[1)] and it has been reasonably understood in terms that *N*-benzylideneaniline takes a nonplanar conformation[1b,1c,2)] in which the anilino benzene ring (ring A) twists from the rest part of the molecule considerably (see Fig. 1) whereas *trans*-stilbene[1c,3)] and *trans*-azobenzene[1c,4)] do not take drastically twisted conformations.

The molecular conformations of *N*-benzylideneanilines have been investigated by several methods. A recent gas phase electron diffraction study has indicated that the twist angle θ_N of *N*-benzylideneaniline **1** is about 52°.[5)] The PCILO[6)] and NDDO[7)] calculations also supported the twisted conformation of **1**.

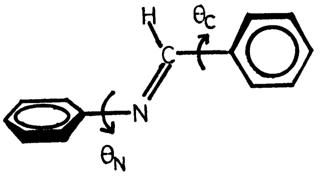


Fig. 1. Twisted conformation of *N*-benzylideneaniline.

In crystalline states, the molecular structures of *N*-benzylideneaniline and some of its derivatives have been determined by X-ray crystallography.[8—14)] For example, it was reported that *N*-benzylideneaniline,[8)] the 4-carboxy derivative,[8)] and the 4-dimethylamino-4′-nitro derivative[9)] take nonplanar conformations with the twist angle θ_N of 55.2, 41.1, and 9.1°, respectively. The 4,4′-dichloro derivative crystallizes in two modifications, and in one modification the molecule has the twist angle θ_N of about 25° and in another modification it takes a planar conformation.[10)] Similar phenomenon is also found for the 4,4′-dimethyl derivative.[12,13)] These facts clearly show that the twist angles θ_N of these compounds in crystals are controlled by the way of molecular packing,[15)] and that it is not suitable for estimating the twist angles θ_N of the molecules dissolved in solutions from those determined in crystalline states.

In solution, the electronic absorption spectra of various *N*-bezylideneanilines have already been reported.[1b,1c,2,9,16,17)] Historically, Wiegand and Merkel[16)] examined for the first time the UV absorption spectrum of *N*-benzylideneaniline and proposed the linear planar model as its structure. Ebara analyzed UV spectra of various substituted *N*-benzylideneanilines including nitro derivatives and postulated that in these compounds the ring A is perpendicular to the rest part of the molecule, the imino nitrogen taking sp hybridization.[2b)] This model was taken later by El-Bayoumi and coworkers also in their extensive study of UV absorption spectra of various substituted *N*-benzylideneanilines.[2g)] On the other hand, Brocklehurst[1b)] and Smith[2c)] proposed the model in which the ring A is rather twisted around the C–N bond by the examination of the UV absorption spectra of *N*-benzylideneaniline and related compounds. And nowadays, this model is reasonable, judging from the results for the other phases mentioned above.

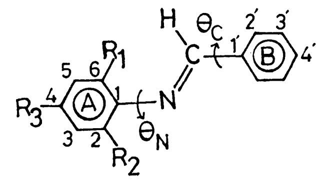
Skrabal and his coworkers compared the UV spectra of several substituted *N*-benzylideneanilines with those of their corresponding 5-substituted 2-aryl-3,3-dimethyl-3*H*-indoles, and suggested that substitution of 4-dimethylamino group will reduce the twist angle θ_N, that 4-nitro group would not change the angle, and that the 4-dimethylamino-4′-nitro derivative takes a nearly planar conformation.[2h)] Ezumi *et al.* reported that the 4-dimethylamino-4′-nitro derivative takes a nearly planar conformation on the basis of the comparison of its UV spectrum with that of 4-dimethylamino-4′-nitro-*trans*-stilbene together with calculations of the transition energies and intensities of their absorptions, and the planarity of the molecule was attributed to the favourable π-delocalization throughout the molecule by intramolecular charge transfer interaction between the substituents.[9)] These results indicate that the substitution on the ring A is quite important in determining the twist angle θ_N.

In order to get deeper insight into the substituent effect on the twist angles θ_N of *N*-benzylideneanilines, an attempt has been made to investigate the effect of 4-nitro group as well as 2-methyl and 2,6-dimethyl groups on the electronic absorption spectra. The electronic absorption spectra of six *N*-benzylideneanilines, that is, *N*-benzylideneaniline **1**, *N*-benzylidene-2-methylaniline **2**, *N*-benzylidene-2,6-dimethylaniline **3**, *N*-benzylidene-4-nitroaniline **4**, *N*-benzylidene-2-methyl-4-nitroaniline **5**, and *N*-benzylidene-2,6-dimethyl-4-nitroaniline **6**, have been measured, and their transition properties have been calculated to interpret the observed spectra.

Table 1. Electronic absorption spectral data for **1**—**6** in cyclohexane[a)]

Compound	$\lambda_{\max}$/nm	$E_{\max}$/eV	$\varepsilon_{\max}$ 10^{-4}/dm^3 mol^{-1} cm^{-1}	f
N-Benzylideneaniline (**1**)	210		1.78	
	222		1.37	
	(236)		1.03	
	264	4.70	1.72	0.36
	315	3.94	0.70	0.18
N-Benzylidene-2-methylaniline (**2**)	212		1.81	
	227.5		1.18	
	(237)		1.24	
	(247.5)		1.41	
	263	4.71	1.71	0.43
	330	3.76	0.59	0.13
N-Benzylidene-2,6-dimethylaniline (**3**)	212.5		2.13	
	253	4.90	2.23	0.42
	340	3.65	0.18	0.04
N-Benzylidene-4-nitroaniline (**4**)	210		1.62	
	223.5		1.47	
	298	4.38	1.65	0.18
	321	3.86	1.47	0.38
N-Benzylidene-2-methyl-4-nitroaniline (**5**)	209		2.18	
	225		1.62	
	(268)		1.20	
	295	4.37	1.69	0.25
	327	3.79	1.34	0.37
N-Benzylidene-2,6-dimethyl-4-nitroaniline (**6**)	207.5		2.81	
	233		1.27	
	254	5.05	1.28	0.29
	(296)	4.13	1.32	0.42

a) $\lambda_{\max}$ and $\varepsilon_{\max}$ are for the apparent band maxima and $E_{\max}$ and f are for the deconvoluted bands.



1: $R_1=R_2=R_3=H$
2: $R_1=H$, $R_2=CH_3$, $R_3=H$
3: $R_1=R_2=CH_3$, $R_3=H$
4: $R_1=R_2=H$, $R_3=NO_2$
5: $R_1=H$, $R_2=CH_3$, $R_3=NO_2$
6: $R_1=R_2=CH_3$, $R_3=NO_2$

Method and Results

The electronic absorption spectra of six *N*-benzylideneanilines **1**—**6** are shown in Figs. 2—7, respectively. The observed absorption spectral data are listed in Table 1. The long wavelength regions of the observed spectra were approximately deconvoluted into the first and second main component bands to estimate their transition energies and oscillator strengths which are also included in Table 1. The intensity ratios of the first bands to the second ones are shown in Table 2.

In order to reproduce the observed spectral patterns, the transition energies and the oscillator strengths have been calculated by the CNDO/S[18)] CI calculations including interactions between sixty-four singly-excited configurations for varying degrees of the twist angle θ_N. In the calculations of **1**, **2**, and **3**, the

Table 2. Calculated and observed intensity ratio, f_1/f_2[a)]

Compound	f_1/f_2	
	Calcd(θ_N/°)	Obsd
N-Benzylideneaniline (**1**)	0.70 (30) 0.42 (35) 0.29 (40) 0.12 (55.2)	0.50
N-Benzylidene-2-methylaniline (**2**)	0.40 (40) 0.26 (45) 0.20 (48.16) 0.17 (50) 0.12 (55.2) 0.04 (76.84)	0.30
N-Benzylidene-2,6-dimethylaniline (**3**)	0.29 (40) 0.24 (70) 0.14 (75) 0.05 (76.84) 0.008 (90)	0.10
N-Benzylidene-4-nitroaniline (**4**)	9.70 (50.2) 6.87 (60) 3.56 (80) 2.89 (90)	2.11
N-Benzylidene-2-methyl-4-nitroaniline (**5**)	7.44 (50.2) 5.73 (60) 2.96 (80) 1.96 (90)	1.48
N-Benzylidene-2,6-dimethyl-4-nitroaniline (**6**)	3.48 (60) 2.57 (76.73) 2.31 (80) 1.70 (90)	1.45

a) f_1 and f_2 correspond to the oscillator strengths for the observed first and second bands, respectively.

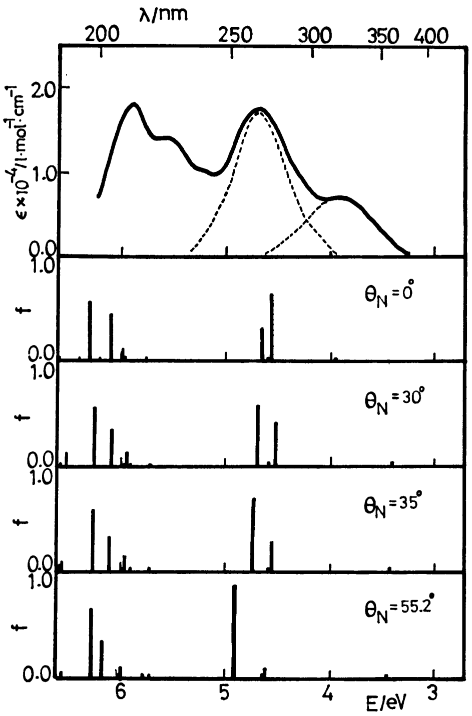


Fig. 2. Observed absorption spectrum and calculated spectral patterns of *N*-benzylideneaniline **1**.

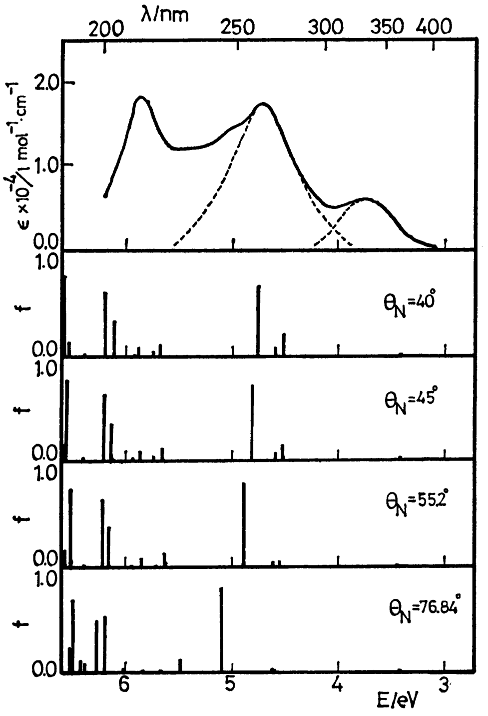


Fig. 3. Observed absorption spectrum and calculated spectral patterns of *N*-benzylidene-2-methylaniline **2**.

twist angles θ_C were kept at the same angle as for crystalline **1**, 10.3°,[8] since, in the preliminary calculations, the spectral pattern was not appreciably changed with its variation from 0° to 10.3°. Likewise, the angles θ_C for **4**, **5**, and **6** were fixed at the same angle as reported for crystalline *N*-(4-methylbenzylidene)-4-nitroaniline, 8.1°.[8]

The calculated results for the spectral patterns at various θ_N are also schematically illustrated in Figs. 2—7, and the ratios of the calculated oscillator strengths of the two strong transitions in the longer wavelength region at the various θ_N are shown in Table 2. Comparison of these calculated ratios with those of the observed ones has enabled us to estimate the twist

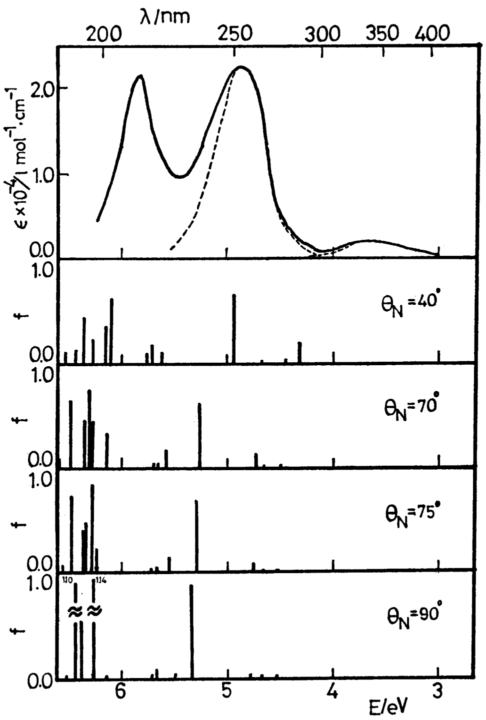


Fig. 4. Observed absorption spectrum and calculated spectral patterns of *N*-benzylidene-2,6-dimethylaniline **3**.

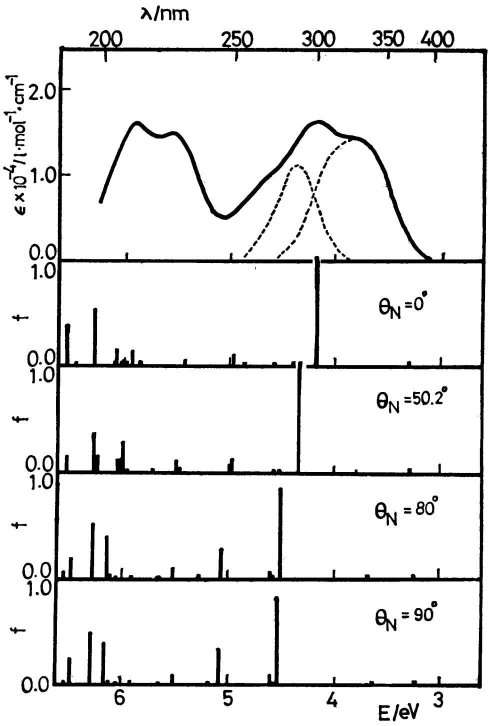


Fig. 5. Observed absorption spectrum and calculated spectral patterns of *N*-benzylidene-4-nitroaniline **4**.

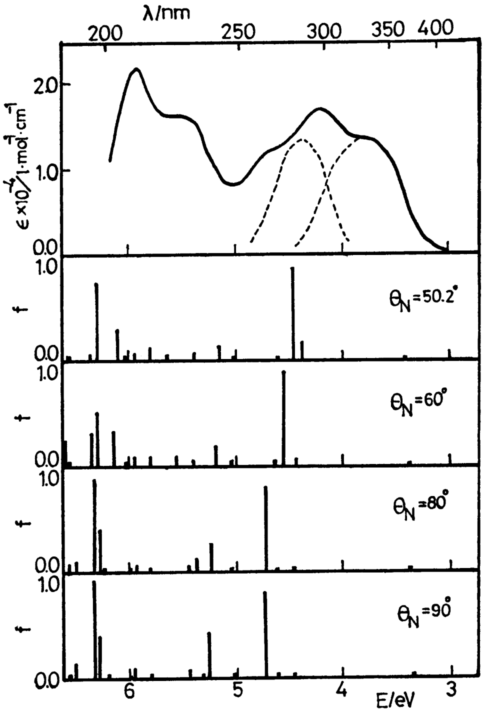


Fig. 6. Observed absorption spectrum and calculated spectral patterns of *N*-benzylidene-2-methyl-4-nitroaniline **5**.

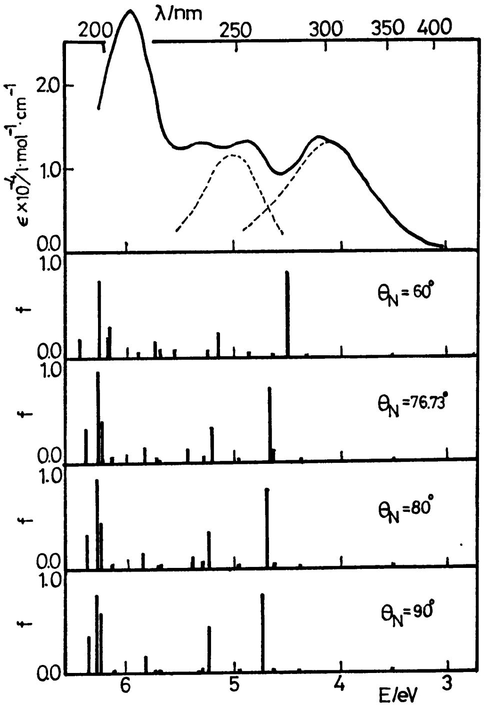


Fig. 7. Observed absorption spectrum and calculated spectral patterns of *N*-benzylidene-2,6-dimethyl-4-nitroaniline **6**.

angle θ_N which can reproduce well the observed results. The twist angles θ_N thus estimated are 30—35, 40—45, 70—80, 90, 90, and 90° for **1**, **2**, **3**, **4**, **5**, and **6**, respectively. Tables 3 and 4 respectively list the calculated transition energies and oscillator strengths for **1** and **4** at the above estimated angles $\theta_N=35°$ and 90°, respectively, together with the CI compositions and types of excitations. Figures 8 and 9 show schematic illustrations of the molecular orbitals calculated for **1** and **4** at the above twist angles, respectively.

Discussion

Compound 1. As Fig. 2 and Table 1 indicate, **1** shows the first absorption band at 315 nm (3.94 eV) and the intense second band at 264 nm (4.70 eV) in cyclohexane. The calculated transitions at 4.56 and 4.75 eV are regarded to correspond to these observed bands. The observed first band can be assigned mainly to the π-π^* transition with predominant configurations of 34—32, 34—33, and 36—33 (Table 3). Although the calculations predict the existence of an n-π^* transition with low intensity in the long wavelength region, this band was not identified probably owing to its low intensity and overlapping with the strong 315 nm band. The higher energy bands may tentatively be assigned as shown in Table 3.

As Fig. 2 indicates, with the increase in the twist angle θ_N, the first band is expected to decrease in intensity, and on the contrary, the second band is to increase in intensity. As Table 2 and Fig. 2 indicate, the calculation with the twist angle θ_N of 30—35° can well reproduce the observed spectral pattern. This estimated twist angle θ_N is smaller than that observed in the gas phase ($\theta_N=52\pm5°$[5]); however, the present result may be taken to show that the twist angle θ_N of **1** in a solution is far from 90°, and may be in qualitative agreement with that estimated from photoelectron spectroscopy as described in a subsequent paper.[19]

The method used in this study seems more suitable for estimating approximately the twist angle θ_N than the previous work by Minkin *et al.*[2f] employing the ASMO PPP CI method which was not successful in reproducing the observed intensity ratio of the first to the second band.

Compound 2. On introduction of an ortho-methyl group on the ring A (in going from **1** to **2**), the first band undergoes bathochromic shift by 15 nm; however, the second band remains unchanged in position (see Table 1). The intensity of the first band ($f=0.13$) is moderately reduced compared with **1** ($f=0.18$), and the intensity ratio of the first to the second band is decreased from 0.50 for **1** to 0.30 for **2**. The results of the calculations (Table 2) show that the twist angle θ_N of **2** may be 40—45° slightly larger than that evaluated for **1**. Accordingly, an ortho-methyl group on the ring A seems to exhibit not so pronounced effect on the twist angle θ_N. The first band is assigned mainly to the π-π^* transition with predominant configurations of 37—33, 37—36, and 38—34. The second band is also assigned mainly to the π-π^* transition with predominant cofiguration of 37—36. Here, molecular orbitals 32—42 of **2** correspond to orbitals 29—39 of **1**, respectively.

Compound 3. For compound **3**, its first band, as compared with **2**, shows bathochromic shift by 10 nm and reduces in intensity. The intensity ratio of the first to the second band is much smaller than

Table 3. Calculated transition energies and oscillator strengths for *N*-benzylideneaniline **1** ($\theta_N = 35°$)

Calcd					Obsd	
		CI Composition a)				
E/eV	*f*	Excitation	Coefficient	Type	*E*/eV	*f*
3.460	0.010	38—29	−0.477	n-π*		
		38—33	−0.671	n-π*		
4.563	0.291	34—32	0.338	π-π*	3.94	0.18
		34—33	0.537	π-π*		
		36—33	0.406	π-π*		
4.610	0.001	34—30	0.469	π-π*		
		34—32	0.306	π-π*		
		35—31	−0.389	π-π*		
		35—33	−0.414	π-π*		
4.748	0.692	34—32	−0.311	π-π*	4.70	0.36
		34—33	0.751	π-π*		
5.738	0.001	34—31	0.634	π-π*		
		35—30	0.315	π-π*		
		36—33	−0.375	π-π*		
		37—33	−0.324	π-π*		
5.905	0.034	34—31	0.445	π-π*		
		36—33	0.532	π-π*		
		37—33	0.310	π-π*		
		38—33	−0.386	n-π*		
5.955	0.146	34—30	0.434	π-π*	5.25 b)	
		35—33	0.797	π-π*		
5.967	0.001	36—31	0.371	π-π*		
		38—31	0.599	n-π*		
6.109	0.336	34—32	0.607	π-π*	5.59 b)	
		36—33	−0.337	π-π*		
		37—33	0.588	π-π*		
6.256	0.580	34—29	−0.403	π-π*	5.90 b)	
		35—30	0.553	π-π*		
		36—32	−0.319	π-π*		
		37—32	0.410	π-π*		
6.555	0.106	34—29	−0.429	π-π*		
		38—30	0.325	n-π*		
		39—33	0.554	σ-π*		
6.557	0.079	34—30	0.328	π-π*		
		36—30	0.360	π-π*		
		38—30	0.533	n-π*		
		39—33	−0.360	σ-π*		
6.656	0.621	34—30	−0.455	π-π*		
		35—29	0.323	π-π*		
		35—31	−0.609	π-π*		
		38—30	0.309	n-π*		
6.715	0.015	34—32	0.442	π-π*		
		36—29	0.307	π-π*		
		37—32	−0.309	π-π*		
		36—32	−0.462	π-π*		
6.748	0.100	36—32	−0.402	π-π*		
		39—31	0.359	σ-π*		
		39—33	0.342	σ-π*		
6.810	0.206	34—29	0.465	π-π*		
		35—30	0.582	π-π*		

a) The transition, indicated *i-j*, refers to a one-electron excitation from orbital *i* to virtual orbital *j*. The second column gives the CI coefficient of the configuration *i-j*. Orbitals 33 and 34 are the LUMO and HOMO, respectively. b) The apparent band maximum.

TABLE 4. CALCULATED TRANSITION ENERGIES AND OSCILLATOR STRENGTHS FOR *N*-BENZYLIDENE-4-NITROANILINE **4** ($\theta_N=90°$)

Calcd					Obsd	
		CI composition[a]				
E/eV	*f*	Excitation	Coefficient	Type	*E*/eV	*f*
3.257	0.000	44—32	0.385	n(NO$_2$)-π*		
		44—36	0.919	n(NO$_2$)-π*		
3.660	0.000	38—31	−0.319	π-π*		
		38—35	−0.609	π-π*		
		41—31	0.361	n-π*		
		41—35	0·617	n-π*		
4.520	0.816	37—35	−0.427	π-π*	3.86	0.38
		38—36	−0.825	π-π*		
4.573	0.000	38—34	−0.653	π-π*		
		40—32	−0.331	π-π*		
		40—36	0.670	π-π*		
4.586	0.081	37—33	−0.644	π-π*		
		38—36	0.361	π-π*		
		39—35	−0.611	π-π*		
5.076	0.310	37—35	0.843	π-π*	4.38	0.18
		38—36	−0.396	π-π*		
5.229	0.001	37—32	−0.415	π-π*		
		37—36	0.813	π-π*		
5.514	0.087	38—34	0.509	π-π*		
		40—32	0.350	π-π*		
		40—36	0.703	π-π*		
5.651	0.005	38—35	0.662	π-π*		
		41—35	0.587	n-π*		
5.893	0.005	38—32	−0.739	π-π*		
		40—34	0.316	π-π*		
		41—36	−0.320	n-π*		
6.030	0.004	37—34	−0.897	π-π*		
		43—34	−0.366	π-π*		
6.109	0.027	40—35	0.931	π-π*		
6.149	0.381	37—33	0.554	π-π*	5.55[b]	
		39—35	−0.698	π-π*		
6.260	0.478	37—31	−0.376	π-π*	5.90[b]	
		39—33	−0.502	π-π*		
		40—34	0.542	π-π*		
6.470	0.236	39—33	0.503	π-π*		
		41—32	−0.391	n-π*		
		41—36	0.579	n-π*		
6.515	0.038	37—32	−0.483	π-π*		
		37—36	−0.379	π-π*		
		40—32	−0.511	π-π*		
		42—36	−0.387	π(NO$_2$)-π*		
6.586	0.007	37—32	0.503	π-π*		
		37—36	0.387	π-π*		
		40—32	−0.454	π-π*		
		42—36	−0.466	π(NO$_2$)-π*		
6.650	0.000	39—36	0.966	π-π*		
6.743	0.569	37—31	0.741	π-π*		
		39—33	−0.402	π-π*		
		43—35	−0.420	π-π*		
6.882	0.006	38—33	−0.963	π-π*		
6.893	0.756	40—32	0.377	π-π*		
		41—34	0.442	n-π*		
		42—36	−0.723	π(NO$_2$)-π*		
6.921	0.200	38—32	0.490	π-π*		
		39—33	0.331	π-π*		
		40—34	0.657	π-π*		
		41—36	−0.345	n-π*		

a) The transition, indicated *i-j*, refers to a one-electron excitation from orbital *i* to virtual orbital *j*. The second column gives the CI coefficient of the configuration *i-j*. Orbitals 36 and 37 are the LUMO and HOMO, respectively. b) The apparent band maximum.

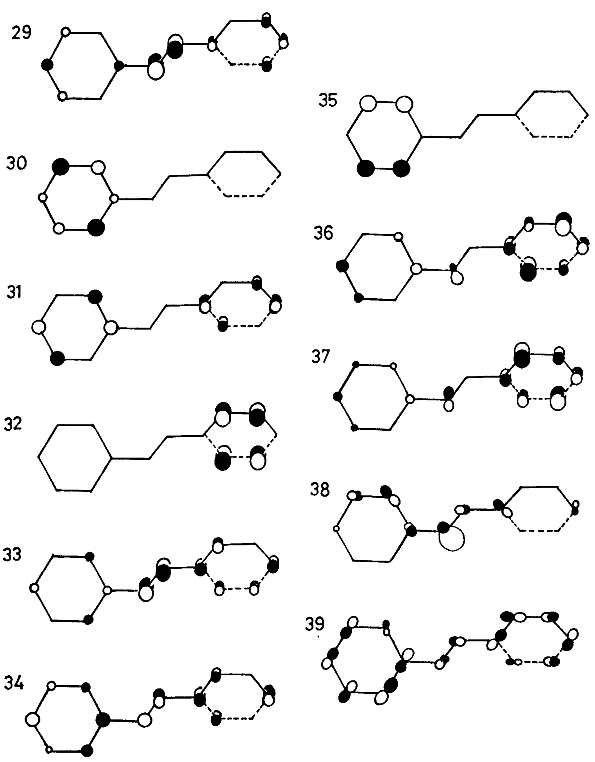


Fig. 8. Molecular orbitals of *N*-benzylideneaniline **1** (θ_N=35° and θ_C=10.3°).

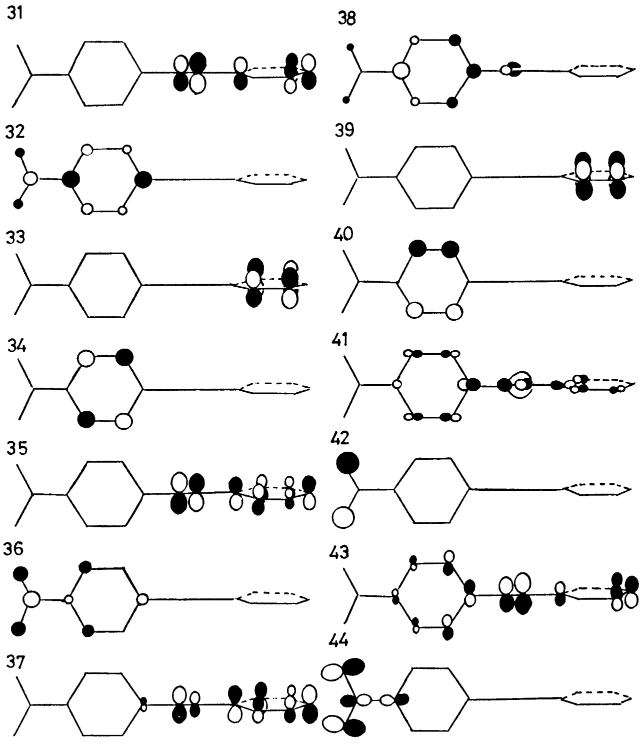


Fig. 9. Molecular orbitals of *N*-benzylidene-4-nitroaniline **4** (θ_N=90° and θ_C=8.1°).

those of **1** and **2**. The present calculations indicate that the first band is assigned mainly to the π-π^* transition with a slight n-π^* character. The π-π^* transition is mainly caused by charge transfer from the ring A to the PhCH=N– group. The second band at 253 nm is also assigned mainly to the π-π^* transition with a slight n-π^* character in which a local excitation in the PhCH=N– group is the main configuration. The most probable twist angle θ_N is estimated to be 70—80° (see Table 2 and Fig. 4). This value corresponds well to that estimated on the basis of the van der Waals radii, $\gtrsim$77°.

It is worth noting that the present calculations provide a quantitative interpretation for the previous UV absorption data by Smith[2c)] which show that the consecutive introduction of ortho-methyl groups on the ring A successively lowers the intensity of the first band.

Compound 4. Compounds **4**, **5**, and **6** carrying 4-nitro group exhibit characteristic absorption bands in the long wavelength region different from those of **1**, **2**, and **3** which do not carry 4-nitro group. Deconvolution of the observed spectra reveals that, in **4**, **5**, and **6**, the first main bands are stronger in intensity than the second bands in contrast with **1**, **2**, and **3** in which the first bands are weaker in intensity than the second bands (see Figs. 2—7).

For **4**, Fig. 5 and Table 2 indicate that the calculated ratio of the oscillator strengths of the first to the second main transition decreases with the increase in the twist angle θ_N, but the observed ratio is still lower than the calculated one even at the perpendicular conformation (θ_N=90°). This suggests that, within the limitation of the CNDO/S CI calculations employed, **4** assumes a considerably twisted conformation in solution. As Table 4 indicates, the first band can be mainly assigned to the charge transfer excitation from the aniline-like group to the nitro group mixed with the local excitation in the PhCH=N– group.

The present result is in contrast with that by Skrabal and his coworkers who reported, without deconvolution of the spectra, that **4** would have a similar twist angle θ_N to that of **1** on comparsion of the apparent spectral patterns between **4**, **1**, and their corresponding 3*H*-indoles which can be regarded to take planar conformations.[2h)] However, as described above, the transition characters of the first and second bands, particularly their intensity ratios, are remarkably different from each other between **1** and **4**. Their postulation, therefore, seems not fully satisfactory.

Compound 5. In the case of **5**, similar trend on the twist angle θ_N was observed (Fig. 6 and Table 2). The observed intensity ratio of the first to the second band (f_1/f_2) is 1.48. The twist angle θ_N predicted by the present calculations to reproduce best this intensity ratio is 90°.

The observed first band can be assigned mainly to the π-π^* transition. The main configurations are the so-called charge transfer ones from the toluidine-like group to the nitro group. The second band is also assigned mainly to the π-π^* transition. The main configuration is a local excitation in the PhCH=N– group.

Compound 6. Comparison of the observed spectrum of **6** with those calculated at various twist angles θ_N (Table 2 and Fig. 7) leads to conclusion that **6** also takes a considerably twisted conformation like

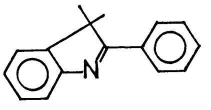
Table 5. Electronic absorption spectral data of *N*-benzylideneaniline **1**, *N*-benzylidene-4-nitroaniline **4**, and the corresponding 3*H*-indoles **7** and **8**[a)]

Compound	λ_{max}/nm	E_{max}/eV	ε_{max} 10^{-4}/dm^3 mol^{-1} cm^{-1}
N-Benzylideneaniline (**1**)	236	5.25	1.030
	262	4.73	1.710
	313	3.96	0.686
3,3-Dimethyl-2-phenyl-3*H*-indole (**7**)	228	5.44	1.530
	235	5.28	1.580
	245	5.06	1.250
	309	4.01	1.660
N-Benzylidene-4-nitroaniline (**4**)	220	5.64	1.650
	295	4.20	1.770
	(325)	3.81	1.540
3,3-Dimethyl-5-nitro-2-phenyl-3*H*-indole (**8**)	229	5.41	1.460
	(234)	5.30	(1.420)
	335	3.70	2.460

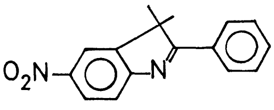
a) Taken from Ref. 2h. λ_{max}, E_{max}, and ε_{max} in this table are all for the apparent band maxima.

those of **4** and **5**. The first band can be mainly assigned to the π-π^* charge transfer transition from the benzylideneaniline group to the nitro group. The second band is assigned mainly to the π-π^* transition. The main configurations are the excitations to the PhCH=N– group π from the delocalized π-orbitals.

*Consideration on the Electronic Absorption Spectra of 2-Phenyl-3,3-dimethyl-3*H*-indoles.* Finally, it is worth noting that the present CNDO/S CI method can well reproduce the reported UV spectral patterns[2h)] of 3,3-dimethyl-2-phenyl-3*H*-indole **7** and 3,3-dimethyl-5-nitro-2-phenyl-3*H*-indole **8** regarded as the model compounds for the planar forms of *N*-benzylideneaniline **1** and *N*-benzylidene-4-nitroaniline **4**, respectively. Their spectral data are shown in Table 5. The spectral patterns calculated by the CNDO/S CI method for planar conformations ($\theta_N=0°$) for **1** and **4** are shown in Figs. 2 and 5, respectively. As shown in Table 5, the planarization in each case (from **1** to **7** and from **4** to **8**) is accompanied by increase in the intensity of the first band, and this trend can be well reproduced by the present calculations (see Figs. 2 and 5).



7



8

This finding may suggest that the CNDO/S CI method employed here is suitable for estimating the twist angles θ_N of *N*-benzylideneanilines in solutions.

In summary, it is concluded from the present results that the twist angle θ_N for *N*-benzylideneaniline **1** may be far from 90° and the introduction of 4-nitro group (compound **4**) remarkably increases the twist angle θ_N in the liquid phase.

Experimental

Materials. *N*-Benzylideneanilines **1**—**6** were prepared by refluxing equimolar amounts of appropriate amine and aldehyde in ethanol or benzene in the presence of molecular sieve (Wako synthetic zeolite; 8—12 mesh). For the preparation of **6**, refluxing in xylene for 3 d was required. The new compounds **5**, mp 119—120 °C, and **6**, mp 108—109 °C, gave satisfactory results of elemental analyses and spectroscopic data.

Spectral Measurements. Electronic absorption spectra were recorded with a JASCO UVIDEC-1 double-beam spectrophotometer in cyclohexane at room temperature.

Theoretical Calculations

The CNDO/S[18)] CI calculations were carried out with a FACOM 230-75 computer at the Institute of Physical and Chemical Research. All the necessary atomic integrals and parameters were taken from or estimated according to Ref. 18. In the configuration interactions all the singly-excited configurations concerning the eight highest occupied and eight lowest unoccupied molecular orbitals were taken into account. In the evaluation of the oscillator strengths also the ZDO approximation was used. The geometrical structures were properly assumed on the basis of the appropriate data given in Ref. 8.

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