The intrinsic photoferroelectric effect in the smectic C* phase of a chiral azobenzene[†]

Alexander Saipa,^{*a*} Mikhail A. Osipov,^{*b*} Kenneth W. Lanham,^{*c*} Catherine H. Chang,^{*c*} David M. Walba^{*c*} and Frank Giesselmann^{**a*}

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The ferroelectric properties in the liquid-crystalline smectic C* phase of the chiral mesogenic azobenzene (S)-4-(4-decyloxy-phenylazo)benzoic acid 4-(1-methylhexyloxy)-3-nitro-phenyl ester ('W470') were studied and found to be strongly dependent on the intensity of incident light. The light-induced *trans* to *cis* isomerization of the azobenzene chromophore which is an intrinsic constituent of this SmC* mesogen leads to a pronounced photoferroelectric effect since the ferroelectric SmC* ordering is considerably disturbed by the presence of bent-shaped *cis*-isomer molecules: At increasing light intensity a strong decrease of both SmC* order parameters, spontaneous electric polarization P_s and director tilt angle θ , is observed. It is further seen that even the nature of the ferroelectric transition is affected by the photoisomerization which leads to a crossover from the nearly tricritrical transition observed in the absence of light to a typical second-order transition. This result is interpreted theoretically taking into account a coupling between the director tilt and the biaxial order parameter which is strongly affected by the light-induced generation of the bent-shaped *cis*-isomers. The dynamics of the intrinsic photoferroelectric effect in W470 was studied by time-resolved measurements of spontaneous polarisation and director tilt.

Introduction

Ferroelectric materials which, as a result of interaction with light, change their ferroelectric properties such as spontaneous electric polarization $P_{\rm s}$ or coercive field are denoted as "photoferroelectrics".¹ In liquid crystals photoferroelectric behaviour can be induced by dissolving small amounts of photochemically isomerizable dopants in ferroelectric liquid crystalline host phases like the chiral smectic C* (SmC*) phase.²

In the SmC* phase of elongated molecules the average direction of the long molecular axis *n* is inclined at a certain director tilt angle θ with respect to the smectic layer normal *k*. The full rotational symmetry about *k* is broken by the director tilt leading in the case of chiral molecules to the polar C_2 point group symmetry.^{3–5} As a result the spontaneous electric polarization P_s is observed along the two-fold symmetry axis, perpendicular to θ and *k*:

$$\boldsymbol{P}_{\rm s} \sim \boldsymbol{k} \times \boldsymbol{n} \tag{1}$$

In the most common ferroelectric liquid crystals the SmC* phase undergoes a second-order transition to the non-tilted

^aUniversity of Stuttgart, Institute of Physical Chemistry, D-70569 Stuttgart, Germany. E-mail: f.giesselmann@ipc.uni-stuttgart.de; Fax: +49 711 685-2563; Tel: +49 711 685-4460 ^bUniversity of Strathclyde in Glasgow, Department of Mathematics, Livingstone Tower, 26 Richmond Street, Glasgow, UK G1 1XH ^cUniversity of Colorado at Boulder, Department of Chemistry and Biochemistry, Campus Box 215, Boulder, Colorado, 80309-0215, USA ^f Electronic supplementary information (ESI) available: full synthesis details. See DOI: 10.1039/b602060g SmA* phase at higher temperatures. As temperature T increases θ and P_s continuously decrease until the non-tilted SmA* phase is reached at the SmA*–SmC* phase transition temperature T_c^* . The connection between director tilt θ and electric polarization P can be obtained from the standard Landau expansion of the free energy density ΔF around T_c^* .^{5,6} In the absence of an external electric field (E = 0) the spontaneous polarization P_s can be expressed as:

$$P_{\rm s} = \varepsilon_0 \chi C \theta \tag{2}$$

where P_s increases linearly with the director tilt θ and basically becomes temperature dependent as a result of the temperature dependence of θ .

It has been experimentally verified that homogeneous mixtures of photoisomerizable dyes with these ferroelectric SmC* phases are photoresponsive ferroelectric materials where macroscopic properties like P_s , θ , or T_c^* can be modulated by irradiation with light of the appropriate wavelength and intensity.^{7–15} In certain cases the ferroelectric SmC* phase can be completely suppressed by light-induced phase transitions into the SmA* phase or even the isotropic phase. Reisomerization of the photosensitive dopant molecules restores the initial properties of the original state before irradiation ('dark state'). This opens the possibility to control the properties and even the phase behaviour of ferroelectric liquid crystal materials by light irradiation.

The mechanism of the induced photoferroelectric effect in these guest/host systems has recently been investigated in our group.^{14,15} A basic result of these investigations is the distinction between the primary and secondary photoferroelectric

effects.¹⁵ The primary effect originates from light-induced changes of the ferroelectric ordering. The secondary effect is a pure thermodynamic consequence of the shift in T_c^* which results from the photoinduced variation in the isomer composition of the photoferroelectric phase. We further reported that the light-induced changes in the spontaneous polarization and the molecular isomerization process both follow simultaneous mono-exponential rate laws with the same rate constants and activation energies. According to eqn (2), changes in P_s could be a result of light-induced variations in θ , in C, or both. However, it was found that the primary photoferroelectric effect actually observed in our guest/host systems mainly results from a light-induced variation of the bilinear coupling coefficient C which is related to the bias of molecular rotations in the SmC* phase.¹⁴ At least for low concentrations of the photoisomerizable dopant no indications of a significant photoinduced change of the director tilt were found. One of the primary goals of the present work has been the study of a different class of photoisomerizable smectic materials where the director tilt can be significantly modified by the irradiation.

In this paper we now report our studies on the photoferroelectric effect in the SmC* phase of a chiral azobenzene mesogen. As such mesogens contain a photoisomerizable azobenzene linkage as an inherent part of their mesogenic core it is not necessary to further induce photoferroelectric behaviour through the addition of photoisomerizable dyes. Instead, photoferroelectricity is expected and proven to be an intrinsic property of SmC* phases constituted by photoisomerizable mesogens.

In clear contrast to the induced photoferroelectric effect in guest/host systems we show that the intrinsic photoferroelectric effect in this chiral azobenzene mesogens is mainly connected with substantial changes of the director tilt. Moreover, this may lead to irreversible re-orientations of the smectic layer configuration (*i.e.*, from the initial 'bookshelf' to the 'chevron' configuration).

We also show that the photoisomerization may even affect the nature of the SmA* to SmC* transition in such materials transforming the initial tricritical behaviour—observed without irradiation—into a typical second-order transition. This transition is interpreted theoretically taking into account a coupling between the director tilt and the biaxial order parameter of the SmC phase which is very sensitive to the presence of *cis*-isomers.

Experimental

In the experiments on the intrinsic photoferroelectric effect we used the chiral azobenzene (S)-4-(4-decyloxyphenylazo)benzoic acid 4-(1-methylhexyloxy)-3-nitro-phenyl ester (abbreviated as 'W470'):¹⁶



UV absorption spectra of the *trans* and *cis* isomers dissolved in chloroform are depicted in Fig. 1. The phase sequence of W470

observed in the polarisation microscope on cooling and under red light (633 nm) to avoid the photoisomerization of the azobenzene moiety is given by:

X 57.1 °C SmC* 87.3 °C SmA* 117.1 °C isotr.

The low-temperature phase designated as 'X' is a peculiar optically isotropic fluid, the nature of which has not been conclusively clarified so far.¹⁷ The W470 material was filled by capillary action into LC test cells (E.H.C. Ltd., Tokyo, Japan) with a 2 μ m cell gap and 16 mm² indium tin oxide (ITO) electrodes. The sample was thermostatted and irradiated with various intensities of monochromatic light. All experiments in this study were carried out with light of 450 nm wavelength where the maximum photoresponse of the W470 sample was obtained. Light- and temperature-dependent values of the spontaneous polarization P_s and the director tilt angle θ were measured in an electro-optic setup which was described previously.¹⁴

Results and discussion

Photostationary state

The formation of bent-shaped *cis*-isomers is stimulated by constant illumination of the W470 sample with light of fixed intensity *I* and wavelength 450 nm. Typically after a couple of minutes the photostationary state is reached where the balance between the photoinduced *trans* \rightarrow *cis* isomerization and the thermally as well as photochemically activated *cis* \rightarrow *trans* re-isomerization leads to a stationary amount of *cis*-isomer molecules, the concentration *x* of which increases with the intensity *I* of incident light.^{13,14} To study the properties of W470 in its photostationary states the spontaneous polarization P_s and the tilt angle θ were continuously measured as a function of the temperature *T* during cooling the sample at a rather slow rate of 0.25 K min⁻¹. The choice of a sufficiently slow cooling rate ensures that the sample readjusts its photostationary state at any temperature in the range of



Fig. 1 UV-vis spectra (absorbance A vs. wavelength λ) of W470 dissolved in chloroform at 25 °C. Solid line: *trans*-isomer before irradiation; dashed line: *cis*-isomer as obtained after 40 min irradiation with light of 366 nm wavelength.



Fig. 2 Temperature-dependent values of (a) spontaneous polarization $P_s(T)$ and (b) tilt angle $\theta(T)$ measured in the photostationary state at different intensities of incident light ($\lambda = 450$ nm).

measurement. These temperature scans of $P_s(T)$ and $\theta(T)$ were repeated at different light intensities *I*.

The results of these measurements are depicted in Fig. 2. The $P_s(T)$ curves in Fig. 2(a) show that W470 has its highest polarization in the absence of light ($I = 0 \text{ W cm}^{-2}$) where P_s reaches 240 nC cm⁻² at 65 °C. This remarkably high value of spontaneous polarization is substantially reduced under the illumination with light ['negative photoferroelectric effect', $(\partial P_s/\partial I) < 0$]. Even far below the ferroelectric transition at 65 °C a moderate light intensity of 0.84 mW cm⁻² stimulates a 55% drop in polarization from 240 nC $\rm cm^{-2}$ down to 110 nC cm⁻². Close to the SmA*–SmC* phase transition the secondary photoferroelectric effect is noticed from the lightinduced lowering of the transition temperature $T_c^*(I)$. Far below the ferroelectric transition the primary photoferroelectric effect is reflected by the flattening of the $P_s(T)$ curve at increasing I. The corresponding $\theta(T)$ curves depicted in Fig. 2(b) are quite similar to the behaviour of $P_s(T)$ and give clear evidence that also the director tilt is substantially reduced by the illumination with light and the subsequent formation of cis-isomers. These light-induced variations of the director tilt angle deserve a closer analysis since they are in clear contrast to the induced photoferroelectric effect in LC-dopant mixtures where only negligible changes of the tilt had been observed.14

Light-induced variations of the director tilt angle

Deeper insight into the consequences of the light-induced reduction of the director tilt is obtained by a detailed analysis of the tilt and polarization data in terms of Landau theory, based on the following expansion of the free energy of the SmC* phase in terms of tilt angle θ and polarization *P*.^{5,6}

$$\Delta F = \frac{1}{2} \alpha \left(T - T_{\rm c}^* \right) \theta^2 + \frac{1}{4} b \theta^4 + \frac{1}{6} c \theta^6$$

$$- CP\theta + \frac{1}{2\varepsilon_0 \chi} P^2 - PE$$
(3)

The first three terms in eqn (3) represent the free energy of the non-chiral SmC phase with Landau coefficients α , *b*, and *c*. The polarization-tilt coupling is reflected by the $-CP\theta$ term, introducing the bilinear coupling coefficient *C*, which measures the orientational ordering of transverse molecular dipoles in the chiral SmC* phase. The $P^2/(2\epsilon_0\chi)$ term introducing the generalised susceptibility χ and the vacuum permittivity ϵ_0 is related to the decrease in entropy due to the polar ordering. The last term in eqn (3) describes the coupling to a non-zero electric field *E*.

Minimisation of the free energy in eqn (3) with respect to θ leads to the following equation:

$$T = T_{\rm c}^* + \frac{1}{\alpha} \left[\frac{\varepsilon_0 \chi CE}{\theta} - b\theta^2 - c\theta^4 \right] \tag{4}$$

which relates the temperature *T* and the equilibrium tilt angle θ at that temperature.^{18,19} According to eqn (2) the product $\varepsilon_0 \chi C$ was calculated from the ratio of the experimental P_s and θ data. The plot of the ratios P_s/θ vs. temperature *T* in Fig. 3 shows a negligible temperature dependence so that for each data set an average value of $\varepsilon_0 \chi C$ is taken into account. The decrease of $\varepsilon_0 \chi C$ at increasing light intensity mainly reflects the light-induced reduction of *C* due to the primary photoferroelectric effect.¹⁴

With given values of $\varepsilon_0 \chi C$, T_c^* , and $E = 2 \text{ V } \mu \text{m}^{-1}$ (the field amplitude applied to measure θ and P_s) eqn (4) is fitted to the experimental $\theta(T)$ data with the Landau coefficients α , b, and cremaining the parameters to fit. The fit parameters α , b, and cobtained for different intensities of incident light are listed in Table 1 together with the respective values of T_c^* and $\varepsilon_0 \chi C$.

5.0 4 5 $(P_s/~ heta)~/~10^{-3}~{
m C~m^{-2}}$ 4.0 3.5 3.0 0.00 mW cm 2.5 0.42 mW cm 0.84 mW cm 2.066 68 70 72 74 76 64 $T / ^{\circ}C$

Fig. 3 The ratio P_s/θ (= $\varepsilon_0 \chi C$) vs. temperature T of the non-irradiated (0.00 mW cm⁻²) and two irradiated (0.42 and 0.84 mW cm⁻²) samples. In the range of interest the temperature dependence of P_s/θ can be neglected in a first approximation.

Table 1 Summary of Landau parameters. Expansion coefficients α , b, and c and phase transition temperature T_c^* result from the fitting of eqn (4) to the experimental tilt data in Fig. 2. Values of $\varepsilon_0 \chi C$ are directly taken from the experiments in Fig. 3

$I/mW \text{ cm}^{-2}$	0.00	0.42	0.84
$\alpha/10^3 \text{ J m}^{-3} \text{ K}^{-1}$	56	22	9
$b/10^3 \text{ J m}^{-3}$	~ 0	64	400
$c/10^3 \text{ J m}^{-3}$	13	7	2
$T_{\rm c}*/^{\circ}{\rm C}$	87.4	83.5	80.5
$\epsilon_0 \chi C / 10^{-3} \text{ Cm}^{-2}$	4.3	4.0	2.9



Fig. 4 $T(\theta)$ curves of the non-irradiated sample and two irradiated samples. Solid curves are the fit results according to eqn (4) with parameters listed in Table 1.

The comparison in Fig. 4 proves the good agreement between the fit results (solid lines) and the experimental data points in the vicinity of the smectic A^*-C^* transition point.

As seen in Table 1, all Landau coefficients are significantly changed in the irradiated states. Both coefficients α and cdecrease by a factor of 6 within the experimental range of the light intensity *I*. It should be noted that this decrease only leads to some quantitative changes of the order parameters in the transition. However, most remarkable is the dramatic change of the coefficient *b*, the sign of which controls the order of the SmA–SmC transition.^{19,20} In the dark state $b \approx 0$ and thus the system is close to the tricritical point. In contrast, in the irradiated state the coefficient *b* is positive and large, and thus a pronounced second-order transition takes place. This lightinduced crossover indicates that the nature of the ferroelectric transition is indeed changed by the light-induced formation of the *cis* isomers. We will discuss this most noteworthy observation from the theoretical point of view in the following section.

Light-induced variation of biaxial order

In this section we show that the light-induced change in the order of the transition can be described theoretically in a qualitative way taking into account that the irradiation with light induces a transformation of *trans* into *cis* isomers. Thus in a photostationary state there exists some (molar) fraction x of *cis* isomers which act as a nonmesogenic dopant. *cis* Isomers are bent-shaped molecules with a weakly pronounced 'long axis', and thus one cannot expect a large degree of nematic orientational ordering of such molecules in the SmC* phase. On the other hand, *cis* isomers are strongly biaxial and

therefore their influence on the SmA*–SmC* phase transition may be related to the biaxial ordering in the SmC* phase. As discussed in ref. 21 typically low values of the Landau coefficient *b* in various smectic C materials¹⁹ can be explained taking into consideration a coupling between tilt and biaxial order of short molecular axes. In the phenomenological theory of ferroelectric smectic C* liquid crystals tilt is described by the pseudovector:⁶

$$w = [n \times k](n \cdot k) \tag{5}$$

where *n* is the director and *k* is the smectic layer normal. The absolute value of the order parameter *w* describes the magnitude of the tilt, *i.e.* $w = (1/2) \sin 2\theta$. At small tilt angles $\theta^2 \ll 1, w \approx \theta$. The direction of *w* corresponds to that of the C_2 axis of the SmC* phase, *i.e.* it is perpendicular to the tilt plane. According to eqn (2) the spontaneous polarisation in the SmC* phase is proportional to *w*, *i.e.* $P_s = \varepsilon_0 \chi C w$ where the coefficient *C* may be positive or negative depending on the molecular structure.

It is well known that the SmC phase is biaxial, and therefore the molecular orientational ordering cannot be completely specified by the nematic tensor order parameter $Q_{\alpha\beta} = S(n_{\alpha}n_{\beta} - \delta_{\alpha\beta}/3)$. In particular, the molecular short axes should be partially ordered in the direction perpendicular (or parallel) to the tilt plane even in a nonchiral SmC phase without any polarisation (see Fig. 5). This biaxial ordering is nonpolar and can be described by the tensor order parameter $B_{\alpha\beta}$ which can be written as:²¹

$$B_{\alpha\beta} = \langle b_{\alpha}b_{\beta} - c_{\alpha}c_{\beta} \rangle = C(n_{\alpha}n_{\beta} - \delta_{\alpha\beta}/3) + B(\hat{w}_{\alpha}\hat{w}_{\beta} - m_{\alpha}m_{\beta})$$
(6)

where the unit vectors **b** and **c**, (**b** · **c**), are in the direction of short molecular axes, the unit vector \hat{w} is parallel to **P** and the unit vector **m** is perpendicular to both **w** and **n** (see Fig. 5). Here **B** is the scalar biaxial order parameter and the order parameter *C* describes the tendency of short molecular axes to order along the director. One notes that in the limit of perfect nematic order $S \rightarrow 1$ and $C \rightarrow 0$. In this limit the biaxial order parameter $B = \langle \cos \varphi \rangle$ where the angle φ specifies the orientation of the short molecular axis about the long axis **a**.

Now the part of the total free energy of the SmC* phase which does not depend on polarisation can be expanded in



Fig. 5 Ordering of the molecular axes a, b, and c of a biaxial molecule with respect to the reference frame n, w, and m where n denotes the director, w is along the direction of spontaneous polarization P and m is orthogonal to both n and w; k is the normal to the smectic layers.

powers of the primary vector order parameter w and the secondary tensor order parameter $B_{\alpha\beta}$:

$$\Delta F(\mathbf{w}, \mathbf{B}) = \frac{1}{2} \alpha (T - T_{c}^{*}) w^{2} + \frac{1}{4} \beta w^{4} + \frac{1}{6} c w^{6} + \frac{1}{2} A B^{2} + G(w_{\alpha} B_{\alpha\beta} w_{\beta}) + \dots,$$
(7)

where the coefficient G describes a coupling between tilt and the biaxial ordering. Substituting eqn (5) and (6) into eqn (7) one obtains for small tilt angles θ :

$$\Delta F(\theta, B) \approx \frac{1}{2} \alpha \left(T - T_c^* \right) \theta^2 + \frac{1}{4} \beta \theta^4 + \frac{1}{6} c \theta^6 + \frac{1}{2} A B^2 + G B \theta^2$$
(8)

Minimising the free energy (8) with respect to B and substituting back into eqn (8) one obtains the full expansion of the free energy in powers of the tilt angle θ :

$$\Delta F(\theta) \approx \frac{1}{2} \alpha \left(T - T_{\rm c}^* \right) \theta^2 + \frac{1}{4} b \theta^4 + \frac{1}{6} c \theta^6 \tag{9}$$

where:

$$b = \beta - \frac{2G^2}{A} \tag{10}$$

Thus the Landau coefficient b is renormalised due to a coupling between tilt and biaxiality order parameters. In the context of this model the nearly tricritical natue of the SmA–SmC transition, observed in many materials,^{19,20} is related to large values of the coupling coefficient G which may lead to abnormally small values of b according to eqn (10).

In the smectic C* material investigated in this paper the coefficient *b* approximately vanishes in the dark state, *i.e.* in the system of predominantly *trans* isomers b = 0. Irradiation with light creates a certain fraction of strongly biaxial bent-shaped *cis* isomers which grows with the increasing light intensity. In the mixture of *trans* and *cis* isomers the coupling between the average tilt and the biaxial order parameters *B* and *B*₁ of the two isomers can approximately written as:

$$(1 - x)GB\theta^2 + xG_1B_1\theta^2$$

where x is the molar fraction of cis isomers and B_1 is the corresponding biaxial order parameter. The coefficient G describes the coupling between tilt and the biaxial order parameter in the system of pure *trans* isomers while the coefficient G_1 describes the corresponding contribution of cis isomers. One notes, however, that cis isomers do not possess a well defined long axis, and therefore the orientational order parameter of such molecules must be low. Thus the cis isomers may only make a small contribution to the stabilization of the average tilt in the SmC phase. The contribution of these isomers to the coupling between tilt and the biaxial order parameter is also expected to be small and thus $G_1 \ll G$. For simplicity we assume that $G_1 = 0$ and thus the coupling between average tilt and average biaxial ordering can approximately be expressed as $G(1 - x)B\theta^2$. The coefficient A in eqn (8) should also depend on the fraction of cis isomers because these molecules are strongly biaxial, and their molecular planes

should be partially ordered in the biaxial SmC phase thus contributing to the average biaxial order. If the fraction of *cis* isomers x is small, the parameter A can be expanded in powers of x keeping the linear term: $A \approx A_0 + xA_1$, where we assume that $A_1 > 0$. Now the effective Landau coefficient b can be expressed as:

$$b \approx \beta - \frac{2(1-x)^2 G^2}{A_0 + x A_1} \tag{11}$$

In the dark state x = 0 and, according to our experimental data, the coefficient *b* vanishes. This means that the coefficient β in eqn (11) can be expressed in terms of *G* and A_0 , *i.e.* $\beta \approx 2G^2/A_0$ and:

$$b(x) \approx \beta \left(1 - \frac{(1-x)^2}{1+\kappa x} \right) \tag{12}$$

where $\kappa = A_1/A_0$ is on the order of 1.

One can readily see from eqn (12) and from Fig. 6 that the Landau coefficient b(x) vanishes at x = 0 and becomes positive for all values of the molar fraction x of *cis*-isomers which are created by the irradiation of light. The coefficient b(x) is also an increasing function of x, at least for small x. These qualitative results enable one to explain why the irradiation with light results in a positive value of the coefficient b (in this particular material) which grows with the increasing light intensity. One also notes that the rapid growth of the coefficient b, which follows from the experiment, is determined by the fact that b is given by a difference between two large terms in eqn (11). In the pure smectic C* without light irradiated sample the balance between the two terms is shifted producing a large effect even at small values of x.

However, it is seen from Table 1 that absolute values of b remain relatively small compared, for example, to the coefficient c. It is also seen in Fig. 6 that if we assume β to be of the same order as $c \ (\approx 104 \text{ kJ m}^{-3})$ the maximum experimental value of $b \approx 400 \text{ kJ m}^{-3}$ is achieved at $x \approx 0.014$



Fig. 6 Increase of the fourth-order Landau coefficient *b* with the molar fraction *x* of bent-shaped *cis*-isomers formed during the irradiation with light. The curve has been calculated according to eqn (12) with $\beta \approx 104$ kJ m⁻³ and $\kappa \approx 1$.

which seems to be a small enough value to maintain the stability conditions of the SmC* phase. Finally, it should be noted that all Landau coefficients may depend on the molar fraction x due to a dilution effect determined by the presence of nonmesogenic molecules. This additional dependence, which has not been taken into account in the present simple model, is expected, however, to be qualitatively the same for all coefficients, and thus it cannot explain the specific behaviour of the coefficient b which determines the order of the transition.

Light-induced bookshelf to chevron transitions

Another interesting consequence of the photoisomerization process seems to be the induction of irreversible changes in the smectic layer arrangement. An example of these light-induced smectic layer re-orientations is depicted in Fig. 7. In the initial dark state the W470 sample was aligned to be in the so-called 'bookshelf' configuration where the smectic layers are all more or less perpendicular to the glass substrates of the LC cell.⁴ The sample is continuously switched by a low-amplitude electric field of 2 V um⁻¹ to measure its polarization. Hence, no SmC* ferroelectric domains are seen in this picture. After the irradiation with light (450 nm, 0.42 mWcm⁻²) and the subsequent formation of the cis-isomers the initial bookshelf configuration transformed into the so-called 'chevron' configuration which is recognised by the characteristic 'zig-zag' defect lines in the texture micrograph.^{5,22} The chevron configuration is signified by smectic layers tilted in opposite directions. Domains of opposite layer tilt directions are separated by zig-zag defects. The chevron configuration is preserved even after the irradiation has been stopped and the polarization relaxed to its initial value. The bookshelf configuration is recovered only after a high *E*-field treatment, where the tilted layers are straightened up by the application of a strong electric field with an amplitude of about 20 V μ m⁻¹.

The reason for this light-induced bookshelf to chevron transition is not clear to us at all. Since the common explanation for the tilting of smectic layers into the chevron configuration is given by the shrinkage of the smectic layer spacing at increasing tilt of the molecules the origin might be related to light-induced variations of the layer spacing due to the formation of the *cis*-isomers.

Time-resolved measurements

After the irradiation is stopped, the *cis*-isomers that have been formed in the photostationary state thermally re-isomerize to the rod-shaped *trans*-state and, simultaneously, the initial dark state properties (except the layer configuration, see above) of the SmC* phase are restored. The thermal *cis* \rightarrow *trans* isomerizations of azobenzenes in diluted isotropic solutions^{23,24} as well as in liquid-crystalline guest/host systems^{13,14} are known to follow simple mono-exponential rate laws, the rate constants *k* of which are described by the Arrhenius law with activation energies typically on the order of $E_A \approx 10^2$ kJ mol⁻¹.

We studied the thermal relaxation of the W470 sample after irradiation by time-resolved measurements of P_s and θ at several temperatures ranging from 85 °C, close to the SmA*– SmC* phase transition, down to 65 °C, 20 K below the transition. The results for five selected temperatures are shown in Fig. 8 where the solid lines represent the best fits



Fig. 7 Texture micrographs in the SmC* phase of the W470 sample at 65 °C showing a light-induced bookshelf to chevron transition of the smectic layers. All pictures are taken with light of 589 nm wavelength to avoid photoisomerization during the microscopic observation. For further explanations see text.



Fig. 8 Relaxation of (a) the spontaneous polarization P_s and (b) director tilt θ after ending the irradiation with light at 65, 70, 75, 80, and 85 °C. Solid curves are the best fits to mono-exponential rate laws with rate constants listed in Table 2.

temperatures T						
exponential rate 1	aws of	the P	s and θ	relaxation	ns at o	different
Table 2 Summary	of ra	te cons	stants K	observed	in the	mono-

65	70	75	80	85
49	59	80	111	115
53	60	78	95	128
	65 49 53	657049595360	657075495980536078	6570758049598011153607895



Fig. 9 Arrhenius plots of the temperature-dependent rate constants listed in Table 2. The slopes of the regression lines $(-E_a/R)$ lead to activation energies in the order of 31 kJ mol⁻¹ for both the relaxation of the spontaneous polarization P_s (a) and the relaxation of the tilt θ (b).

to mono-exponential rate laws. Indeed, both $P_s(t)$ and $\theta(t)$ are well-described by these rate laws with similar time constants of, *e.g.* 12–13 s at 75 °C. All rate constants obtained from fitting the $P_s(t)$ and the $\theta(t)$ relaxations are listed in Table 2. The temperature dependence of these rate constants is analysed in the Arrhenius plots shown in Fig. 9. It is readily seen from Fig. 9 that both processes follow the Arrhenius law with almost identical activation energies around 31 kJ mol⁻¹ which is roughly one third of the typical activation energies found in diluted azobenzenes with similar substituents at the *p* and *p'* positions.^{23,14}

The fact that the $P_s(t)$ as well as the $\theta(t)$ relaxation are both described by single-exponential rate laws with identical activation energy and, at a given temperature, very similar rate constants clearly indicate that both relaxations are directly coupled to the same rate-determining process, *i.e.* the thermal $cis \rightarrow trans$ isomerization of the azobenzene mesogens.

Conclusions

Experimental data indicate that in contrast to the induced photoferroelectric effect in FLC-dopant mixtures,¹⁴ the

intrinsic photoferroelectric effect in the one-component SmC^* phase of W470 is mainly determined by the lightinduced change of the director tilt angle which then also gives rise to a change of the spontaneous polarization. In addition, a light-induced decrease of the bilinear coupling coefficient *C* (between polarisation and tilt) has also been observed.

The temperature variation of the tilt angle $\theta(T)$ in the dark state and in the irradiated states has been fitted using the standard Landau expansion of the free energy. All coefficients of this expansion have been found to depend significantly on the intensity of light. In particular, a dramatic change of the coefficient b has been observed which signifies a change in the order of the SmA*-SmC* transition from the tricritical one in the dark state to the pronounced second-order one in the irradiated states. This change in the nature of the transition has been interpreted theoretically taking into account that the bent-shaped cis-isomer molecules (generated through the irradiation with light) possess a strong biaxiality. The effective coefficient b, which determines the deviation from the tricritical point, is strongly affected by the coupling between the tilt and the biaxial order parameters. The corresponding coupling coefficient depends on the molar fraction of cisisomers, and this enables us to explain qualitatively the experimentally observed strong dependence of the coefficient b on the intensity of light.

It has been found that the light-induced variation of the tilt angle is connected with an irreversible change of the smectic layer configuration from the initial bookshelf geometry to the chevron one. In addition, close to the SmA*–SmC* transition point the secondary photoferroelectric effect has been observed which corresponds to a shift of the transition temperature.

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