

EFFECTS OF SUBSTITUENTS ON THE ULTRAVIOLET SPECTRA OF THE PHOTOISOMERS OF BENZYLIDENEANILINES

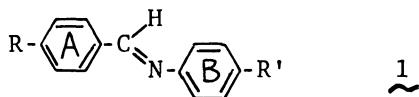
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The UV spectra of the photoisomers of substituted benzylidene-anilines are determined in solid matrix at 77K, and the conformations of the photoisomers are estimated from the effects of substituents on the spectra.

Although the structure of benzylideneaniline (1a) is similar to those of stilbene and azobenzene, isolation of cis and trans isomers of 1a has not been reported in the literature. Formation of an unstable photoisomer upon irradiation of 1a at low temperature was reported,<sup>1,2</sup> but the structure of this photoisomer was not established.

We have investigated the photoisomerism of many substituted benzylideneanilines 1, and found that various 1 are converted to their photoisomers upon irradiation of UV light in a solid E. P. A. matrix (ether:isopentane:ethyl alcohol = 5:5:2) at 77K.



UV spectra at low temperatures were determined in a sample cell cooled to 77K with liquid nitrogen in a quartz Dewar bottle.<sup>3</sup> The E. P. A. matrix at 77K was transparent. For volume contraction, a correction factor of 0.8 was used according to the literature.<sup>3</sup> A 500 W high-pressure mercury lamp and suitable filters were used, and in some cases monochromatic lights of a few nm width were produced by use of quartz prisms and slits. The duration of irradiation varied from 10 min. to several hours.

The photoisomers are stable for a long time at 77K, but when they are warmed up to 233K, their UV spectra changed to those of the original 1. When they were re-cooled to 77K and irradiated, the UV spectra of the photoisomers are reproduced. These procedures can be repeated for many times, and therefore the changes observed are not ascribable to hydrolysis or photocondensation of 1.

When 1 is irradiated at the wavelength corresponding to the longest-wavelength absorption maximum of 1, it changes to its photoisomer, but the photoisomer also absorbs the light. Therefore, the ratio between the amounts of the photoisomer and the original 1 depends upon the wavelength of the light used. This is illustrated in Fig. 1, which shows the UV spectrum of 1e (R=NO<sub>2</sub>, R'=Me), that of a 1e - photoisomer mixture at photo-equilibrium produced with the light at 300 nm, and that of a 1e - photoisomer mixture at photo-equilibrium produced with the light of wave-

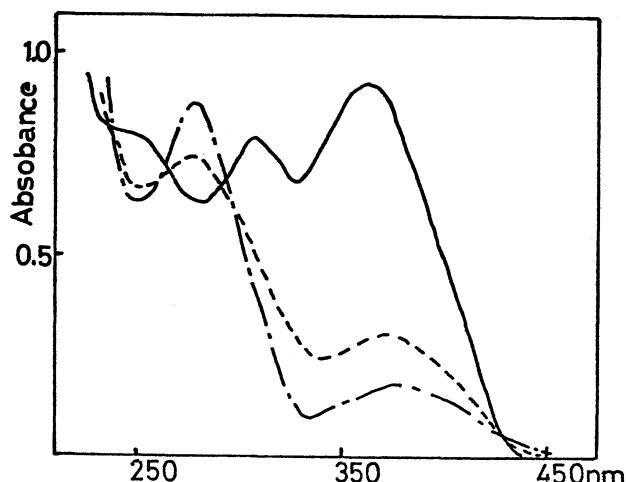


Fig. 1. The U. V. Spectrum of  $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH=N-C}_6\text{H}_4\text{Me-p}$

— Before irradiation

- - - At photo-equilibrium with the light at 350 nm

- - - - At photo-equilibrium with the light greater than 280 nm

lengths greater than 280 nm.

This photoisomerism is greatly affected by the substituents, R and R'. For example,  $\text{lg}$  ( $\text{R=NO}_2$ ,  $\text{R}'=\text{NMe}_2$ ) showed no change in its UV spectrum when it was irradiated under various conditions at 77K.

In order to determine the characteristics of the UV spectra of these photoisomers, it is desirable to have almost 100% conversions to photoisomers. This could be achieved by choosing  $\text{l}$  with suitable substituents and also choosing suitable wavelengths for irradiation lights. Fig. 2A shows the UV spectra of  $\text{la}$  ( $\text{R=H}$ ),  $\text{lb}$  ( $\text{R=OMe}$ ), and  $\text{lc}$  ( $\text{R=NMe}_2$ ); Fig. 2B is the UV spectra of their photoisomers (in this series,  $\text{R}'$  is kept constant;  $\text{R}'=\text{H}$ ). The wavelengths of the absorption maxima of the photoisomers are shorter than those of original  $\text{la-c}$  and vary considerably with the substituents (H, OMe, and NMe<sub>2</sub>).

Figure 3A shows the UV spectra of  $\text{ld}$  ( $\text{R}'=\text{H}$ ),  $\text{le}$  ( $\text{R}'=\text{Me}$ ), and  $\text{lf}$  ( $\text{R}'=\text{OMe}$ ); Fig. 3B shows the UV spectra of their photoisomers (in this series,  $\text{R}$  is kept constant ( $\text{R=NO}_2$ )). In contrast with the UV spectra shown in Fig. 2B, the UV spectra of these photoisomers do not vary with the substituents, whereas those of original  $\text{ld-f}$  vary with the substituents. These findings indicate that in these photo-isomers the benzylidene benzene rings and the C=N groups are conjugated but there is almost no conjugation between the imino benzene rings and the C=N groups. This hypothesis is further supported by the following observations:

1) The absorption maxima of  $p\text{-R-C}_6\text{H}_4\text{CH=N-t-Bu}$  are observed at 243 ( $\text{R=H}$ ), 265 ( $\text{R=OMe}$ ), and 280 nm ( $\text{R=NO}_2$ ), and the absorption maxima of the photoisomers of the corresponding  $p\text{-R-C}_6\text{H}_4\text{-CH=N-Ph}$  ( $\text{la}$ ,  $\text{lb}$ , and  $\text{ld}$ ) are also observed at similar wavelengths. Thus, the conjugation systems of photoisomers should be composed of the ring A and the C=N group without the ring B.

2)  $p\text{-R-C}_6\text{H}_4\text{CH=N-C}_6\text{H}_2\text{-Me}_2\text{-2,6-R'-4}$  ( $\text{2}$ ) were synthesized, in which the ring B

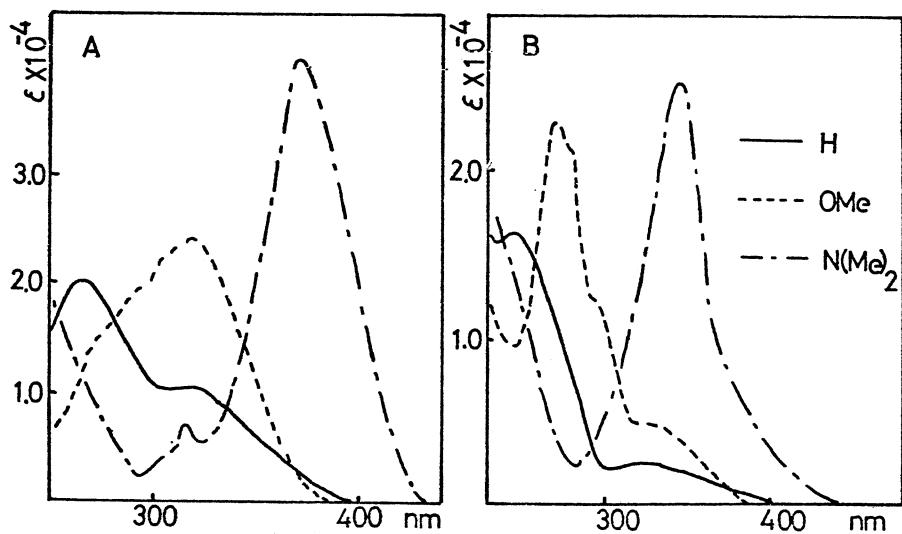
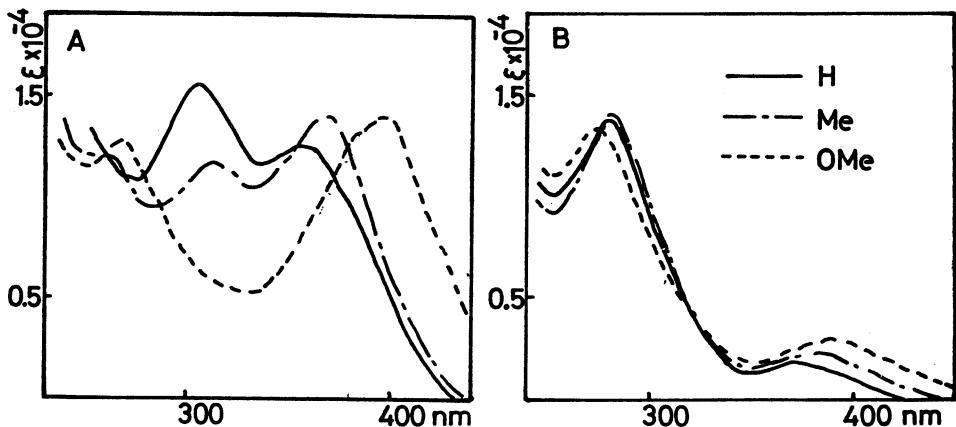
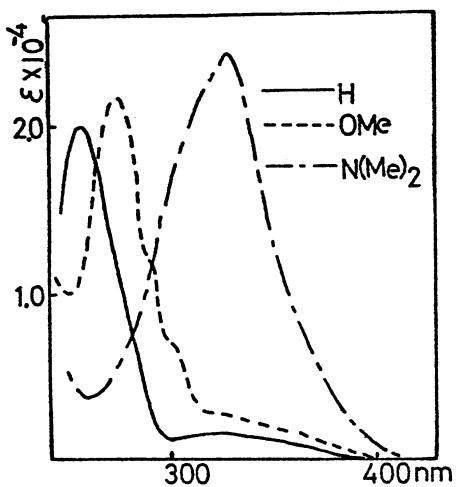
Fig. 2. The UV Spectra of  $p$ -R- $C_6H_4CH=N-C_6H_5$  (A) and Its Photoisomer (B).Fig. 3. The UV Spectra of  $p$ -O<sub>2</sub>N- $C_6H_4CH=N-C_6H_4-R'$ -p (A) and Its Photoisomer (B).

Fig. 4. The UV Spectrum of

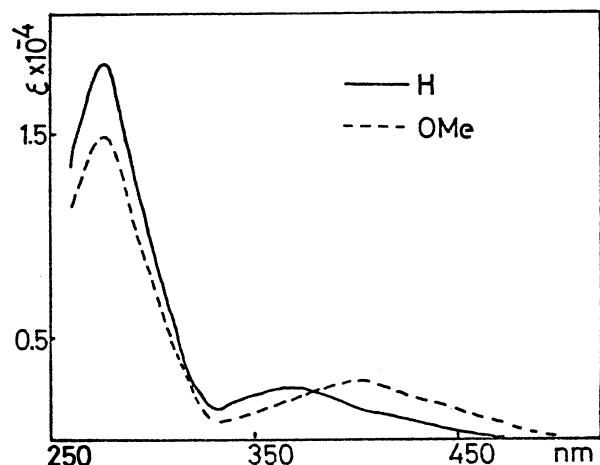
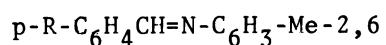
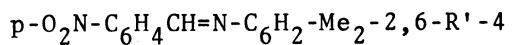
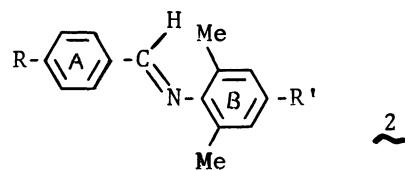


Fig. 5. The UV Spectrum of





is expected to be rotated from the plane of the ring A and the C=N group, and the ring B is not involved in the conjugation of the ring A and the C=N group. As Fig. 4 shows, the UV spectra of 2a (R=H, R'=H), 2b (R=OMe, R'=H), and 2c (R=NMe<sub>2</sub>, R'=H) were almost the same as those of the photoisomers of 1a, 1b, and 1c shown in Fig. 2B, respectively.

3) The UV spectra of 2d (R=NO<sub>2</sub>, R'=H) and 2e (R=NO<sub>2</sub>, R'=OMe) shown in Fig. 5 are almost the same as those of the photoisomers of 1d and 1f shown in Fig. 3B, respectively.

Thus, the UV spectra of photoisomers are affected by substituents R but not by substituents R'. Therefore, in the photoisomers of 1, the plane of the ring B is probably rotated from the plane of the ring A and C=N group by about 90°. One of the factors responsible for stabilizing this rotated conformation is the conjugation between the lone pair of the imino-nitrogen and the ring B. This problem is currently being studied in our laboratories by use of INDO calculations and studies on solvent effect.

We have shown that in the photoisomers of 1 the plane of the ring B is rotated from the plane of the ring A and the C=N group by about 90°, but it is not yet clear whether or not they have cis structure. We wish to solve this problem in our future investigations.

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