August, 1981] © 1981 *The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *54*, *2395—2398 (1981)* 2395

Configuration and Conformation of the Photoisomers of *N*-[*p*-(Dimethylamino)benzylidene]anilines

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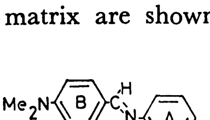
(Received December 5, 1980)

The UV, ^{1}H-NMR, and ^{13}C-NMR spectra of the photoisomers produced by irradiation of *N*-[*p*-(dimethylamino)benzylidene]anilines at low temperature have been studied. The results suggested that the photoisomers have Z structures and the imino benzene rings are twisted around the Ar–N axis out of Ar–CH=N plane due to the steric repulsion between the two rings.

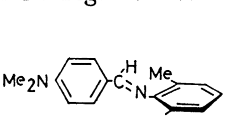
N-Benzylideneanilines (Ar'CH=NAr) are formally related to stilbenes (Ar'CH=CHAr) and azobenzenes (Ar'N=NAr), but differ from the latter in that *Z* (cis) isomers have not yet been isolated. The possibility of the existence of *E*-*Z* isomerism in *N*-benzylideneanilines has interested chemists for many decades. It was reported that the irradiation of a solution of (*E*)-*N*-benzylideneaniline at 200 K converts it reversibly into a photoisomer with a different UV absorption.[1] We investigated the photoisomerism of many substituted *N*-benzylideneanilines (p-R'–C_6H_4CH=NC_6H_4–R-p) by the measurement of UV spectra, and found that various *N*-benzylideneanilines are converted into their photoisomers upon irradiation by a high pressure mercury lamp at 77 K (liq. N_2) or 200 K (Dry Ice–EtOH or Dry Ice–acetone).[2] Recently, ^{1}H-NMR spectroscopy has been applied to the problem of configuration of the photoisomers of *N*-benzylideneanilines.[3,4] In this paper we report UV, ^{1}H-NMR, and ^{13}C-NMR spectra of the photoisomers of *N*-[*p*-(dimethylamino)benzylidene]aniline and its methyl or dimethyl derivatives produced by photoirradiation, and discuss the configuration and conformation of the photoisomers. *N*-[*p*-(Dimethylamino)benzylidene]aniline and its methyl or dimethyl derivatives were chosen for this study because they have strong absorption maxima at wavelengths greater than 300 nm, and are most easily converted to the photoisomers.

Results and Discussion

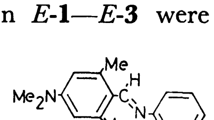
The UV spectra of the following three compounds and their photoisomers produced by photoirradiation at 77 K in M. P. (methylcyclohexane–isopentane 1 : 1) matrix are shown in Fig. 1. When *E*-**1**—*E*-**3** were irradiated at the wavelength corresponding to the longest wavelength absorption maxima, they were converted to their photoisomers; these also absorbed the light and reverted to *E* forms. Therefore, the photoequilibrium between the photoisomer and the *E* form depends upon the wavelength of the light used. In order to determine the characteristics of the UV spectra of these isomers, it is desirable to have almost 100% conversion to photoisomers. This could be achieved by choosing monochromatic light of 366 nm for irradiation.



E-1



E-2



E-3

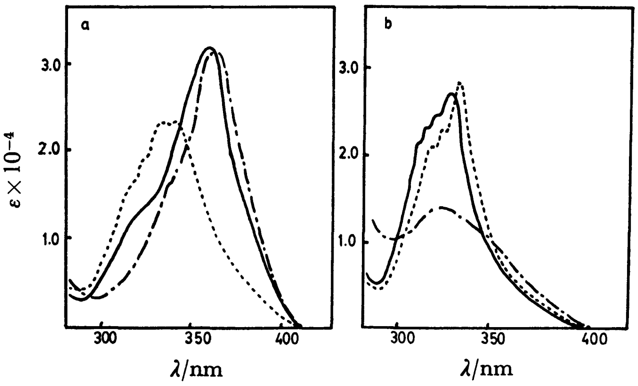
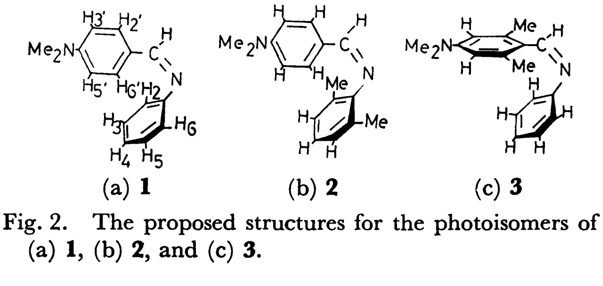


Fig. 1. The UV spectra of (a) *E*-**1** (——), *E*-**2** (- - -), and *E*-**3** (—•—), and (b) their photoisomers in methylcyclohexane–isopentane 1 : 1 at 77 K.

Compound *E*-**1** was shown to have a planar structure from the UV spectra.[5] As described in our previous paper, the UV spectrum of *E*-**2** is quite similar to that of *N*-[*p*-(dimethylamino)benzylidene]-*t*-butylamine, and so we conclude that the UV absorption band of *E*-**2** shown in Fig. 1a is due to the conjugated system of the benzylidene benzene ring (ring B) and C=N group, with little contribution from the imino benzene ring (ring A).[2] The UV spectrum of *E*-**3** is similar to that of *E*-**1**, so it should also have a planar structure. In the photoisomers, the UV spectrum of **1** is quite similar to that of **2**, but different from that of **3** (Fig. 1b). And the UV spectra of the photoisomers of **1** and **2** are almost the same as that of *E*-**2**. These features of the photoisomers of *N*-[*p*-(dimethylamino)benzylidene]anilines can be explained by the structure of the photoisomers proposed in Fig. 2. The photoisomer of **1** has *Z*-configuration and ring A is greatly twisted around the Ar–N axis; ring B and CH=N group compose a conjugated system with little contribution from ring A. The conformation of ring A of the photoisomer of **2** is the



(a) **1** (b) **2** (c) **3**

Fig. 2. The proposed structures for the photoisomers of (a) **1**, (b) **2**, and (c) **3**.

TABLE 1. ^{1}H-NMR CHEMICAL SHIFTS OF **1**, **4**, AND THEIR PHOTOISOMERS[a)]

	1	Photoisomer of **1**	$\Delta\delta^{b)}$	**4**	Photoisomer of **4**	$\Delta\delta^{c)}$
H_α	8.41	8.21	0.20	8.63	8.53	0.10
$H_{2'}$	7.85$^{d)}$	7.09$^{d)}$	0.76			
$H_{6'}$	7.85$^{d)}$	7.09$^{d)}$	0.76	8.03$^{e)}$	6.65$^{e)}$	1.38
$H_{3'}$	6.84$^{d)}$	6.59$^{d)}$	0.25	6.64	6.63	0.01
$H_{5'}$	6.84$^{d)}$	6.59$^{d)}$	0.25	6.71$^{e)}$	6.20$^{e)}$	0.51
$H_{2,6}$	*ca.* 7.4	f)		*ca.* 7.3	*ca.* 6.8	
$H_{3,5}$	7.44	7.42	0.02	7.42	7.32	0.10
H_4	*ca.* 7.4	f)		f)	f)	

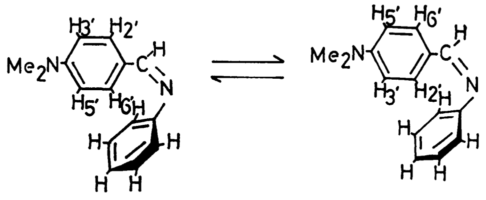
a) In ppm downfield from internal TMS. b) $\Delta\delta=\delta$ of **1**$-\delta$ of the photoisomer of **1**. c) $\Delta\delta=\delta$ of **4**$-\delta$ of the photoisomer of **4**. d) $J_{H_{2'},H_{3'}}=J_{H_{5'},H_{6'}}=8.79$ Hz (AA′ BB′ quartet). e) $J_{H_{5'},{}_{6'}}=8.79$ Hz (AA′BB′ quartet). f) These chemical shifts could not be determined since the signals were multiplet.

same as that of the photoisomer of **1**, because the 2- and 6-methyl groups on ring A do not act as steric hindrances. On the other hand, ring B of the photoisomer of **3** is twisted due to the steric repulsion between the 2- and 6-methyl groups on ring B and ring A.

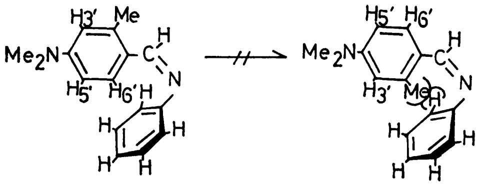
As shown in our previous paper, the UV spectra of the photoisomers of *p*-substituted *N*-benzylideneanilines (p-R′-C_6H_4CH=NC_6H_4-R-p) do not vary with the substituents R but with the substituents R′, and are quite similar to those of corresponding *N*-benzylidene-2,6-dimethylanilines (p-R′-C_6H_4CH=NC_6H_2-Me_2-2,6-R-4). These results support the idea that the photoisomers of *N*-benzylideneanilines have the structure shown in Fig. 2a.

^{1}H-NMR chemical shifts of *E*-**1** and (*E*)-*N*-(4-dimethylamino-2-methylbenzylidene)aniline (**4**) and their photoisomers were also studied. The aromatic protons of these compounds were assigned by comparison with ^{1}H-NMR chemical shifts of **1**-2,4,6-d_3, **4**-2,4,6-d_3, and **4**-2,4,6,3′,5′-d_5 and their photoisomers. The chemical shifts are summarized in Table 1.

$H_{2'}$ and $H_{6'}$ of the photoisomer of **1** resonate at a field higher than those of *E*-**1**. The significant change in $H_{2'}$ and $H_{6'}$ (0.76 ppm) can be ascribed to the diamagnetic shielding by ring A, since $H_{2'}$ or $H_{6'}$ in photoisomer is located above ring A, as shown in Fig. 2a. In **1** or its photoisomer, the signals of $H_{2'}$, $H_{6'}$, $H_{3'}$, and $H_{5'}$ are AA′BB′ type quartets. This shows that ring B freely rotates around the Ar–C bond within the NMR time scale, although this ring lies in the plane common to the C=N bond most of the time (Eq. 1). Therefore, the upfield shifts observed in $\delta_{H_{2'}}$ and $\delta_{H_{6'}}$ in **1** upon irradiation must be the average of the shifts of the $H_{6'}$, affected by the diamagnetic shielding from the ring A, and of $H_{2'}$, little affected by such shielding. If the rotation of ring B around the Ar–C bond could be restricted, the real upfield shift in $H_{6'}$ upon irradiation should be observed. So the NMR spectra of (*E*)-*N*-(4-dimethylamino-2-methylbenzylidene)aniline and its photoisomer were investigated. In the photoisomer of **4** the 2-methyl group should be situated far from ring A and thus should avoid the steric repulsion of the methyl group and ring A, as shown in Eq. 2. A large upfield shift of 1.38 ppm upon irradiation was observed in $H_{6'}$. This is approximately twice that observed in the $H_{2'}$ and $H_{6'}$ in **1** (0.76 ppm), in accordance with our expectation. The upfield shift in $H_{5'}$ (0.51 ppm) is also about two times that observed in the $H_{3'}$ and $H_{5'}$ in **1** (0.25 ppm). The fact that $H_{5'}$ is not equivalent to $H_{3'}$ shows the restriction of the rotation.



(1)



(2)

4

If one assumes that the ring A is twisted around the Ar–N axis by 90° and that ring B and CH=N group are on the same plane, the theoretical shielding effect on $H_{6'}$ according to the ring currents model proposed by Johnson and Boby[6)] is more than 4 ppm (ρ(Å)$=0.79$, z(Å)$=1.46$; ρ and z are two components of the radius vector from the center of shielding ring A to $H_{6'}$. ρ lies in the plane of ring A and z is the component along the hexad axis.). This theoretical value is quite different from the observed one (1.38 ppm). However, the shielding on $H_{6'}$ from ring A is sensitive to the dihedral angle of the Ar–C axis (θ_C). For example, the theoretical shielding is about 2 ppm at $\theta_C=30°$ (ρ(Å)$=1.52$, z(Å)$=1.60$) and about 0.5 ppm at $\theta_C=45°$ (ρ(Å)$=2.01$, z(Å)$=1.80$). So it is reasonable to assume a little twist of ring B, although ring B is conjugated with C=N.

From the results obtained by the studies with UV and ^{1}H-NMR, the following conclusions may be drawn about the configuration and conformation of the photoisomers of *N*-[*p*-(dimethylamino)benzylidene]-anilines.

1) The photoisomer of *N*-[*p*-(dimethylamino)benzylidene]aniline has *Z*-configuration and is stable only below 200 K; consequently, it has not been isolated.

2) For the steric repulsion of two rings in *Z*-configuration, ring A is twisted greatly around Ar–N axis, so

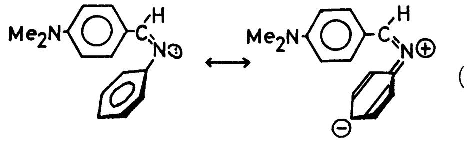
Table 2. ^{13}C-NMRchemical shifts of **1**, **2**, and their photoisomers$^{a)}$

Position of aromatic ring	*E*-**1**	*Z*-**1**	*E*-**2**	*Z*-**2**
C-2,6	121.5	118.2	b)	b)
C-3,5	129.7	130.2	128.5	128.7
C-4	125.6	123.0	123.5	122.6
C-2′,6′	130.9	133.0	130.5	131.7
C-3′,5′	111.8	111.2	111.8	111.6

a) In ppm downfield from internal TMS. b) δ_{C-1}, $\delta_{C-1'}$, $\delta_{C-4'}$, and $\delta_{C-\alpha}$ in **1** and **2**, and $\delta_{C-2,6}$ in **2** could not be determined because of their long spin-lattice relaxation times.

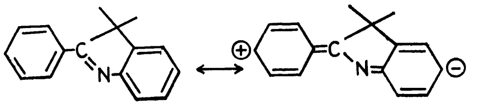
that ring A does not conjugate with C=N; but the twist of ring B around Ar–C axis is small enough to allow conjugation with C=N.

Such ease of twist of ring A in (*Z*)-*N*-[*p*-(dimethylamino)benzylidene]aniline may be ascribed to the energy gain by delocalization of the N lone pair electrons to ring A upon the twist of the ring, as shown in Eq. 3. In order to investigate the electron density of ring A, we determined ^{13}C-NMR chemical shifts of *E*- and *Z*-**1**, and *E*- and *Z*-**2**; the results are summarized in Table 2.

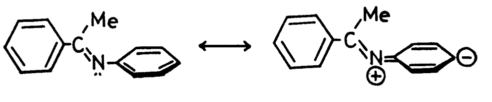


(3)

δ_{C-4} of *Z*-**1** resonates at a field higher than that of *E*-**1** by 2.6 ppm, while there is no difference in the δ_{C-4} of 2 between *E* and *Z* forms. The δ_{C-4} of *Z*-**1** is also similar to those of *Z*-**2** and *E*-**2**. $\delta_{C-2,6}$ of *Z*-**1** resonates at a field higher than that of *E*-**1** by 3.3 ppm while $\delta_{C-3,5}$ of *Z*-**1** is similar to that of *E*-**1**. Ring A of *E*-**2**, *Z*-**1**, and *Z*-**2** are greatly twisted around the Ar–N axis, as stated before, and the twist of ring A causes the upfield shifts of $\delta_{C-2,6}$ and δ_{C-4}. In order to find the reason of the upfield shift of δ_{C-4} by the twist of ring A, ^{13}C-NMR chemical shifts of *N*-benzylideneanilines with various dihedral angles (θ_N) around the Ar–N axis were determined (Table 3). An X-ray diffraction study has shown that ring A in **6** is twisted about 50° around the Ar–N axis.[7] The smaller extinction coefficients in **8** and **9** compared with that of **6** have been ascribed to the greater twist of ring A around the Ar–N axis, because of the steric hindrance involving methyl groups and ortho or alpha hydrogens.[8] The extinction coefficent of **7** is not much different from that of **6**, and this suggests that the extents of twist of ring A are similar in **6** and **7**. This is reasonable because the methyl group of **7** can be situated far from the methine hydrogen and no interaction between them may take place. The higher field resonance in C-4 of **5** than that of benzene (δ=128.5) should be due to the resonance shown in Eq. 4. Twisting of ring A around the Ar–N axis is expected to decrease such resonance, and downfield shifts of the C-4 signals should be expected. However, δ_{C-4} values of **8** and **9**, in which ring A is twisted around the Ar–N axis, are observed at a much higher field than that in **5** (δ_{C-4}(**5**)$-\delta_{C-4}$(**8**)$=2.19$, and δ_{C-4}(**5**)$-\delta_{C-4}$(**9**)$=2.61$). This difference cannot be ascribed to the electron-donating effect of the methyl groups. Because methyl substituents do not affect δ_{C-meta} greatly[9] and also δ_{C-4} value in **7** is similar to that of **6**. The finding that δ_{C-4} of **9** possessing α-methyl group is similar to that of **8** possessing methyl groups at **2** and **6** positions on ring A suggests that the twist of ring A around the Ar–N axis causes the upfield shifts observed in **8** and **9**. The upfield shifts actually observed for the C-4 signals of **8** and **9**, in comparison with that of **5**, indicate the existence of the delocalization of N-lone pair electrons to ring A by the resonance shown in Eq. 5. In **8** or **9**, the resonance shown in Eq. 4 should not be possible and the resonance shown in Eq. 5 must be important. The greater electron density on C-4 of **8** and **9** in comparison with that of **5**, which is reflected in the ^{13}C-NMR chemical shift, suggests that the increased contribution of resonance (5) outweighs the decreased contribution of resonance (4). In **6** or **7**, in which ring A is twisted by about 50°, the chemical shift of C-4 is about the same as that of **5**. These results indicate that increased contribution of resonance (4) is approximately equal to the decreased contribution of resonance (5). So we have clarified that the upfield shifts of δ_{C-4} of *N*-benzylideneanilines by the twist of ring A were caused by the delocalization of the N-lone pair to ring A.

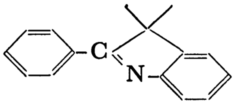
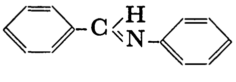
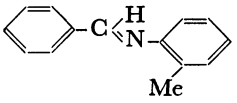
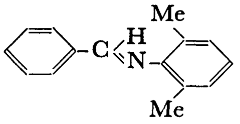
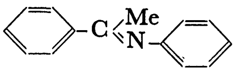


(4)



(5)

Table 3. ^{13}C-NMR chemical shifts and UV data of *N*-benzylideneanilines

	 **5**	 **6**	 **7**	 **8**	 **9**
$\delta_{C-4}$$^{a)}$	125.7	125.8	125.6	123.5	123.1
λ_{max}/nm	309$^{b)}$	314$^{c)}$	325$^{c)}$	331$^{c)}$	320$^{c)}$
ε	16600	6940	4230	1740	1840

a) Chemical shifts of the other carbons of these compounds have been reported in our previous paper : M. Yoshida, H. Minato, and M. Kobayashi, *Chem. Lett.*, **1976**, 1097. b) Ref. 5. c) Ref. 8.

The steric repulsion of the two rings in (*Z*)-*N*-[*p*-(dimethylamino)benzylidene]aniline should be decreased by the preferential twist of ring A around Ar–N axis, because the twist of ring A is energetically more favorable than that of ring B for the stabilization by the delocalization of N-lone pair to ring A. The delocalization of the N-lone pair was reflected in the ^{13}C-NMR chemical shifts of *Z*-**1** and *Z*-**2**.

Experimental

UV spectra were taken with a Hitachi EPS-3T spectrometer. ^{1}H- and ^{13}C-NMR spectra were taken with a JEOL Fx-60 FT-NMR spectrometer.

UV spectra at low temperatures were measured in a sample cell cooled to 77 K with liquid nitrogen in a quartz Dewar bottle. As a solvent, M. P. (methylcyclohexane–isopentane 1 : 1) was used. For volume contraction, a correction factor of 0.8 was used.[10]

An acetone-d_6 solution ($\approx 10^{-3}$ mol dm^{-3}) of an *N*-benzylideneaniline in a Pyrex tube (10 mm) was cooled in a Dry Ice–acetone bath and irradiated through a quartz Dewar bottle with a 500 W high pressure mercury lamp until about 100% isomerization was attained. Then ^{1}H-NMR spectrum of the photoisomer of an *N*-benzylideneaniline was immediately determined at 198 K. Since this photoisomerization is complete only in dilute concentrations, spectra were determined by use of a Fourier transform NMR spectrometer (accumulation 100—500).

The ^{13}C-NMR spectrum of the photoisomer of an *N*-benzylideneaniline was determined in a similar way (Concentration of the solution, 10^{-2} mol dm^{-3}; pulse flipping angle, 60°; sampling time, 900 ms; data points, 4096; accumulation, 5000; pulse interval, 1 s).

N-[*p*-(Dimethylamino)benzylidene]anilines were prepared by heating mixtures of corresponding aldehydes and amines. Samples were purified by repeated recrystallization. The details were described in our previous papers.[3] (Melting points in °C: **1**, 99—101; **2**, 41—43; **3**, 84.5—85.5; **4**, 83—85.)

References

1) E. Fisher and Y. Frei, *J. Chem. Phys.*, **27**, 808 (1959).

2) M. Kobayashi, M. Yoshida, and H. Minato, *Chem. Lett.*, **1976**, 185.

3) M. Kobayashi, M. Yoshida, and H. Minato, *J. Org. Chem.*, **41**, 3322, (1976).

4) K. Maeda and E. Fisher, *Isr. J. Chem.*, **16**, 294 (1977); K. Maeda, K. A. Musuzkat, and S. Sharafi-Ozeri, *J. Chem. Soc., Perkin Trans. 2*, **1980**, 1282.

5) D. Skrabal, J. Steiger, and H. Zollinger, *Helv. Chim. Acta*, **58**, 800 (1975).

6) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

7) H. B. Bürgi and J. D. Dunitz, *Helv. Chim. Acta*, **54**, 1225 (1971).

8) W. F. Smith, *Tetrahedron*, **19**, 445 (1963).

9) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Interscience, New York (1972), p. 81.

10) A. Kuboyama, R. Yamazaki, and S. Matsuzaki, *Bull. Chem. Soc. Jpn.*, **42**, 10 (1969).