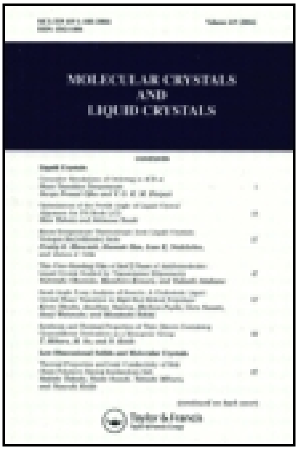

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Studies of Photochemically Induced Structure Transfer from Stilbene Chromophores onto a Liquid Crystalline Phase

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Studies of Photochemically Induced Structure Transfer from Stilbene Chromophores onto a Liquid Crystalline Phase

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The photoinduced structure transfer from different stilbene chromophores onto a nematic liquid crystalline phase was investigated depending on the specific chromophore structure and the rate constants of the E-Z photoisomerization. No linear correlation was found between the rate constants of the E-Z isomerization and the overall molecular lengths of the 4-N,N-dialkylamino-4'-alkoxystilbenes. The rate constants decreased with an increasing number of carbon atoms in both hydrocarbon chains of the 4-N,N-dialkylamino group. In contrast, the length of the 4'-alkoxy group only had a small influence on the rate constants of the E-Z photoisomerization.

The light transmittance of the stilbene-LC system in a display changed as a consequence of the photochemically induced structure transfer from stilbene chromophores onto the liquid crystalline molecules. The effect of the structure transfer from the chromophore onto the LC phase has a tendency to grow with the increasing stilbene molecular length.

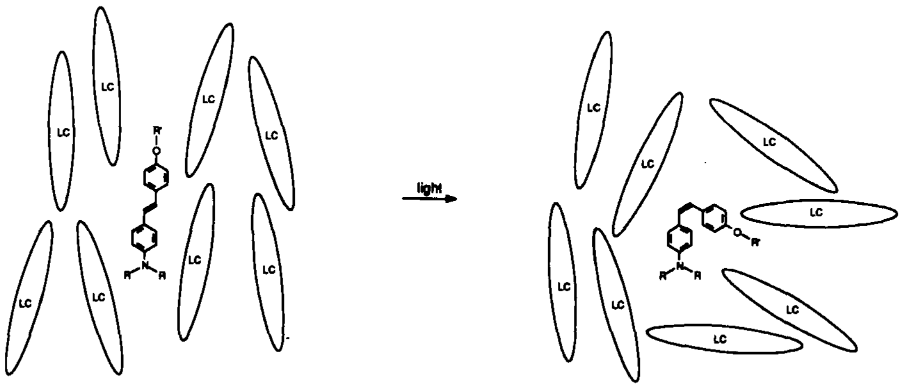
Keywords: Liquid crystal, chromophore, structure transfer, E-Z photoisomerization, rate constant, light transmittance.

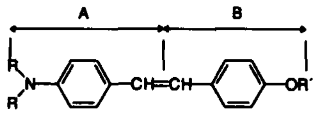
1. INTRODUCTION

The photochemical E-Z isomerization of chromophores, such as stilbene and azo compounds embedded in a liquid crystalline (LC) volume[1,2] or polymer dispersed liquid crystals (PDLC)[3], is well known. A photoinduced phase transition is observed between the nematic and the isotropic state in some azobenzene doped LC systems.[4,5] A photoinduced alignment change which is controlled by the photoisomerization of surface-attached azobenzene moities[6–8] or azobenzene Langmuir-Blodgett mono- and multilayers[9–12] is described.

The purpose of the present work is to investigate the photoinduced structure transfer from different stilbene chromophores embedded in an LC bulk onto the nematic liquid crystalline phase, depending on the specific chromophore structure and the rate constants of the E-Z photoisomerization (Fig. 1).

Therefore a homologous series of stilbene derivatives (I) with distinguished substituents was synthesized. On the one hand the stilbene derivatives had different overall molecule lengths and on the other had different distances, A and B, between the





(I)

$R = CH_3, C_2H_5, n\text{-}C_4H_9$ $R' = CH_3, n\text{-}C_4H_9, n\text{-}C_7H_{15}, n\text{-}C_{12}H_{25}$

FIGURE 1 Photoinduced structure transfer from stilbene chromophores onto an LC.

photochemically active carbon double bond and the endposition of the R or R' groups, respectively. The position of the carbon double bond varied in relation to the molecule length as a result.

The influence of the specific chromophore structure on the rate of the photochemically induced E-Z isomerization was studied. In order to gather additional information about the possibility of using these chromophore-LC-guest-host systems in liquid crystalline displays (LCD), the photoaddressed displays were characterized. A photodiode was used to determinate the change of light transmittance depending on the structure transfer from the chromophore onto the LC.

2. EXPERIMENTAL

4-N,N-dialkylamino-4'-alkoxystilbenes (I) with different structures were synthesized as chromophores.

The synthesis of the stilbenes started from 4-hydroxybenzylalcohol through the reaction with n-alkylbromides (Williamson-reaction). Then the 4-n-alkoxybenzylalcohols obtained were treated with thionyl chloride in the presence of pyridine to produce 4-n-alkoxybenzylchlorides. The following reaction of 4-n-alkoxybenzylchlorides with triphenylphosphine produced 4-n-alkoxybenzyltriphenylphosphonium chloride. The latter reacted in toluene under dry argon with butyllithium, the resulting

4-n-alkoxyphenylmethylenetriphenylphosphoranes reacted with N,N-dialkylaminobenzaldehydes (Wittig-reaction) to the corresponding stilbenes. After addition of the N,N-dialkylaminobenzaldehydes, the following procedures were carried out under dark-room illumination to prevent E-Z photoisomerization of the stilbenes thus built. The stilbenes were isolated and recrystallized four times in n-hexan. They 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 toluene in the range of 353 and 360 nm (Table I). The UV-visible spectra of the synthesized stilbenes indicated that the predominant majority of the stilbene molecules were E-isomers.

A mixture of several 4-alkylcyclohexyl-4'-cyanocyclohexanes with positive Δn and $\Delta\varepsilon$ values was used as liquid crystal ZLI 1695 (Merck). The prepared chromophore/LC guest-host systems contained 0.079 mole stilbene. The LC-stilbene mixtures were filled into commercially available testing cells (E.H.C. Co., Japan) with a cell gap of 5 μm. The dimensions of these cells were 12 × 25 mm.

Irradiations were carried out by using 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 were arranged on an optical bench between lamp and sample.

UV/VIS absorption spectra were recorded on a Perkin-Elmer Lambda 18 spectrophotometer.

For the determination of the rate constants of the E-Z photoisomerization, the changes in absorbance of the E-isomers were recorded depending on the irradiation time. The first order rate constants k were then calculated from the slope of the plot of logarithm of absorbance versus irradiation time according to equation (1)[13]:

$$-\ln A = k \cdot t, \tag{1}$$

with A = absorbance and t = irradiation time.

TABLE I
Melting points and maximum of absorbance in toluene of 4-N,N-dialkylamino-4'-alkoxystilbenes

Sample	Stilbene R	Stilbene R'	Melting point of the E-isomers (°C)	Maximum of absorbance in toluene (nm)
1	CH_3	CH_3	182–184	353
2	C_2H_5	CH_3	121–122	359
3	n-C_4H_9	CH_3	91–94	360
4	CH_3	n-C_4H_9	156–157	353
5	C_2H_5	n-C_4H_9	113–115	359
6	n-C_4H_9	n-C_4H_9	52–53	360
7	CH_3	n-C_7H_{15}	134–135	353
8	C_2H_5	n-C_7H_{15}	72–73	359
9	n-C_4H_9	n-C_7H_{15}	48–49	360
10	CH_3	n-$C_{12}H_{25}$	127–128	353
11	C_2H_5	n-$C_{12}H_{25}$	81–82	359
12	n-C_4H_9	n-$C_{12}H_{25}$	58–60	360

To investigate the photoinduced structure transfer from the stilbenes onto the LC phase, the cells were irradiated with polychromatic light of the wavelength range 300–500 nm, selected by a band pass filter. In all experiments the irradiated sample area was constant with a 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 using a Si-photodiode, type SEL 100 from International Light Incorporated, connected with an IL 1400A radiometer. The transmitted light intensity was measured in μW. The corrected light intensities at 450 nm were obtained by multiplying the measured μW with the factor 2.1105. This factor was determined from a calibration curve where the relative sensitivity of the photodiode is plotted versus the wavelength of light.

3. RESULTS AND DISCUSSION

The 4-N,N-dialkylamino-4′-alkoxystilbenes represent the photoreactive compounds in the guest-host mixture. On irradiation, the stilbenes undergo E-Z photoisomerization to produce the Z-isomer. This transformation takes place until a photostationary state is reached. Irreversible photochemical side reactions, such as the cyclization of Z-stilbene[14] or the [2 + 2] photocycloaddition,[15] are of minor importance and may be neglected in these investigations.

Irradiation of the stilbene with light of the wavelength 350 nm causes a decrease in the absorbance of E-isomers and an increase in the absorbance of Z-isomers. The decrease in absorbance of the E-isomers after irradiation is characterized by a first order reaction as expected for intramolecular conversions such as E-Z isomerization. In Table II the obtained first order rate constants *k* are listed together with the

TABLE II

First order rate constants of the E-Z photoisomerization of stilbenes 1–12 in LC ZLI 1695 and in toluene in relation to the calculated molecular lengths of the E-isomers and the B/A ratio, respectively

	Stilbene		Molecular length of the E-isomer in Å	Ratio of the length B/A (Fig. 1)	Rate constants[1] in LC ZLI $1695^2 \cdot 10^4$ s	Rate constants[3] in toluene$^4 \cdot 10^3$ s
Sample	R	R′				
1	CH_3	CH_3	15.8	1.04	4.09	10.15
2	C_2H_5	CH_3	16.6	0.93	1.73	8.68
3	n-C_4H_9	CH_3	18.6	0.77	1.33	7.06
4	CH_3	n-C_4H_9	19.2	1.50	2.96	10.16
5	C_2H_5	n-C_4H_9	20.1	1.35	1.46	8.12
6	n-C_4H_9	n-C_4H_9	22.0	1.11	1.04	7.20
7	CH_3	n-C_7H_{15}	23.2	1.97	2.65	8.40
8	C_2H_5	n-C_7H_{15}	24.0	1.76	1.45	7.64
9	n-C_4H_9	n-C_7H_{15}	25.9	1.46	1.04	7.12
10	CH_3	n-$C_{12}H_{25}$	29.2	2.74	–	9.24
11	C_2H_5	n-$C_{12}H_{25}$	29.9	2.46	1.34	8.25
12	n-C_4H_9	n-$C_{12}H_{25}$	31.8	2.03	0.95	7.21

[1] 1 measurement, [2] 0.079 molar stilbene mixtures, [3] average of 2 measurements, the standard deviation is $\pm 0.2 \cdot 10^{-3}$ s^{-1}, [4] $5 \cdot 10^{-4}$ molar stilbene solutions.

molecular lengths and the ratios B/A of the stilbene chromophores according to Figure 1.

The specific structure of the chromophore has a significant influence on the rate constants of the E-Z photoisomerization. However, there is no correlation between the rate constants of the E-Z isomerization and the molecular lengths of the stilbenes (Table II). Although the shortest stilbene 1 has the greatest rate constant $k = 4.09 \cdot 10^{-4} s^{-1}$ in ZLI 1695 and the longest stilbene 12 has the smallest rate constant $k = 0.95 \cdot 10^{-4} s^{-1}$, the stilbene 7 has a considerably greater rate constant than the shorter stilbenes 2,3,5 and 6. Also stilbene 4 has a greater rate constant than the shorter stilbenes 2 and 3. Furthermore, the stilbenes 6 and 9 have the same rate constant but differ in molecular length.

Therefore a correlation was sought between the specific position of the photochemically active carbon double bond in the molecule in relation to the molecule overall length and the rate constants of the E-Z photoisomerization. A correlation between the length ratio B/A and the rate constants k could not be observed. Therefore the rate constants for stilbenes 4 with $2.96 \cdot 10^{-4} s^{-1}$ and 9 with $1.04 \cdot 10^{-4} s^{-1}$ differ from each other but have nearly the same B/A ratio of 1.50 and 1.46, respectively. The rate constants for the stilbenes 1 and 2 differ in the same way by the factor 2.36 although they have similar B/A ratios of 1.04 and 0.93, respectively. Otherwise similar rate constants, $1.33 \cdot 10^{-4} s^{-1}$ and $1.34 \cdot 10^{-4} s^{1}$, were found for the smallest (sample 3) and greatest (sample 11) B/A ratio of 0.77 or 2.46.

However, the number of the carbon atoms in both hydrocarbon chains (R in Figure 1 and Table II) of the 4-N,N-dialkylamino group has a specific influence on the rate constants. They decrease with an increasing number of carbon atoms in the 4-N,N-dialkylamino group of the stilbene chromophore. For instance, in the case of 4-N,N-dialkylamino-4′-methoxystilbenes (samples 1–3) the rate constants decrease from $4.09 \cdot 10^{-4} s^{-1}$ to $1.73 \cdot 10^{-4} s^{-1}$ or $1.33 \cdot 10^{-4}$ s^{-1}, if both methyl groups were substituted by ethyl or n-butyl groups. The same decrease in rate constants was observed for all 4-N,N-dialkylamino-4′-n-butoxystilbenes (samples 4–6), 4-N,N-diakylamino-4′-n-heptoxystilbenes (samples 7–9) and 4-N,N-dialkylamino-4′-n-dodecyloxystilbenes (samples 10–12) if both methyl groups in the 4-N,N-dialkylamino group were substituted by ethyl or n-butyl groups respectively. In general, the differences of the rate constants (Table II) between comparable 4-N,N-dimethylamino-4′-alkoxy-stilbenes and 4-N;N-diethylamino-4′-alkoxystilbenes are higher than the differences between analogous 4-N,N-diethylamino-4′-alkoxystilbenes and 4-N,N-di-n-butylamino-4′-alkoxystilbenes.

In contrast to this the influence of the chain length of the 4′-alkoxy group at a constant 4-N,N-dialkylamino group on the rate of isomerization is relatively low. Therefore the differences in rate constants for all 4-N,N-diethylamino-4′-alkoxystilbenes (samples 2,5,8 and 11) and 4-N,N-di-n-butylamino-4′-alkoxystilbenes (samples 3,6,9 and 12) are very small and unspecific. Only for the case $R=CH_3$ the rate constants decrease from $4.09 \cdot 10^{-4} s^{-1}$ to $2.96 \cdot 10^{-4} s^{-1}$ or $2.65 \cdot 10^{-4} s^{-1}$ if the methyl group in the 4′-alkoxy group is substituted by n-butyl or n-heptyl group.

An explanation of the different influence of the 4-N,N-dialkylamino or 4′-alkoxy group on the rate constants of E-Z photoisomerization seems to be possible with the help of the following view. The effects of the 4-N,N-dialkylamino group and 4′-alkoxy group are consciously separated, knowing that the rate constants of the E-Z photoisomerization are influenced by the simultaneous action of both sides of the stilbene molecule. In the case of the 4'-alkoxy group, only one phenylalkoxy group moves against the resistance of the surrounding LC medium during the E-Z isomerization. This means that only one alkoxy chain has to displace the liquid crystalline molecules. With increasing length of the alkoxy chain more LC molecules must be displaced. Therefore the rate constants of isomerization decreases slightly in ZLI 1695 with an increasing length of the alkoxy chain.

Considering the other part of the stilbene molecules, one has to take into account that in the 4-N,N-dialkylamino group two alkyl chains, which are positioned by each other like an open pair of scissors, influence the movement of the 4-N,N-dialkylaminophenyl group during E-Z isomerization. The resistance against the movement is considerably greater in comparison with the alkoxy group because the two alkyl groups act like an open pair of scissors.

The same tendency of influencing the rate constants of the photoinduced E-Z isomerization by the chromophore structure is found in isotropic solutions of toluene (Table II). In comparison with the case of an LC medium, the rate constants in isotropic toluene are about 25 to 75 times greater than in the anisotropic mesophase. The influence of the medium viscosity on the rate constants was expected and is in agreement with the literature.[16]

The photochemically induced E-Z isomerization of the stilbene chromophores in the LC phase is connected with a reorientation of the liquid crystalline molecules (see Fig. 1 for illustration). Ichimura *et al.*[7] assume that the photoisomerization of one surface-attached azobenzene unit brings about the reversible reorientation of about 10^4 LC molecules.

In Figure 2, the photoinduced changes in light transmittance of the liquid crystalline matrix are illustrated depending on the irradiation time for guest-host mixtures of the stilbene chromophores 1, 8 and 12. The light transmittance, expressed in μW, increases as a consequence of the photoinduced reorientation of the liquid crystal.

The stilbenes have a different influence on the light transmittance. The shortest stilbene 1 causes a faster increase in light transmittance during the first 6 min of irradiation than the longest stilbene 12. Nevertheless for all 3 systems the photoinduced structure transfer is completed after 30–40 min. Furthermore, the increase in light transmittance correlates with the length of the stilbene chromophores in the case of the stilbenes 1, 8 and 12. Therefore, the difference in light transmittance increases with the increasing length of the stilbenes. However, in general the values for Δ μW are not linearly connected with the molecular lengths. Figure 3 shows the Δ μW values depending on the stilbene chromophore molecular length. As shown, there is no linear correlation between the Δ μW values and the molecular lengths of the stilbenes. But a general tendency can be identified. The differences in light transmittance after irradiation increase fundamentally with increasing molecular length in comparison with the value before irradiation. The smallest Δ μW value ($\Delta = 4.45$ μW) was obtained for the shortest stilbene 1 and the highest ΔμW value ($\Delta = 7.05$ μW) for the longest stilbene 12. But the stilbene 2 with a molecular length 16.6 Å has a greater difference in light transmittance ($\Delta = 4.98$ μW) in comparison with the somewhat longer stilbenes 3 and 4 ($\Delta = 4.75$ μW or $\Delta = 4.85$ μW). Similarly, the Δ μW value for stilbene 5 is greater

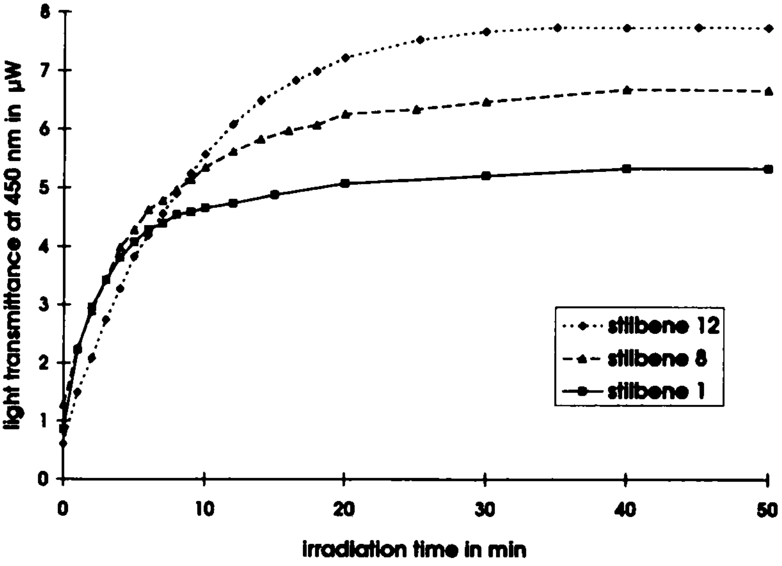


FIGURE 2 Photoinduced changes of light transmittance after irradiation of stilbene-LC mixtures depending on irradiation time.

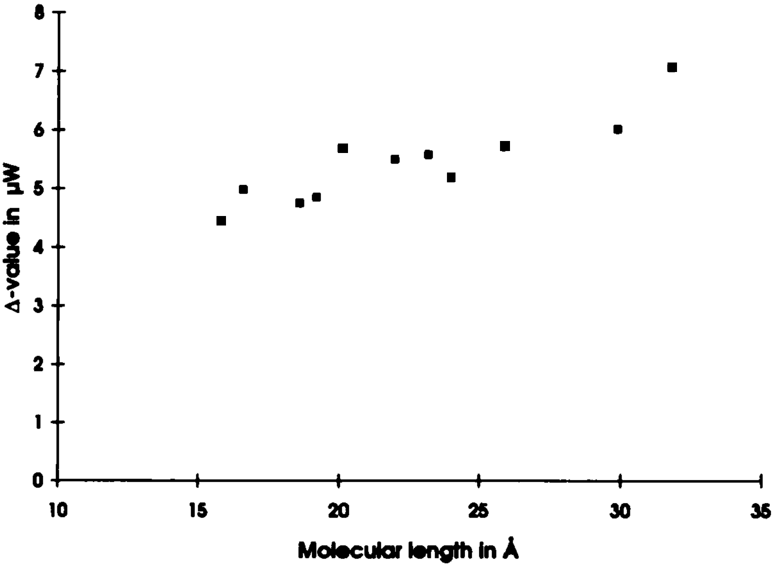


FIGURE 3 Differences in light transmittance before and after irradiation depending on the molecular length of the stilbenes.

than the Δ µW values for the stilbenes 6, 7 and 8. No correlation was registered between the Δ µW values of the display and the observed rate constants of the E-Z isomerization.

A corresponding effect, that is to say the influence of the specific chromophore structure on light transmittance, was observed for photoinduced alignment change which is controlled by the photoisomerization of surface-attached azobenzene units.[7]

Some other interesting questions remain unanswered and will be investigated by us in future, among them the multi-switching behaviour of photoaddressed LCD and the application of chromophores with two or more photoactive centers.

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