tion of the cyclohexene part–NCH_3 in the anti conformer. Since the lone pair electrons of the nitrogen atom have such an important effect on the β carbon situated in the anti-coplanar position, this effect could be used in the investigation by C-13 spectroscopy of the preferential orientation of the nonbonded electrons in different cyclic amines.

Experimental Section

The cannivonine b (1) sample was isolated as previously described.[1] Nickel bisacetylacetonate (Aldrich Chemical Co.) was dried under reduced pressure for 24 h at the temperature of boiling acetone. The ^{13}C NMR spectra were obtained on Brucker HF-X-10 and Jeolco FT spectrometers (22.6 and 25.1 MHz, respectively) with an internal lock ^2H. The δ_C were measured in parts per million using Me_4Si as a standard. Solutions of 1 (10.0%) in $CDCl_3$ in standard tubes (10 mm or 8 mm) at a temperature of 25 ± 1 °C were used. The $Ni(acac)_2$ relative induced shifts for all carbons were measured from the slopes of linear plots of observed ^{13}C contact shifts vs. concentration of acetylacetonate (induced ^{13}C contact shifts in hertz plotted vs. concentration of $Ni(acac)_2$ expressed in millimoles). The "true" shift of 2.20 ppm was observed for 0.025 mol of $Ni(acac)_2$ for C-1 and was normalized to unity.

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Registry No.—1, 52340-94-0.

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Configuration of the Photoisomers of Benzylideneanilines

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Benzylideneanilines (ArCH=NAr′) are formally related to stilbenes (ArCH=CHAr′) and azobenzenes (ArN=NAr′), but are different from the latter two in the respect that *Z* (cis) and *E* (trans) isomers have not been isolated. It was reported that the irradiation of a solution of benzylideneaniline at low temperature converts it reversibly to a photoisomer of different uv absorption,[1a] but no concrete evidence as to its structure has been presented although a *Z* structure has been assigned to the photoisomer of 4,4′-dichlorobenzylideneaniline on the basis of dipole moment measurements.[2]

We have determined the uv spectra of photoisomers of many substituted benzylideneanilines in an EPA matrix (ether–isopentane–ethanol) at −196 °C and showed that the imino arene ring of the photoisomer is about 90° rotated from the ArCH=N– plane around the N–Ar′ bond.[3] However, it was not possible to determine whether or not the photoisomer has a *Z* structure.

As described in our previous paper,[3] the photoisomers are stable in a matrix at −196 °C for a long period and stable for several hours in solutions (EPA, methylcyclohexane, or acetone) at −72 °C. Therefore, the configuration of the photoisomers was studied by determining ^1H NMR spectra in acetone-d_6. Since this photoisomerization is complete only in dilute concentrations (~10^{-3} M), spectra were determined by use of a Fourier transform instrument (accumulation, 500–1000 sweeps). When the photoisomers produced at −196 or −72 °C were warmed to room temperature, the ^1H NMR and uv spectra showed that the photoisomers were completely converted back to the original *E* isomers. This change can be reproduced many times.

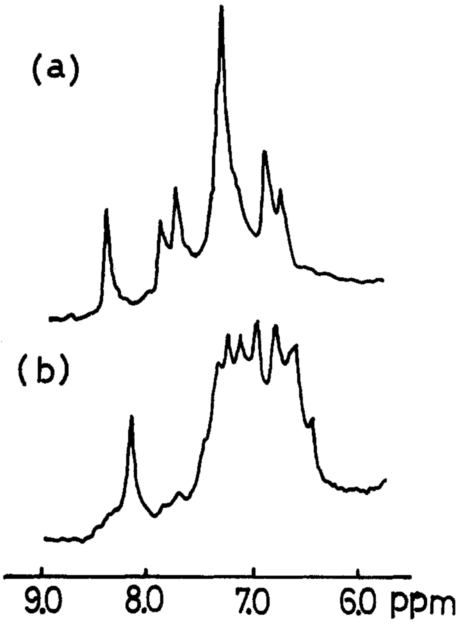
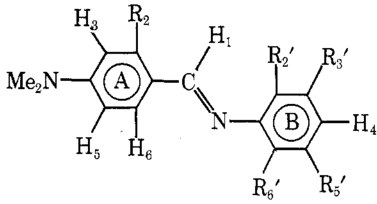
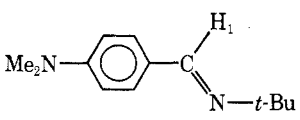


Figure 1. NMR spectra of (a) 1 and (b) its photoisomer **1a**.

p-Dimethylaminobenzylideneaniline (1) and its methyl derivatives were chosen for our study because they have strong absorption maxima at wavelengths greater than 300 nm, and are almost completely converted to their photoisomers upon irradiation in acetone-d_6 solutions with a high-pressure mercury lamp. In order to ascertain the assignments of aromatic NMR absorptions, some derivatives of 1 deuterated at suitable positions were synthesized and their spectra were determined.



1, $R_2 = R_2' = R_3' = R_5' = R_6' = H$
2, $R_2' = R_6' = Me; R_2 = R_3' = R_5' = H$
4, $R_2 = R_2' = R_6' = H; R_3' = R_5' = Me$
5, $R_2 = Me; R_2' = R_3' = R_5' = R_6' = H$



3

Results and Discussion

Figure 1a is the NMR spectrum of 1 in acetone-d_6 at −75 °C; H_1 (s, 8.41 ppm from internal Me_4Si); H_2 and H_6 (q, 7.85 ppm); H_3 and H_5 (q, 6.84 ppm); other ArH (m, ca. 7.4 ppm). Figure 1b is the NMR spectrum of the photoisomer of 1 (**1a**),

Table I. Chemical Shifts of Benzylideneanilines and Their Photoisomers[a]

		δ			$\Delta\delta$	δ		$\Delta\delta$	δ		$\Delta\delta$	δ		$\Delta\delta$
	1	1-2′,4′,6′-d_3	1a	1a-2′,4′,6′-d_3	(1 − 1a)	2	2a	(2 − 2a)	4	4a	(4 − 4a)	5	5a	(5 − 5a)
H_1	8.41	8.41	8.21	8.21	0.20	8.15	8.37	−0.22	8.42	8.18	0.24	8.63	8.53	0.10
H_2	7.85	7.85		7.09	0.76	7.87[b]	7.03[b]	0.8	7.88[c]	7.13[c]	0.24			
H_6												8.03[d]	6.65[d]	1.38
H_3	6.84	6.84		6.59	0.25	*e*	6.58[b]		6.8[c]	6.58[c]	0.2	6.64	6.63	0.01
H_5												6.71[d]	6.20[d]	0.51
$H_{2'},H_{6'}$	7.4								6.86	6.39	0.47	7.31	6.82	0.49
$H_{3'},H_{5'}$	7.4	7.44		7.42	0.02	*e*	7.03					7.42	7.32	0.10
$H_{4'}$	7.4					*e*			6.8			?	?	

[a] Downfield shift from internal Me_4Si in acetone-d_6 in parts per million. [b] $J_{H_2,H_3} = J_{H_5,H_6} = 8.79$ Hz (quartet). [c] $J_{H_2,H_3} = J_{H_5,H_6} = 8.79$ Hz (quartet). [d] $J_{H_5,H_6} = 8.79$ Hz (quartet). [e] 7.08–6.96.

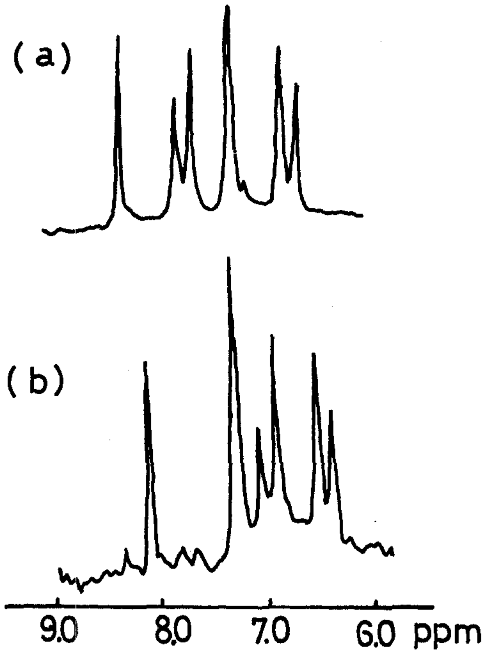


Figure 2. NMR spectra of (a) 1-2′,4′,6′-d_3 and (b) its photoisomer.

in which the absorption of H_1 is shifted to higher field (8.21 ppm). In order to assign other aromatic absorptions, 2′,4′,6′-trideuterated 1 was prepared, and its NMR spectrum and that of its photoisomer were determined (Figure 2). The chemical shifts of 1 and 2′,4′,6′-trideuterated 1 and their photoisomers are compared in Table I.

The absorptions of H_2, H_6, H_3, and H_5 are AA′BB′ type quartets, and this shows that ring A freely rotates around the Ar–C bond within the NMR time scale: $J_{H_2,H_3} = J_{H_5,H_6} = 8.79$ Hz. In the NMR spectrum of 1-2′,4′,6′-d_3, $H_{3'}$ and $H_{5'}$ are equivalent, and this can be interpreted in two ways: ring B also rapidly rotates around the Ar–N bond, or as proposed in our previous paper[3] the stable conformation of **1a** has ring B about 90° rotated around the Ar–N bond. The data shown in Table I can be reasonably explained if one assumes that **1a** has the *Z* structure shown in Figure 3. Although the possibility of the rapid rotation of ring B in **1a** cannot be rejected from the NMR data alone, examination of its molecular model suggests that it is unlikely, since its uv spectrum shows that ring A and the CH═N– group lie in the same plane.

In the case of *cis*-stilbenes no such twist of ring B has been invoked. One of the factors for stabilizing this twisted conformation for the photoisomers of benzylideneanilines must be the conjugation between the lone pair of the imino nitrogen and ring B. An x-ray analysis showed that ring B of benzylideneaniline (*E* isomer) itself is rotated by about 50° from the PhCH═N– plane.[4]

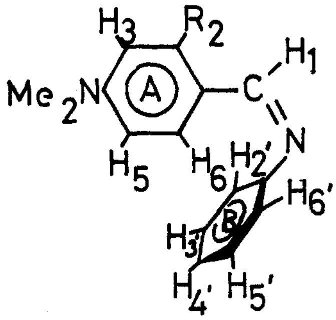


Figure 3. Structures proposed for photoisomers **1a** and **5a**: **1a**, R_2 = H; **5a**, R_2 = ME.

Although ring B in 1 is probably rotated around the Ar–N bond to some extent from the ArCH═N– plane,[5] H_1 must be strongly shifted to a lower field by the paramagnetic deshielding of the ring current. In accordance with such estimation, the methine proton H_1 of p-$Me_2NC_6H_4CH$═N-*t*-Bu (**3**) (to be discussed later) absorbs at 8.21 ppm at −75 °C in acetone-d_6. If **1a** has the *Z* structure shown above, the H_1 should not be affected by the ring current of ring B; the upfield shift (0.20 ppm) observed is quite reasonable.

The significant changes in H_2 and H_6 (0.75 ppm) can be ascribed to the diamagnetic shielding by ring B. If **1a** has the *Z* structure, H_2 and H_6 may be situated right above ring B, and such diamagnetic shielding is expected. H_3 and H_5 must be affected similarly by such diamagnetic shielding, but owing to the greater distance from ring B the upfield shift observed was smaller (0.25 ppm).

The comparison of the NMR spectra of 4-dimethylaminobenzylidene-2′,6′-dimethylaniline (**2**) and its photoisomer (**2a**) shown in Table I further supports our assignment of **1a** to the *Z* structure. **2** has an *E* structure as to the C═N bond, but because of the steric repulsion between 2′,6′-methyls and H_1 the ring B is greatly rotated around the Ar–N bond from the ArCH═N– plane. This can be readily understood from its molecular model, but is also further supported from the fact that the uv spectrum of **2** is quite similar to those of p-$Me_2NC_6H_4CH$═N-*t*-Bu (**3**) and **1a**. Therefore, H_1 of **2** is affected by the diamagnetic shielding effect of ring B and the downfield shift upon irradiation (0.22 ppm) can be ascribed to the loss of such diamagnetic shielding in H_1 of *Z*-structured **2a**. The upfield shift (0.8 ppm) of H_2 and H_6 upon irradiation is about the same as that observed in the case of 1 to **1a**.

Then, in order to clarify the changes in the absorptions of $H_{2'}$ and $H_{6'}$, the NMR spectra of 4-dimethylaminobenzylidene-3′,5′-dimethylaniline (**4**) and its photoisomer (**4a**) were

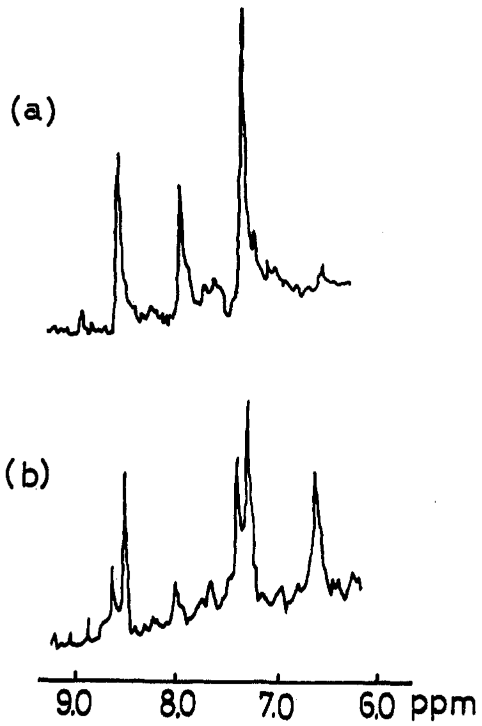


Figure 4. NMR spectra of (a) **5**-*3,5,2′,4′,6′-d_5* and (b) its photoisomer (because of incomplete isomerization, a weak signal of the original azomethine signal is observed.)

investigated. The magnitude of the upfield shift in H_1 (0.24 ppm) upon irradiation is about the same as that observed in the case of **1**. The large upfield shift in H_2 and H_6 (0.75 ppm) upon irradiation is comparable to those observed in the case of 1 and **2**. The comparison of the NMR spectra of **4** and **4a** shows that the absorptions of H_2' and H_6' of ring B suffer an upfield shift of 0.47 ppm. This upfield shift can be explained as follows. The paramagnetic deshielding due to the ring current of the C=N bond affects the H_2' and H_6' in **4**, but not the H_2' and H_6' in **4a**, which has a twisted *Z* structure as shown in the case of **1a**. H_2' and H_6' are greatly rotated out of the ArCH=N- plane.

In **1**, **2**, **4**, or their photoisomers, ring A rotates around the Ar-C bond rapidly within the NMR time scale. Therefore, the upfield shift observed in the absorptions of H_2 and H_6 of 1 and 4 upon irradiation must be the average of the shifts of the H_6 affected by the diamagnetic shielding from the ring B and the H_2 not affected by such shielding. If the rotation of ring A around the Ar-C bond could be restricted, the real upfield shift in H_6 upon irradiation would be shown. Therefore, the changes in the NMR spectra of 2-methyl-4-dimethylaminobenzylideneaniline (**5**), its 2′,4′,6′-trideuterio derivative, and 3,5,2′,4′,6′-pentadeuterio derivative upon irradiation were investigated. If the photoisomer of **5** has a *Z* structure shown in Figure 3, the 2-methyl group should be situated far from ring B. Figure 4 shows the NMR spectra of **5**-*3,5,2′,4′,6′-d_5* and its photoisomer.

The absorption of H_6 suffers a large upfield shift of 1.38 ppm, which is approximately twice the upfield shift observed in the H_2 and H_6 in **1**, **2**, or **4** (0.75 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 or 4 (0.2–0.25 ppm). This is reasonable because H_5 in **5** is not equivalent with H_3 owing to the restriction of the rotation. The structure of **5a** postulated is consistent with the fact that the absorption of the H_3 was not shifted upon the photoisomerization. The upfield shift in H_2' and H_6' (0.49 ppm) is comparable to that observed in 4 (0.47 ppm), and this can be explained in terms of the loss of the paramagnetic deshielding by the C=N group upon isomerization.

Thus, the shifts observed in the absorptions of the methine proton and aromatic protons in **1**, **2**, **4**, and **5** upon irradiation can be rationalized if one assumes that the photoisomer has the *Z* structure and the ring B is rotated around the Ar-N bond from the ArCH=N plane by about 90°. Therefore, we may conclude that, as in the cases of stilbenes and azobenzenes, benzylideneanilines do have *Z* isomers, which are stable only below −70 °C and consequently have not been isolated as such.

Experimental Section

Materials. Benzylideneanilines **1**, **2**, **4**, and **5** and their deuterated derivatives were prepared by heating equimolar mixtures of the corresponding aldehydes and amines without solvent at 150 °C for 10 h, and recrystallized several times from hexane. The melting points follow: **1**, 98–99 °C (lit.[7] 99–100.5 °C); **1**-*2′,4′,6′-d_3*, 97–100 °C; **2**, 68–69 °C; **4**, 68–70 °C; **5**, 83–85 °C; *5-2′,4′,6′-d_3*, 81.5–84 °C; **5**-*3,5,2′,4′,6′-d_5*, 81–83 °C. **2**, **4**, and **5** are new compounds, and their identities are supported by their satisfactory elemental analyses data and NMR spectra. **3** was prepared by heating *p*-dimethylaminobenzaldehyde and *tert*-butylamine at the boiling point of the amine for 48 h, and purified by vacuum distillation at 143–145 °C (7.5 mmHg).

4-Dimethylamino-2-methylbenzaldehyde, used for synthesizing **5**, was prepared from *m*-toluidine by methylation with methyl phosphate and formylation of the 3-methyl-*N*,*N*-dimethylaniline[8] with formaldehyde and *p*-dimethylaminonitrosobenzene according to the method of formylating *N*,*N*-dimethylaniline.[9]

2,4,6-Trideuterioaniline was prepared by refluxing anilinium chloride in D_2O[10] (the extent of exchange, over 95%). 2-Methyl-3,5-dideuterio-4-dimethylaminobenzaldehyde was prepared by refluxing 2-methyl-4-dimethylaminobenzaldehyde in excess D_2O and acetic acid (the extent of exchange, over 95%).

An acetone-d_6 solution of a 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 till about 100% isomerization (5–10 h). Then its ^1H NMR spectrum was immediately determined at −75 °C with a JEOL Fourier transform NMR spectrophotometer FX-60.

Registry No.—1, 1613-99-6; 1-*2′,4′,6′-d_3*, 59812-52-1; **1a**, 40339-45-5; **1a**-*2′,4′,6′-d_3*, 59812-53-2; **2**, 59812-54-3; **2a**, 59812-55-4; **3**, 59812-56-5; **4**, 59812-57-6; **4a**, 59812-58-7; **5**, 59812-59-8; **5**-*3,5,2′,4′,6′-d_5*, 59812-60-1; **5a**, 59812-61-2; **5a**-*3,5,2′,4′,6′-d_5*, 59813-33-1; *p*-dimethylaminobenzaldehyde, 100-10-7; *tert*-butylamine, 75-64-9; 4-dimethylamino-2-methylbenzaldehyde, 1199-59-3; 2,4,6-trideuterioaniline, 7291-08-9; 2-methyl-3,5-dideuterio-4-dimethylaminobenzaldehyde, 59812-62-3.

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