

Photochemically induced structure transfer from analogous azobenzenes and stilbenes onto a liquid crystalline phase

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Thorsten Fischer, Ralf Ruhmann and Arno Seeboth*

Institut für Angewandte Chemie, Abteilung Funktionsmaterialien, Rudower Chaussee 5, 12489 Berlin, Germany

The photoinduced structure transfer from different 4-*N,N*-diethylamino-4'-alkoxyazobenzenes and analogous stilbenes onto a nematic liquid crystalline phase has been investigated. The structure transfer caused by the azobenzenes was found to be 7–8 times smaller than for the corresponding stilbenes. The photoinduced *E*→*Z* isomerization of the azobenzenes occurred in the liquid crystal more slowly than the thermal back reaction. In contrast, despite lower rate constants for the *E*→*Z* photoisomerization, the stilbenes under investigation brought about a greater structure transfer because no thermal back reaction was found at 25 °C.

Investigations carried out with the azobenzenes in ethanol and cyclohexane showed the great influence of the polarity of the surrounding medium on the ratio between the rate constants for the *E*→*Z* photoisomerization and the thermal *Z*→*E* back reaction. This ratio $k_{E \rightarrow Z}/k_{Z \rightarrow E, \text{therm}}$ increased at 25 °C from *ca.* 0.15–0.5 in the highly polar liquid crystal to *ca.* 13–19 in ethanol and nearly 500 in the apolar cyclohexane.

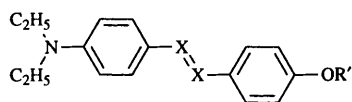
This paper concludes that only the investigated stilbenes are suitable for photoaddressed displays using highly polar, thermotropic liquid crystals.

Introduction

The photochemical *E*→*Z* isomerization of chromophores embedded in a thermotropic liquid crystal (LC), bulk or polymer dispersed LC, is well known. Usually azobenzenes and stilbenes are used as chromophores.^{1–3} A photoinduced alignment change is described, which is controlled by the photoisomerization of surface attached azobenzene moieties^{4–6} or azobenzene LC mono- and multi-layers.^{7–10} Ichimura and co-workers assumed that the photoisomerization of one surface-attached azobenzene unit brings about the reversible reorientation of 10⁴ LC molecules.⁵

More recently, the photoinduced structure transfer from different 4-*N,N*-dialkylamino-4'-alkoxystilbenes embedded in an LC bulk onto the nematic LC molecules has been investigated.¹¹ It was shown that the structure transfer from the chromophore onto the LC phase is influenced by the specific stilbene structure.¹¹ The structure transfer was determined by measuring the changes in light transmittance of the stilbene–LC system in a display with the help of a Si photodiode.

The purpose of the present work was to advance the previous research by answering the following questions. (1) Do



X = N, CH R' = CH₃, C₄H₉, C₇H₁₅, C₁₂H₂₅

investigations of chromophores with a different photoactive group in the molecule, but a comparable overall molecular length, yield additional findings regarding the structure transfer from the chromophore onto the LC phase? (2) What conclusions can be drawn from the results regarding photo-addressed displays?

The chromophores we selected for this research are 4-*N,N*-diethylamino-4'-alkoxystilbenes and the analogous azobenzenes.

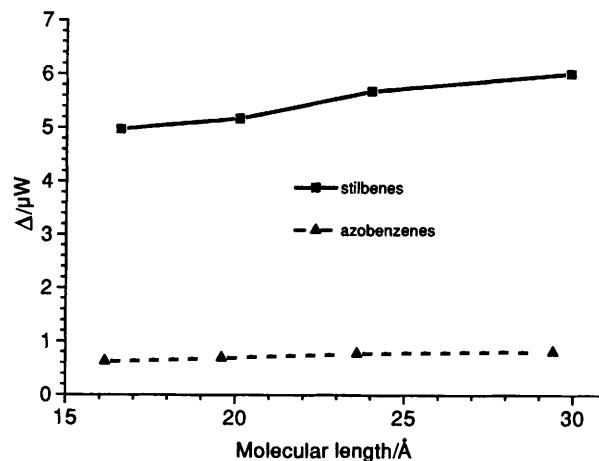


Fig. 1 Differences in light transmittance after and before irradiation depending on the molecular length of the azobenzenes and stilbenes

Results and discussion

The photochemically induced *E*→*Z* isomerization of the stilbene and azo chromophores in the LC phase leads to a reorientation of the liquid crystalline molecules.

In Fig. 1, the photoinduced changes in light transmittance of the liquid crystalline matrix are illustrated for the stilbene and azo chromophores. The light transmittance, expressed in μW , increased as a consequence of the photoinduced reorientation of the liquid crystal. The stilbenes and azobenzenes with comparable molecular structure each had a unique influence on the increase in the light transmittance. The difference in light transmittance after irradiation compared with the value before irradiation (Δ value) rises slightly with the increasing length of the stilbenes. The smallest Δ value ($\Delta = 4.98 \mu\text{W}$) was obtained for the shortest stilbene and the highest Δ value ($\Delta = 6.0 \mu\text{W}$) for the longest stilbene. Otherwise, the differences in light transmittance were very small for all azobenzenes and differed from the Δ values of the stilbenes by a factor of 7–8. The differences in light transmittance after irradiation compared with the value before irradiation increased for the azobenzenes

Table 1 First-order rate constants for the $E \rightarrow Z$ photoisomerization and the thermal $Z \rightarrow E$ isomerization of azobenzenes and stilbenes in ZLI 1695 under investigation

	Sample	R'	$k_{E \rightarrow Z}/10^{-2} \text{ s}^{-1}$	$k_{Z \rightarrow E, \text{therm}}/10^{-2} \text{ s}^{-1}$	$k_{E \rightarrow Z}/k_{Z \rightarrow E, \text{therm}}$
Azobenzenes	1	CH ₃	0.42	2.14	0.20
	2	C ₄ H ₉	0.32	2.11	0.15
	3	C ₇ H ₁₅	0.44	1.76	0.25
	4	C ₁₂ H ₂₅	0.60	1.27	0.47
Stilbenes	5	CH ₃	0.017	—	—
	6	C ₄ H ₉	0.015	—	—
	7	C ₇ H ₁₅	0.014	—	—
	8	C ₁₂ H ₂₅	0.013	—	—

Table 2 First-order rate constants for the $E \rightarrow Z$ photoisomerization and the thermal $Z \rightarrow E$ isomerization of azobenzenes in ethanol and cyclohexane

Azobenzenes		Rate constants in ethanol			Rate constants in cyclohexane		
Sample	R'	$k_{E \rightarrow Z}/10^{-2} \text{ s}^{-1}$	$k_{Z \rightarrow E, \text{therm}}/10^{-2} \text{ s}^{-1}$	$k_{E \rightarrow Z}/k_{Z \rightarrow E, \text{therm}}$	$k_{E \rightarrow Z}/10^{-2} \text{ s}^{-1}$	$k_{Z \rightarrow E, \text{therm}}/10^{-2} \text{ s}^{-1}$	$k_{E \rightarrow Z}/k_{Z \rightarrow E, \text{therm}}$
1	CH ₃	4.08	0.31	13	10.67	0.0211	506
2	C ₄ H ₉	4.78	0.29	16.5	10.72	0.0205	523
3	C ₇ H ₁₅	4.80	0.28	17.1	10.25	0.0208	493
4	C ₁₂ H ₂₅	4.80	0.25	19.2	10.32	0.0204	506

with increasing molecular lengths as well, although in a very moderate way. Thus, a Δ value of 0.62 μW was found for the shortest azobenzene and a Δ value of 0.81 μW for the longest azobenzene.

The different behaviour of stilbenes and azobenzenes indicates that the structure transfer is strongly influenced by the kind of chromophore. Obviously, the length of the molecules is only important for the structure transfer through molecules with the same photoactive centre, whether a stilbene or azo group.

Kinetic measurements were carried out in order to explain the minimal effectiveness of the structure transfer induced by the $E \rightarrow Z$ photoisomerization of (*E*)-4-*N,N*-diethylamino-4'-alkoxyazobenzenes compared with the analogous stilbenes. In this way, the rate constants for the photoinduced $E \rightarrow Z$ isomerization and for the thermal back reaction were determined. A fast thermal $Z \rightarrow E$ isomerization compared with the $E \rightarrow Z$ photoisomerization would explain the small differences measured in light transmittance. The fact that the light transmittance began to decrease rapidly immediately after the irradiation light was switched off, indicates a fast thermal back reaction.

It is known that many of the aminoazobenzene-type molecules seem not to isomerize on irradiation as a result of the fast thermal back-isomerization of the *Z* isomer.^{12,13} In polymer matrices with aminoazobenzene groups pending, or in the backbone, the isomerization can be monitored at room temperature.¹⁴ Albin *et al.* have measured the $E \rightarrow Z$ quantum yields of 4-*N,N*-diethylamino-4'-methoxyazobenzene in cyclohexane solutions at different wavelengths.¹⁵ They found values of 0.72 (434 nm), 0.21 (366 nm), 0.25 (313 nm) and 0.23 (254 nm).

Unfortunately, there is no corresponding report for other, more polar solvents such as ethanol or LC media.

The determined rate constants for the $E \rightarrow Z$ photoisomerization and for the thermal $Z \rightarrow E$ isomerization in the liquid crystalline phase are summarized in Table 1. The corresponding rate constants in the polar solvent, ethanol, and in the apolar solvent, cyclohexane, are shown in Table 2. These investigations were carried out to explain the influence of the medium on the ratio of the photoinduced $E \rightarrow Z$ isomerization to the thermal back reaction $k_{E \rightarrow Z}/k_{Z \rightarrow E, \text{therm}}$.

The rate constants for the thermal $Z \rightarrow E$ isomerization of all

investigated 4-*N,N*-diethylamino-4'-alkoxyazobenzenes were generally higher in the liquid crystalline phase than the corresponding rate constants for the $E \rightarrow Z$ photoisomerization. The ratio $k_{E \rightarrow Z}/k_{Z \rightarrow E, \text{therm}}$ ranged between 0.15 and 0.47. The molecular length of the azobenzenes had no influence on the rate constants for the $E \rightarrow Z$ isomerization. However, it should be mentioned that an accurate determination of the rate constants for the photoinduced $E \rightarrow Z$ isomerization was not possible since there was a fast competitive thermal back reaction. The rate constants for the thermal back reaction decreased slightly with increasing molecular length of the azobenzenes, since more LC molecules must be displaced as the length of the alkoxy chain of the azobenzenes increases. Such an influence by the chain length on the rate constants is also found in ethanol (Table 2). In contrast, in the apolar solvent cyclohexane, the alkoxy chain length had no influence on the rate constants.

The rate constants for the $E \rightarrow Z$ photoisomerization of the 4-*N,N*-diethylamino-4'-alkoxystilbenes in the LC medium were 21–46 times smaller than the corresponding rate constants of the azobenzenes (Table 1). Otherwise, no thermal back reaction was found for the stilbenes at 25 °C. Therefore, despite lower rate constants, the stilbenes under investigation underwent an efficient $E \rightarrow Z$ photoisomerization and a high structure transfer was observed from the chromophore onto the liquid crystalline phase.

In ethanol, the ratio between the rate constants of the photoinduced $E \rightarrow Z$ isomerization and the thermal back reaction ranged between 13 and 19 for the azobenzenes (Table 2). Obviously, the photoreaction predominates over the thermal $Z \rightarrow E$ isomerization. The rate constants for the photoinduced $E \rightarrow Z$ isomerization in ethanol were generally 8–15 times higher than the corresponding rate constants in the LC bulk. In contrast, the rate constants for the thermal back reaction were 5–7 times smaller in ethanol compared with in the LC ZLI 1695.

In the apolar cyclohexane, the photoinduced $E \rightarrow Z$ isomerization of the 4-*N,N*-diethylamino-4'-alkoxyazobenzenes was very fast compared with the thermal back reaction. Values between 490 and 525 were obtained for the ratio $k_{E \rightarrow Z}/k_{Z \rightarrow E, \text{therm}}$. The rate constants for the $E \rightarrow Z$ photoisomerization increased by a factor of 2.1–2.6 compared with the corresponding rate constants in ethanol. In contrast, the rate

constants for the thermal back reaction decreased 10-fold compared with ethanol and by 100-fold compared with the LC phase.

The following conclusions can be drawn from this determination of the rate constants for the photoinduced $E \rightarrow Z$ isomerization and for the thermal back reaction in different media. Aminoazobenzene-type molecules do not undergo an effective $E \rightarrow Z$ isomerization in the highly polar liquid crystalline bulk since there is a fast thermal back-isomerization of the Z isomers. An efficient $E \rightarrow Z$ photoisomerization of aminoazobenzenes can be realised only in an apolar medium such as cyclohexane.

The large solvent effect on the rate for thermal isomerization agrees with results published by Wildes *et al.* and Nishimura *et al.*^{16,17} Wildes *et al.* observed a large solvent effect on the rate and activation energy for the thermal isomerization of *para*-donor-*para'*-acceptor-substituted azobenzenes. The isomerization rate of 4-*N,N*-diethylamino-4'-nitroazobenzene was *ca.* 10^5 times faster in *N*-methylformamide than in hexane.¹⁶ The results of Nishimura *et al.*¹⁷ are virtually in line with those of Wildes *et al.*

We can conclude therefore, that 4,4'-substituted aminoazobenzenes cannot be used for photoaddressed displays since all anisotropic, thermotropic liquid crystals are strong polar compounds.¹⁸

In contrast, the analogous stilbenes undergo an efficient $E \rightarrow Z$ photoisomerization in the LC medium since there is an absence of the thermal back reaction at room temperature. Therefore, the stilbenes under investigation are more suitable than the corresponding azobenzenes for use in photoaddressed displays.

Experimental

Materials

The synthesis of the 4-*N,N*-diethylamino-4'-alkoxystilbenes has been described in a previous work.¹¹ The stilbenes had a purity of 98–99.5%, checked by HPLC (HPLC-instrument from Perkin-Elmer, series 1050, equipped with an RP 18 column) and a maximum absorbance of the E -isomers in ethanol at 355 nm. The synthesis of the 4-*N,N*-diethylamino-4'-alkoxyazobenzenes started from 4-aminophenol through the reaction with *N,N*-diethylaniline to give 4-*N,N*-diethylamino-4'-hydroxyazobenzene according to the method described by Meretoja and Linko.¹⁹ 4-*N,N*-Diethylamino-4'-hydroxyazobenzene (0.015 mol), potassium hydroxide (0.0165 mol) and a trace of potassium iodide were dissolved in a mixture of 40 ml water and 40 ml ethanol. The mixture was stirred and refluxed. The corresponding ω -bromoalkane or methyl iodide, diluted with 40 ml ethanol, was added dropwise. Then the mixture was refluxed for 4 h. After cooling, the precipitate was collected, dried in air and purified by column chromatography (dichloromethane, silica gel 60) and by recrystallization from propan-2-ol. The synthesized azobenzenes had a maximum absorbance of the E -isomers in ethanol at 411 nm.

A mixture of several 4-alkylcyclohexyl-4'-cyanocyclohexanes (ZLI 1695, Merck) was used as liquid crystal.

Sample preparation and irradiation procedure

All prepared chromophore/LC guest–host systems contained 0.079 mol of chromophore. The LC-chromophore mixtures were placed in commercially available testing cells (E. H. C. Co., Japan) with a cell gap of 5 μm . The dimensions of these cells were 12 \times 25 mm.

Irradiations were carried out with a xenon high pressure lamp XBO-101. An IR filter, a band pass filter and a metal interference filter for selecting the wavelength 350 nm (stilbenes) or 400 nm (azobenzenes) were arranged on an optical bench between lamp and sample.

Determination of the photoinduced structure transfer

The filled LC-chromophore testing cells were irradiated where the irradiated sample area had a constant diameter of 3 mm. The changes in transmitted light intensity of a xenon high pressure lamp through the display cells and crossed polarizer were recorded, depending on the irradiation time, at 450 nm (stilbenes) or 525 nm (azobenzenes) using a Si photodiode (type SEL 100 from International Light Incorporated) connected with an IL 1400A radiometer. The measurements were carried out until no further changes in light transmittance were registered. The transmitted light intensity was measured in μW . The corrected light intensities at 450 and 525 nm were obtained with the help of a calibration curve, where the relative sensitivity of the photodiode is plotted against the wavelength of light.

Kinetic measurements

For the determination of the rate constants for the $E \rightarrow Z$ photoisomerization, the changes in absorbance of the E -isomers were recorded with irradiation time. The absorption spectra were recorded on a Perkin-Elmer Lambda 18 spectrophotometer. The first-order rate constants k were calculated from the slope which resulted when the logarithm of absorbance was plotted *versus* irradiation time according to eqn. (1)²⁰ with A = absorbance and t = irradiation time. The

$$-\ln A = kt \quad (1)$$

rate constants for the thermal reaction were obtained from a slope of the straight line obtained by plotting $\ln(A_0 - A)$ *vs.* t where A_0 = absorbance of pure E -isomer and A = absorbance at the time t .²¹

Kinetic runs were performed at 25 °C. At least 10 points were recorded for each run and correlation coefficients were always better than 0.99. All rate constants were checked by duplicate runs, accuracy being within $\pm 3\%$.

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