Short Communication

Investigations of the *cis–trans* isomerization of benzylidene aniline. III

U.v. and n.m.r. spectra of *cis*-benzylidene anilines

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Since 1957 it is known from the experiments of Fischer and Frei [1] that the irradiation of *N*-aryl benzylidene solutions at low temperatures results in a reversible change of the u.v. spectrum which is due to the photochemical *trans–cis* isomerization of these Schiff bases:

$$Ph{-}CH = N{-}Ph \xrightarrow{\ h\nu\ } Ph{-}CH = N{-}Ph \tag{1}$$
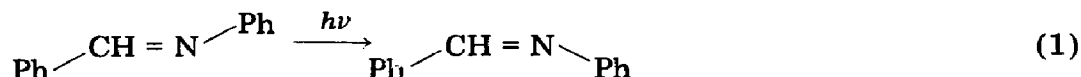
In the course of our investigations concerning the thermal *cis–trans* isomerization of benzylidene anilines [2, 3], it was necessary to obtain reliable spectral data for the *cis*-isomers of benzylidene anilines. In this paper we present the u.v. absorption spectra of *cis*-benzylidene aniline (BA), and *cis-p,p'*-dichlorobenzilidene aniline in methylcyclohexane, the conjugate acid of BA in concentrated sulphuric acid and the n.m.r. spectrum of the latter compound. We hope our results provide some data for the discussions of theoretical chemists [4 - 9] about the geometrical configuration of the benzylidene aniline molecule and its resonance conditions.

Experimental and Results

U.v. absorption spectra of the cis-*isomers of the Schiff bases*

The u.v. spectra were obtained from benzylidene aniline solutions in a 1 : 1 methylcyclohexane /3-methylpentane mixture. Prior to the measure-

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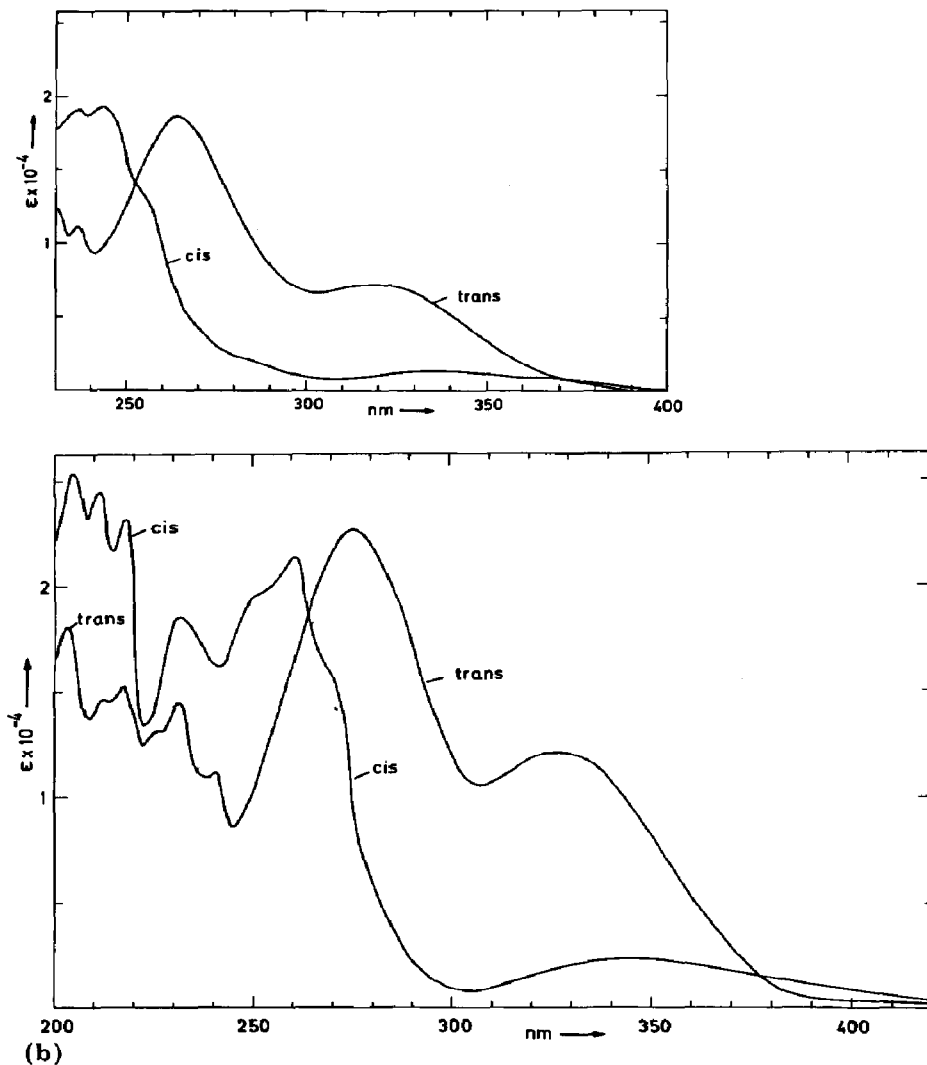
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(b)

Fig. 1 (a). Absorption spectra of benzilidene aniline in 1 : 1 methylcyclohexane/
3-methylpentane at —100 °C.

Fig. 1 (b). Absorption spectra of p,p'-dichlorobenzilidene aniline in 1 : 1 methylcyclo-
hexane/3-methylpentane at —100 °C.

ments the solvent was thoroughly degassed by the freeze–pump–thaw
technique and was dried by stirring over a liquid sodium–potassium alloy.

The benzylidene aniline solutions were cooled down to —100 °C and ir-
radiated directly in the cell compartment of a Cary 17 spectrophotometer
with monochromatic light of different wavelengths. At the applied temper-
ature the thermal *cis–trans* isomerization is completely suppressed and does
not interfere with the photochemical *trans–cis-* and *cis–trans*-reactions.

Under our conditions (100 W medium pressure mercury lamp, 125 mm

monochromator) the photostationary equilibrium is reached after approximately 3 hours.

By applying the procedure outlined by Fischer [10] the u.v. absorption spectra of cis-benzylidene aniline [Fig. 1(a)] and cis-p,p'-dichlorobenzylidene aniline [Fig. 1(b)] were obtained from the absorption spectrum of the respective trans-isomer and the spectra of the photostationary equilibria as obtained from irradiation at the two wavelengths $\lambda_1 = 313$ nm, and $\lambda_2 = 366$ nm. Figures 1(a) and 1(b) show the absorption spectra of the cis- and trans-isomers of both compounds at $-100\ °C$.

U.v. and n.m.r. spectra of the cis- *and* trans-*isomers of the benzylidene anilinium cation*

The pK_a values of the conjugate acids of the benzylidene anilines are about 2 to 4 [11]. Thus, in concentrated sulphuric acid (96%) benzylidene aniline is completely protonated and owing to the low water activity of this solvent the conjugate acid of the Schiff base is not hydrolyzed and is fairly stable even at elevated temperatures (80 to 90 °C). The u.v. spectrum of the benzylidene anilinium differs markedly from that of the unprotonated Schiff base and closely resembles that of stilbene [12] (Fig. 2). Upon irradiation the u.v. absorption spectra of the sulphuric acid solutions change drastically. This spectral change is in all probability due to the photochemical *trans—cis* isomerization of the conjugate acid of the Schiff base whose thermal *cis—trans* reaction is completely suppressed owing to the protonation of the nitrogen lone electron pair [3]. This assumption can be verified by the following two observations: (a) by heating the irradiated solutions above 100 °C the original u.v. absorption spectrum of the *trans*-benzylidene anilinium cation is re-established [3]; (b) the change in the n.m.r. spectrum of the benzylidene anilinium cation which accompanies the spectral change upon irradiation clearly proves that the light induced reaction is the *cis—trans* isomerization.
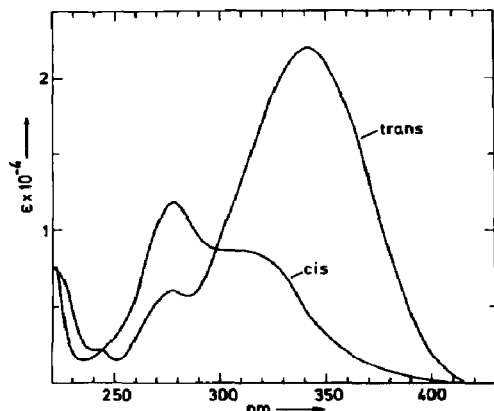

Fig. 2. Absorption spectra of benzilidene aniline in 96% sulphuric acid at 23 °C.
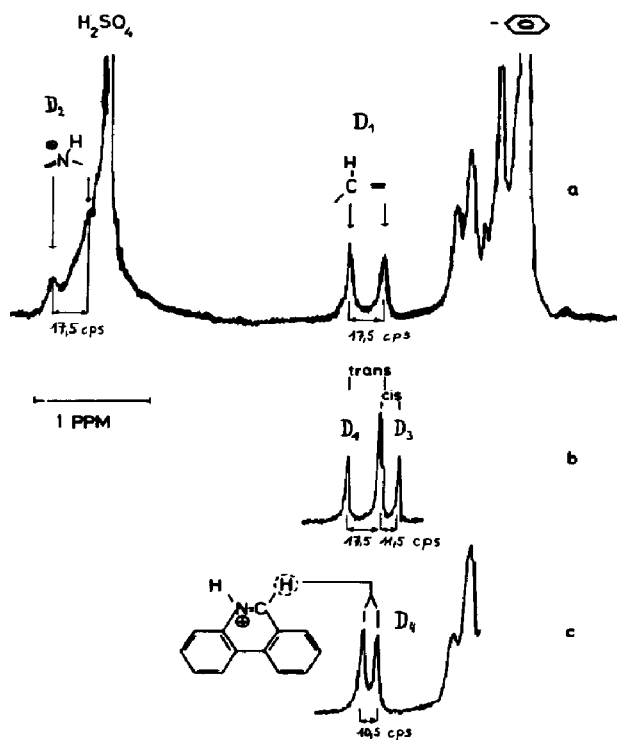
Fig. 3. N.m.r. spectra in 96% sulphuric acid. (a) 1 M *trans*-benzilidene aniline before illumination; (b) same as (a) after illumination, containing 46% *cis*-isomer; (c) 1M phenanthridine.

In Fig. 3(a) the n.m.r. spectrum of the *trans*-benzylidene anilinium cation in H_2SO_4 at 25 °C is depicted. One clearly distinguishes between the phenyl protons and the sulphuric acid protons two doublets [D_1 and D_2 in Fig. 3(a)], with the spin-coupling constants $J_1 = J_2 = 17.5$ cps. The one at higher field (D_1) belongs to the benzylidene proton. The poorly resolved doublet D_2 which is superimposed on the sulphuric acid proton signal is to be attributed to the acidic proton which is attached to the nitrogen atom. This proton is obviously exchanged only very slowly with the bulk of the solution, otherwise both doublets, D_1 and D_2, would show exchange broadening. After irradiation a second doublet D_3 emerges [Fig. 3(b), spin coupling constant $J = 11.5$ cps] which is shifted approximately 0.1 ppm to higher field strengths. The n.m.r. signals of vinyl protons of substituted ethylenes show a very similar difference in the coupling constants for the *trans*- and *cis*-isomers [14]. If the solutions are heated above 100 °C both the u.v. spectral change and the second doublet in the n.m.r. spectrum disappear. Neither the signal form nor the signal intensity of the phenyl protons change upon irradiation. These observations and the comparison with the n.m.r. spectrum of the phenanthridinium cation [Fig. 3(c)] show that the photoproduct is neither the conjugate base of phenanthridine nor that of the dihydrophenanthridinium cation which could both form photo-

chemically from benzylidene aniline in concentrated H_2SO_4 [13]. If the dihydrophenanthridinium cation were formed, the n.m.r. signals of the phenyl protons would be changed drastically. Thus it is quite clear that the photoreaction which is observed in the reported spectral changes is indeed to be attributed to the photochemical *trans–cis* isomerization of the benzylidene anilinium cation:

$$Ph-CH = \underset{\oplus}{NH}-Ph \xrightarrow{h\nu} Ph-CH = \underset{\oplus}{NH}-Ph \qquad (2)$$
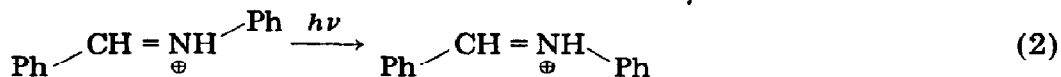
The n.m.r. spectra allow us to determine directly the *cis/trans* ratio in the irradiated solutions with an accuracy of about 10%. With this known ratio the u.v. spectrum of the *cis*-isomer can be calculated (see Fig. 2).

Discussion

Recently it has been demonstrated by X-ray analysis [15] that *trans*-benzylidene aniline is not planar. The *N*-phenyl ring is twisted 60° out of the plane of the C=N double bond owing to its interaction with the nitrogen lone electron pair. This twist causes a marked decrease of the transition moment for the absorption band with $\lambda_{max} \approx 320$ nm [5 - 8] which is assumed to belong to a $\pi \rightarrow \pi^*$ transition which is mainly a charge transfer from the *N*-phenyl system to the C=N bridge [5]. For the *cis*-isomer the transition moment clearly is still smaller. According to the approximate $\cos^2 \theta$ dependence (θ = angle of twist) of the absorption coefficient [5] an increase of the angle of twist up to a value of $\theta_{cis} = 71°$ is estimated for *cis*-benzylidene aniline and of $\theta_{cis} = 80°$ for *cis-p,p'*-dichlorobenzylidene aniline. It is noteworthy that the energy of this long wavelength transition is nearly the same for the *cis* and the *trans* form of both compounds. In contrast to the neutral molecule, the benzilidene anilinium cation is very similar to stilbene.

Brocklehurst has already pointed out [12] that the conjugate acid of benzilidene aniline is planar, since the values $\lambda_{max} = 340$ nm and $\epsilon_{max} = 2.2 \times 10^4 \, M^{-1} \, cm^{-1}$ of the first absorption band are very similar to those of the (planar) *trans*-stilbene ($\lambda_{max} = 300$ nm, $\epsilon_{max} = 2.9 \times 10^4 \, M^{-1} \, cm^{-1}$). The first absorption band of the *cis*-form is — again very similar to *cis*-stilbene — shifted to shorter wavelengths ($\lambda_{max} = 310$ nm) and the extinction coefficients are smaller ($\epsilon_{max} = 0.85 \times 10^4 \, M^{-1} \, cm^{-1}$) (*cis*-stilbene: $\lambda_{max} = 280$ nm; $\epsilon_{max} = 1 \times 10^4 \, M^{-1} \, cm^{-1}$).

Thus, the optical properties of the benzilidene anilinium cation can be interpreted similarly to those of stilbene. We therefore assume, according to the treatment of Beveridge and Jaffé [16] that the small extinction coefficients of the *cis* form are due to a propeller-shaped conformation of the molecule.

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