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Surface memory effect in nematics with smectic C short-range order and hydrogen bonded molecules

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A surface memory effect (SME) is found in the dimerized nematic with short range smectic C order of 4-*n*-octyloxybenzoic acid (OOBA) in a cell whose walls have been covered with an obliquely evaporated SiO or ITO layer. The recording and erasure processes are discussed and erasure in the nematic phase is realized. A mechanism for the surface memorization is presented which takes into account the specific character of dimerized nematics preceding cooling into a smectic C phase.

1. Introduction

There are mainly three types of memory (storage) effect in liquid crystals: electro-optical (bulk effect), thermo-optical (bulk effect) and surface memory. The electro-optical effect has been observed in nematic-cholesteric mixtures with negative dielectric anisotropy ($\varepsilon_a < 0$) [1] or in smectic A [2]. It consists in creating a dynamic scattering texture which is preserved even after switching off the electric field applied to the liquid crystal cell (LCC). The thermo-optical storage effect was also found in cholesteric–nematic mixtures [3] or in smectic A [4]. Rapid cooling of the disordered isotropic phase in this case permits preservation of the disorder (expressed in scattering centres) in the liquid crystal phase. Recently, we have found dynamic scattering with storage in a smectic C phase and in nematics with short range smectic C order [5,6].

The surface memory effect (SME) was first reported by Friedel [7]. He found that an initially isotropic glass surface can be rendered anisotropic by having contact with a liquid crystal. Such glass orientationally orders at its surface the molecules of the nematic liquid crystal phase obtained by melting the liquid crystal substance. Later Clark [8] demonstrated an analogous SME on unrubbed polymer surfaces exposed to smectic A or smectic G phases. He realized a stable anisotropization of the surface by exposing it to an oriented phase (writing process) where the multidomain smectic texture had been imprinted on the polymer surface. This surface then reproduced a similar defect texture in the nematic state. Using optical second harmonic generation and ellipsometry, Ouchi *et al.* [9] examined the asymmetric ordering and anchoring of the liquid crystal molecules at the memory-imprinted unrubbed polymer surface and observed a rather weak azimuthal anisotropy in their orientational distribution. Ouchi *et al.* found that (i) the imprinted surface can align a bulk nematic and (ii) the liquid crystal molecules are anchored to the imprinted surface. These facts suggest that one or several molecular layers immediately at the interface liquid crystal–unrubbed polymer must be aligned. Based on the rotational diffusion model, and taking into account that the orientational distribution of the molecules arises from reorientation in the local surface potential wells caused by the bulk alignment, Ouchi *et al.* succeeded in determining the mean value of these wells: $U = 2{\cdot}1\,\mathrm{eV}$ (which is equivalent to $202\,\mathrm{kJ\,mol^{-1}}$ or $50\,\mathrm{kcal\,mol^{-1}}$). The surface memory effect in liquid crystal cells where both surfaces consist of rubbed polymers has been reported by Myrvold [10], estimating the activation energy for rotational diffusion to be $U = 0{\cdot}25\,\mathrm{eV}$ ($24\,\mathrm{kJ\,mol^{-1}}$ or $5{\cdot}7\,\mathrm{kcal\,mol^{-1}}$). For an unrubbed surface, as used by Clark [8] and Ouchi *et al.* [9], there is no preferred azimuthal direction. Thus when the bulk of the more ordered smectic phase imposes its easy direction, there is no azimuthal force acting on the molecules after heating back the LC into the nematic phase. Therefore the studies of Clark and Ouchi *et al.* looked at the transition from uniform (SME writing) to disordered (erasing) state, while Myrvold looked at the transition from disordered (writing) to uniform (erasing) state, since the rubbing process strongly limits the number of possible orientations of the liquid crystal molecules at the surface.

The mechanism of the SME is till now not clear. We summarize here some ideas concerning only the case

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when the walls of the LCC are covered with polymer. According to Clark [8], in an LCC formed by plates with a hydrophobic polymer surface, there is a close-to-the-surface-layer which is plastically deformable under a torque required to deviate the director from its preferred S_A orientation, rotating it through a certain angle. The deformable surface in this case is probably a mixed polymer–liquid crystal layer. This is possible if the substance exhibits some solvent character leading to partial miscibility, so producing an interfacial region where the liquid crystal solvent softens the polymer. The smectic liquid crystal therefore has printed its ordering at the liquid crystal–polymer interface. The very weak surface ordering of liquid crystal found by Ouchi *et al.* [9] suggests that the imprinted surface is a result of reorientation of the molecules in the close-to-the-surface-layer, induced by the bulk in the smectic phase through molecule–molecule interaction in thermal equilibrium, signifying a rotational diffusion of molecules jumping over potential barriers between the local wells, leading in this manner to reversibility of the SME. Thus a surface imprinted by a bulk smectic alignment along a certain direction can be reprinted along another direction by reorienting the bulk smectic alignment. The SME forces the molecules at the surface into a non-equilibrium state and thus there should be a tendency to restore the equilibrium.

The role of adsorption in the surface induced alignment of nematic liquid crystals on evaporated SiO films has been examined by Yokoyama *et al.* [11]. They found that the textures obtained in this case are invariably stable to the nematic–isotropic phase transition, indicating the presence of a firmly adsorbed layer of liquid crystal molecules. The memory effect could then be due to the well known adsorption of a first layer of nematic molecules on the surface with forces larger than the typical nematic forces.

Until now the SME has been observed only in nematics preceding on cooling a smectic A, where the cell plates are coated with unrubbed [8, 9] or rubbed [10] polymer. SME still has not been reported for a nematic which is oriented either by cell walls covered with obliquely evaporated and suitably thick SiO layers (where the boundary conditions can be controlled by the parameters of the SiO evaporation [12–16]) or by the capillary forces when filling an LCC consisting of glass plates covered with ITO layers.

Moreover, until now, nothing is reported in the literature about the recording (memorization) process; only thermal erasure through annealing has been partially examined (e.g. the values of the activation energy U were determined in some cases, as already mentioned).

Some data about the SME taken from the literature are summarized in Table 1.

The purposes of the present paper are (i) to investigate the SME using a substance demonstrating dimerized nematic and smectic C phases—4,*n*-octyloxybenzoic acid OOBA, (ii) to study the SME in OOBA when the cell walls are covered with obliquely evaporated SiO, as well as (iii) when they are covered with ITO layers. In addition, (iv) we investigate the role of the dimer↔monomer transformation in the nematic phase of OOBA in the processes of writing and erasing. We carry out some standard experiments on thermal erasure through annealing, and determine the activation energy U. However, (v) we also try for the first time to analyze the recording process, using data from erasure without annealing.

2. Experiments and comments

2.1. *General description, techniques and conditions*

2.1.1. *Liquid crystal cell (LCC)*

In the present study we used only the liquid crystal substance OOBA which has the following phase transition characteristics [18]: solid state (SS)–smectic C (S_C) transition, $T_{\mathrm{SS-S}}{}^{\mathrm{C}} = 101^\circ\mathrm{C}$ ($2{\cdot}6\,\mathrm{kcal\,mol^{-1}}$); smectic C–nematic (N) transition, $T_{\mathrm{S}}{}^{\mathrm{C}}{}_{\mathrm{N}} = 108^\circ\mathrm{C}$ ($0{\cdot}3\,\mathrm{kcal\,mol^{-1}}$); nematic–isotropic phase (I) transition, $T_{\mathrm{N-I}} = 146^\circ\mathrm{C}$ ($0{\cdot}6\,\mathrm{kcal\,mol^{-1}}$).

The cell was 20 μm thick and filled with OOBA by capillary forces, always using the I phase at 160°C. Then the LCC was cooled down to the SS phase, heated up to I phase and at the end cooled very carefully to S_C phase in order to obtain large domains and a well defined and resolved optical texture, which made observation and description easier. The S_C state of the LCC so obtained ('initial S_C texture') was the starting point in our experiments.

The cell was formed by two glass plates covered with ITO or with ITO and SiO. Rubbing of the surface was applied only to the ITO layers, but it did not affect our experimental results and therefore we did not use it systematically. The plates were cleaned with ethanol and then with acetone in an ultrasonic bath.

In cases where the LCC had been annealed for a long time (several hours) at relatively high temperatures (180–190°C and more) the liquid crystal began to evaporate. We could, of course, fill the cell with more OOBA, but we then observed the following interesting feature of the cell: the quality of the S_C-texture, as well as the stability of the memory effects, were good only in those parts of the cell, where the initial filling was preserved; secondary filling could never ensure the same quality of the SME.

2.1.2. *Experimental techniques*

The behaviour and the characteristics of the LCC were studied by thermocycling (heating and cooling),

Table 1. Basic data about the SME from several sources.

Authors	Liquid crystal substance	Meso-phases	Cell wall covering	Type of memorized texture	Recording		Observation of the SME in phase:	Erasure:		Ratio eras.time/rec.time	Erasure activation energy: value and physical meaning		
					Phase	Time		Phase	Time		/eV	/kJ mol^{-1}	/kcal mol^{-1}
Clark [8]	70·4	SA, SG, N	Polyimide (unrubbed)	Mosaic	SA, SG	⩽1 min	N, I	I	—	—	—	—	—
Ouchi *et al.* [9]	8CB	SA, N	Polyimide (unrubbed, rubbed)	Homogeneous	SA	⩽1 min	N	I	Several hours	≫1	Potential barrier height between walls 2·1	202	48
Myrvold [10]	*n*-Alkyl-nitro-esters as 10% solutions	N	Polyimide (rubbed)	Mosaic	SS	—	N	—	5–50 min	—	Barrier to reorientation of the liquid crystal molecules 0·25	24	5·7
Yokoyama *et al.* [11]	5CB	N	SiO($\alpha=0°$), SiO($\alpha=60°$C)	Homogeneous	N	⩽10 s	N	I	>0·5 h at 80°C, >12 h at 40°C	≫1	Energy comparable to a heat of adsorption of the order [17]: 0·8–1·8	85–170	20–40
Present paper	OOBA	S_C, N	SiO($\alpha=60°$, 66°, 86°), ITO	Mosaic	S_C	2–60 min	N	I and N	Several hours	>1	Erasure activation energy for rotational diffusion 4	385	90

combined with microscopic optical examination of the textures between crossed polarizers at magnifications ranging between 150 × and 600 × .

The standard thermocycling procedure occupied the predominant part of the experiment's duration and was carried out slowly at a rate of 2–3°C min^{-1}. Special care was taken only at the transition from N to S_C phase, where the cooling rate was reduced to 0·5°C min^{-1} in order to obtain larger domains in the initial texture. On the other hand in certain cases denoted here as thermoprobe or thermosounding, we accelerated the heating and the cooling process up to 10°C min^{-1}. Such probe had to be relatively short in duration in comparison with the whole experiment and thus is to be considered only as a perturbation which does not affect essentially the main process.

We used thermocycling in many different variants. It is easier to describe and to understand them if we introduce suitable schematic diagrams. Let us assume a coordinate system with the following axes: 'temperature T of the LCC' (ordinate) versus 'duration t of the experiment' (abscissa). The diagrams will be connected with these axes, although the latter will not be drawn explicitly. The phases of the liquid crystal will be denoted as usually by SS, S_C, N, I respectively and will be connected with arrows, indicating the direction of the thermal treatment. The slope of the arrow symbolizes the rate of temperature change. After the notations N and S_C we shall sometimes add certain numbers (in parentheses) identifying a specific texture which has been created or memorized in the corresponding phase. The fact of erasing can be expressed by omitting this number or especially emphasized by the sign (-).

2.1.3. *Essence of the SME: definition*

Let us produce an initial S_C texture as described in §2.1.1, denote it by the number 1 and keep it at a temperature T ($T_{SS\text{-}SC} < T < T_{SC\text{-}N}$) during a certain time interval t_{rec}. Then, if we heat the LCC to the N phase, we see the same mosaic picture with a specific contrast. We denote this N-picture again by the number 1. This is an expression and a demonstration of the SME in the simplest case. The picture has been recorded (memorized) in the LCC during the time t_{rec} at the temperature T_{rec} and it continues to exist, not vanishing at higher temperatures in the N phase (figures 1 (*a*) and 1 (*b*)). The erasure of such a picture occurs either by additional heating in the N phase or even in the I phase or, on the contrary, by cooling the LCC down to the S_C or SS phase. The situation is described in Scheme 1.

2.2. *Different types of experiments*

2.2.1. *Behaviour of the recorded texture in the N phase: stability and thermal erasure*

We studied the stability of the image during a monotonous increase in the temperature in the N phase according to scheme 2. Two kinds of result were obtained:

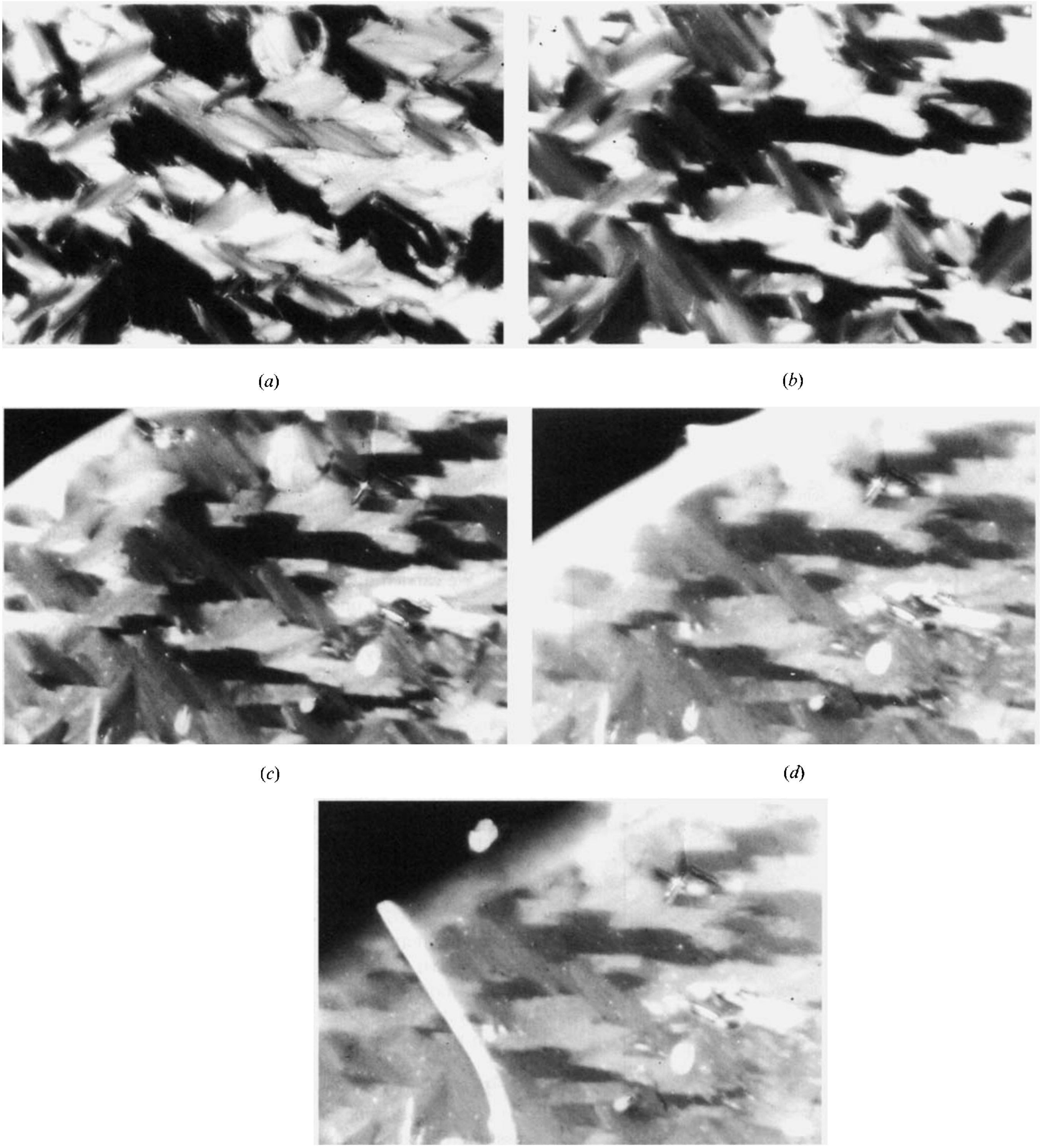
(*a*) At a certain temperature $T < T_{N\text{-}I}$, the contrast became so low that the picture became practically invisible. A decrease in temperature at this point did not restore the image. We can formulate such an irreversible situation as thermal erasure (dynamic erasure or, more precisely, erasure without annealing).

(*b*) The texture remained visible up to $T = T_{N\text{-}I}$ although its contrast was reduced.

Which of these situations will be realized depends on the recording time: the longer t_{rec}, the more stable is the image and vice versa. The accurate examination of this dependence requires an exact criterion for the vanishing contrast. We do not argue over such a criterion and estimated the erasure by visual observation only. We define the vanishing contrast state practically as the state where the mosaic picture becomes extremely hard to distinguish, i.e. its contrast in fact is not exactly zero, but the eyes see the picture at the lower limit of perception. Nevertheless our experience enabled us to follow the relationship between erasure temperature T_{er} and recording time t_{rec} even in this imperfect way. The data are shown in figure 2 for several different cell walls.

The function $T_{er} = f(t_{rec})$ has two important features. First, it is an increasing dependence, i.e. at any fixed recording temperature T_{rec}, some microscopic process is in progress in the LCC during the whole recording time t_{rec}. This process both realizes the recording and stabilizes it, but it remains invisible through the microscope. Second, the above mentioned dependence is evidently not linear; it has two parts differing in their slope: (a) a very abrupt initial part for recording times in the interval $0 < t_{rec} < 2$ min, and (b) a slanted second part for $t_{rec} > 2$ min. The process just mentioned has two stages, respectively: initial fast memorization and a secondary slower one. We could not examine the first stage precisely due to the thermal inertia of our experimental set-up.

The dynamic erasure procedure without annealing was in fact used by us as an instrument for investigating the recording process. However another erasure procedure proved to be possible, a static one—just by keeping the LCC for a certain interval t_{er} at a fixed and sufficiently high temperature T_{er}. This is an erasure with or through annealing. Such a procedure allowed us to reach some conclusions about the mechanism of thermal erasure in itself. Several experiments of this kind are presented in scheme 3 denoted by different indices. It was possible to approximate the results with an exponential type formula [9] $t_{er} = \tau \exp[U/(k_B T)]$, where U and τ are parameters. U is an energy barrier which has to be surpassed by the thermal activation $k_B T$ in order to

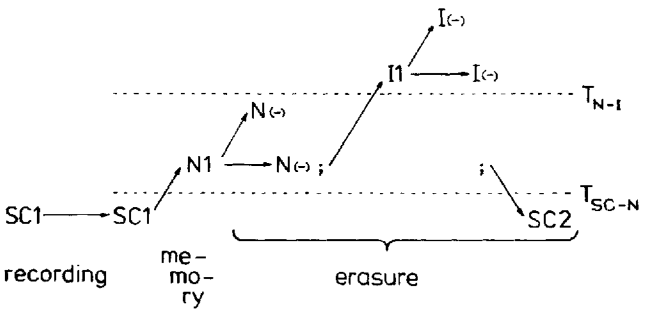


(*a*) (*b*)

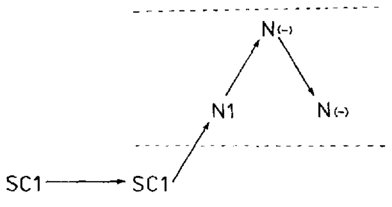
(*c*) (*d*)

(*e*)

Figure 1. Surface memory effect with a single texture (No. 1). The cell walls are covered with SiO evaporated at an angle of 86°. Recording time 2 h at 105°C. Magnification 400 × . The cell is placed between two crossed polarizers. (*a*) Texture No. 1 in the S_C phase at 105°C: recording process. (*b*) Texture No.1 in the N phase at 110°C: demonstration of the memory effect. (*c*) Texture No.1 at 146°C, exactly at the transition N→I: the phase front is moving from left to right due to the presence of a horizontal temperature gradient. (*d*) Texture No.1 after the front in figure 1(*c*) has been stopped for 30 min. (*e*) Texture No.1 exactly at the transition I←N after a 10 min stay at 148°C in the I phase: the phase front is moving from right to left.



Scheme 1.



Scheme 2.

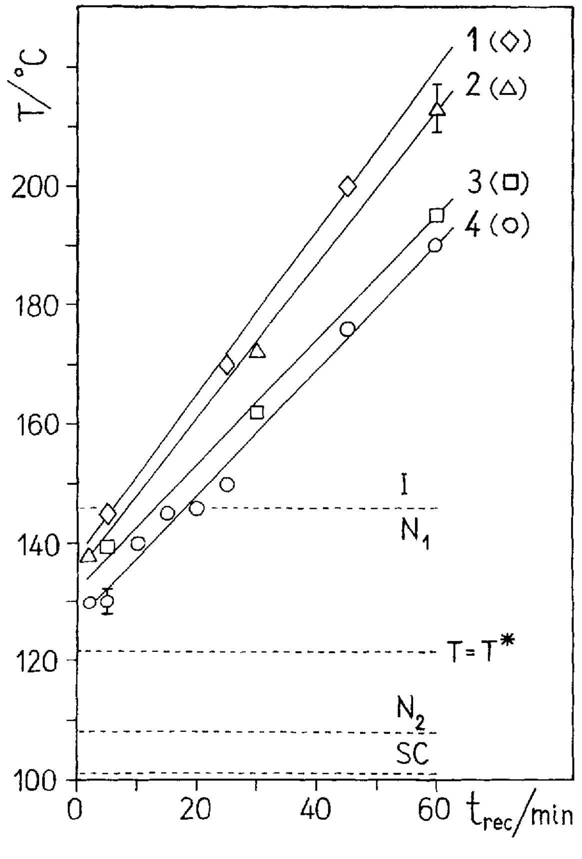
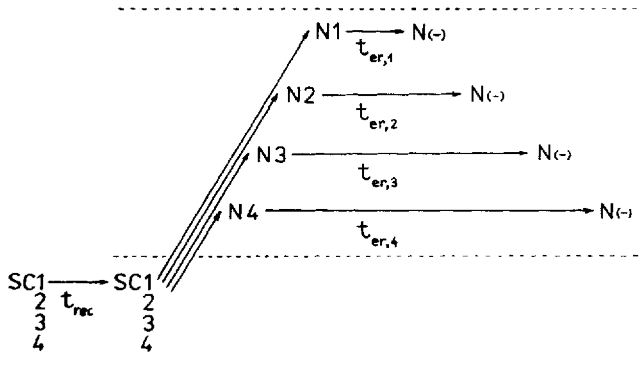


Figure 2. Relation between dynamic erasure temperature T and recording time t_{rec} for different covering layers on the liquid crystal cell plates: 1—SiO, $\alpha = 60°$; 2—SiO, $\alpha = 66°$; 3—ITO; 4—SiO, $\alpha = 86°$.



Scheme 3.

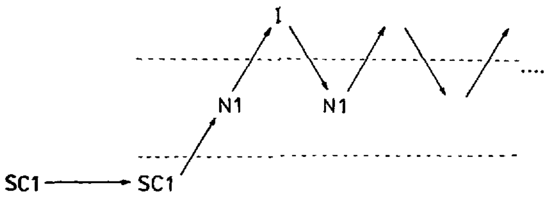
provoke effectively the destruction of the picture through rotational diffusion during a time interval t_{er}. τ is an extrapolation parameter: when the temperature tends to infinity, the erasure time tends not to zero, but to τ. τ is extraordinarily sensitive to experimental accuracy—it requires T to be extrapolated to infinity, while we work only in the interval between 100 and 200°C. At the same time τ loses any physical meaning above 300°C due to decomposition of the liquid crystal.

We carried out two sequences of static erasure experiments: the first one for $t_{rec} = 2$–3 min and the second one for $t_{rec} = 30$ min. In both cases, the energy U proved to be practically the same, approximately 4 eV or 385 kJ mol^{-1} or 92 kcal mol^{-1}.

An important remark has to be added here. We succeeded in erasing the textures in practically acceptable intervals t_{er} only at temperatures between 125 and 148°C. At temperatures around 125–130°C, t_{er} became so long (say 6 h) that the liquid crystal began to evaporate. In contrast with this behaviour, we could not see any contrast decrease even after 6 h at temperatures between 108 and 120°C. Thus, we could not realize erasure through annealing, check the diffusion type formula and find the barrier U. As will be discussed further, it is very interesting that at temperatures below 120°C, the OOBA molecules exist as dimers, while above 120°C they dissociate into monomers. Probably this fact is connected in some way with the possibility of erasing the recorded image in the N phase.

2.2.2. *Behaviour of the image at the N↔I transition: visible and latent image*

Assuming a sufficiently stable recording, say $t_{rec} = 2$ h, let us increase the temperature to the transition N↔I and vary it around T_{N-I} according to scheme 4. In the I phase the image becomes invisible just as if it has been completely erased. However if we bring back the LCC into the N phase, a few minutes later, the mosaic picture becomes visible again, i.e. neither the phase transition nor the short stay in the isotropic phase succeeds in



Scheme 4.

completely destroying the memorizing structures. Obviously 'invisible' does not necessarily always mean 'erased'. The transition N↔I converts the image into an invisible state and the back transition I→N visualizes the latent image again (figures 1(*c*), 1(*d*) and 1(*e*). The existence of the memory effect in visible and invisible form and even in the I phase essentially complicates the study of these phenomena.

We made up to 15 thermo-oscillations around $T_{\mathrm{N-I}}$ without losing the recorded picture. When we kept the LCC very close to $T_{\mathrm{N-I}}$, but still below $T_{\mathrm{N-I}}$, the fluctuations became so strong that they were noticeable in the microscope. They could in principle strongly affect the memorizing structures at the molecular level and destroy them. Nevertheless the image remained resistant and stable over a rather long period (say 1 h).

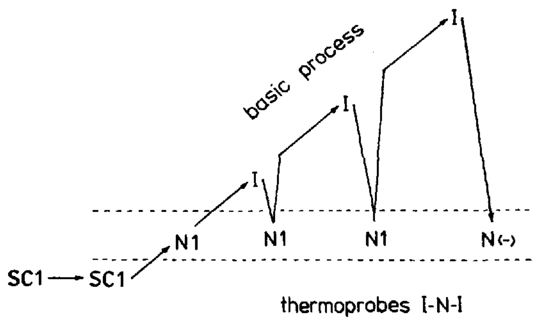
Several important conclusions could be drawn from these experiments. The existence of the recorded texture in the N phase means that the bulk liquid crystal is well oriented and thus is visible between the crossed polarizers. The transition to the I phase destroys the orientation in the bulk and the image becomes invisible. The restoration of the picture after transition back into the N phase means that the bulk orientation has been regenerated. Therefore we may assume that the memorization process takes place only in some parts of the cell, having microdimensions (probably several molecular layers adsorbed at the walls) and a rather strong structure. The transition N→I disorders the bulk liquid crystal and makes the picture invisible, but it does not destroy the micromemorizing structure which persists as a latent image. This structure is able to rebuild the orientation and the ordering in the bulk in the entire LCC, regenerating the visible picture in the N phase. Obviously this small 'memorizing nucleus' (latent image) includes in some way all the information necessary to regenerate the entire bulk texture. The bonds between the liquid crystal molecules and the cell walls within the memorizing nucleus are evidently very strong: they endure the pretransitional fluctuations in the N phase, the phase transition itself, the thermal attack in the I phase and yet they still have the ability to order and to orient the bulk N phase according to the information which has been recorded in the nucleus in $\mathrm{S_C}$ phase.

2.2.3. *Behaviour of the image in the I phase: thermoprobe, erasure with or without annealing*

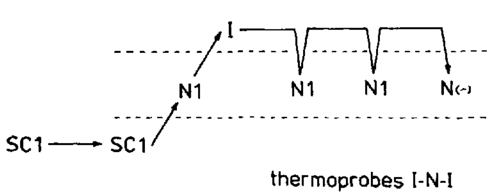
Before starting the study of our system in the I phase, we had to find a technique to register the memory effect in its invisible state. The most straightforward procedure was called by us 'thermoprobe': the LCC was relatively quickly cooled down to the N phase where the recorded picture became visible and then immediately heated back to the I phase.

The experiments on erasure without annealing were carried out according to scheme 5. The relation between t_{rec} and T_{er} at $T > T_{\mathrm{N-I}}$ is shown in figure 2. We followed this function up to temperatures where the liquid crystal began to evaporate (say 180–200°C). The accuracy of determining T_{er} in the I phase was, of course, lower than in the N phase, but still remained within the acceptable interval of ±5°C. The experiments confirmed the second slanted part of the dependence $T_{\mathrm{er}} = f(t_{\mathrm{rec}})$ up to $t_{\mathrm{rec}} = 1\,\mathrm{h}$ and $T_{\mathrm{er}} = 200°\mathrm{C}$. Evidently the memorization is a two-stage process: fast imprinting and slow stabilization.

Erasure through annealing in the I phase was also possible according to scheme 6. We did not study the static erasure in detail. In an LCC made of two glass plates covered only with ITO, we observed dynamic erasure at 190°C as well as static erasure at 160°C for 1 h. We have to note here that the LCC was heated from $T_{\mathrm{N-I}} = 148°\mathrm{C}$ to $T_{\mathrm{er}} = 190°\mathrm{C}$ in 15 min (i.e. approximately $3°\mathrm{C\,min^{-1}}$).



Scheme 5.



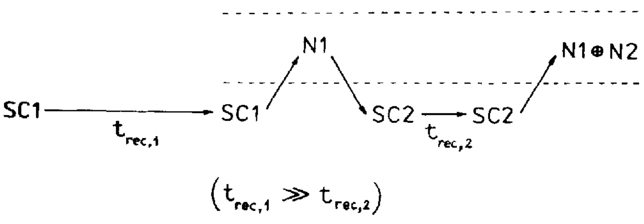
Scheme 6.

2.2.4. *Behaviour of the image on cooling the LCC back to the S_C phase: mixing of recorded images, visible and latent pictures in the S_C phase*

In the previous experiments we made a recording in the S_C phase, then checked its memorization in the N phase and followed the behaviour of the image on increasing temperature in the N as well as in the I phase. We found out that (i) the temperature increase can cause thermal erasure in N and in I phase, (ii) the image can remain even in the I phase, although in a latent state.

In this section we are interested in the evolution of the recording with decreasing temperature when the recording has not been erased during its stay in the N phase. We wanted to examine what would happen to the image when the LCC was brought back to the S_C phase. The accurate quantitative study of these phenomena is rather complicated. We are presenting here preliminary qualitative results in order to give an idea about the possible processes. In the simplest case the experiment had two stages as shown in scheme 7. First we made a recording in the S_C phase for, say $t_{\mathrm{rec},1} = 1$ h, and checked it in the N phase. Then we cooled the LCC to give the S_C phase and observed microscopically that picture No.1 (figure 3(*a*)) had vanished and been replaced by a completely new and different picture No.2 (figure 3(*d*)). This observation could lead to the conclusion that the former picture No.1 had been erased. Logically our next step was to prove this assumption in the N phase. Thus we came to the second stage of our experiment: after keeping the LCC in the S_C phase for an interval $t_{\mathrm{rec},2} \ll t_{\mathrm{rec},1}$, say $t_{\mathrm{rec},2} = 10$ min, we heated it up to the N phase again. This resulted in a surprise: in the N phase, we observed a strange texture (figure 3(*f*), denoted here as N$\oplus$, which was a complex combination containing elements from texture No.2, as well as from texture No.1! Most of the elements originated from texture No.1 due to its longer recording time and higher stability.

Obviously the N$\leftrightarrow S_C$ transition had transformed image No.1 from visible to latent state. The decrease in temperature could not activate the standard thermal erasure mechanism and therefore the simple erasure by loss of contrast was impossible. We observed instead a novel and peculiar 'erasure' process: the old image was replaced by a new image element by element (figure 3). The destruction of the old image (No. 1) and the memorization of the new one (No. 2) proceeded simultaneously; destruction of the first picture was monitored by recording the second picture over it. Instead of 'thermal erasure', we have here 'erasure through new recording' or 'erasure through overwriting'. Based on this curious result we can consider the second stage of our experiment as a thermoprobe ($S_C \rightarrow N \rightarrow S_C$), which, however leads to a stronger perturbation in the LCC in comparison with the thermoprobe I$\rightarrow$N$\rightarrow$I.



Scheme 7.

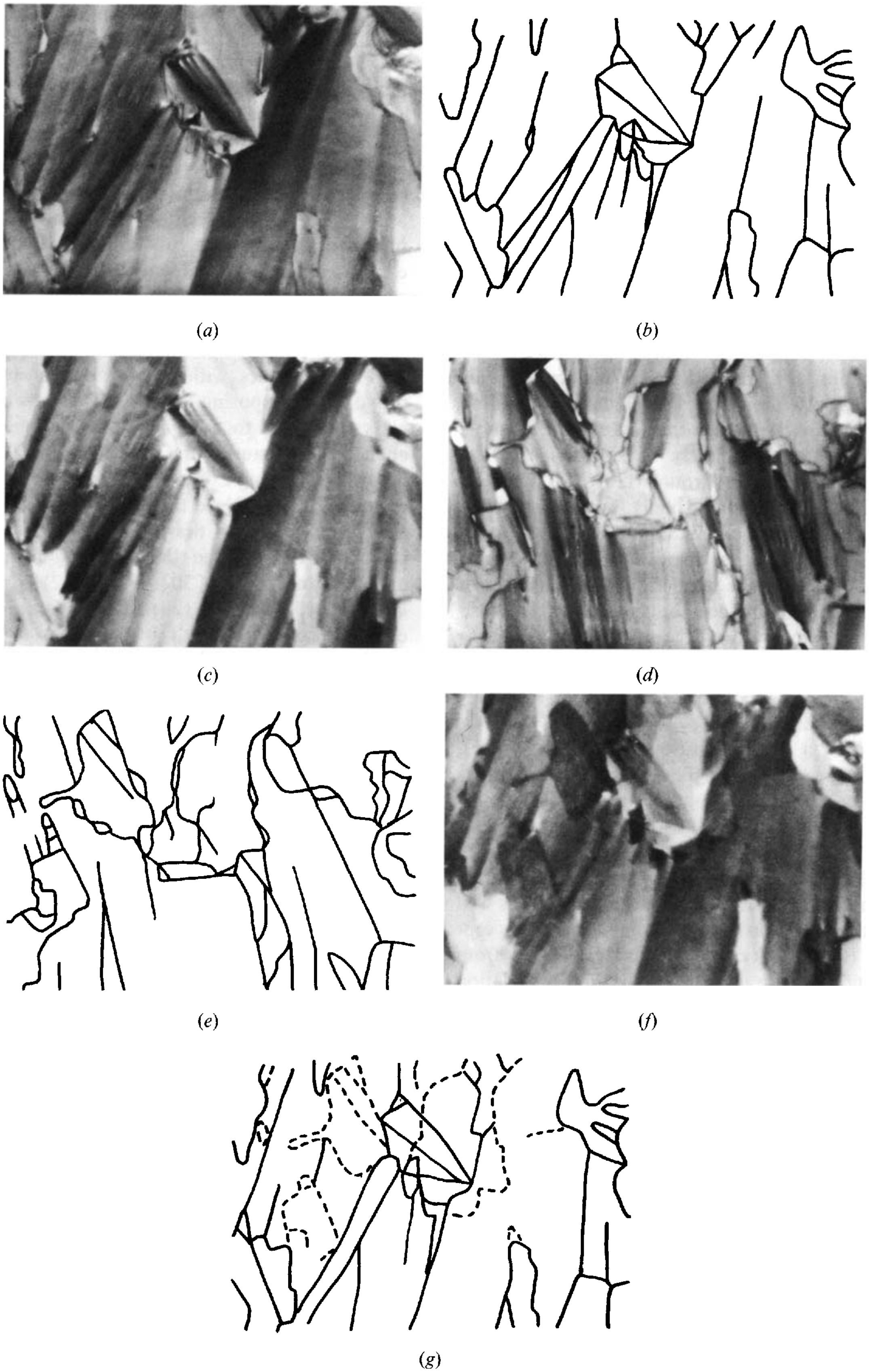
The behaviour of the image at the transition N$\leftrightarrow S_C$ offers an interesting possibility which still has a definite hypothetical character. By means of repeated recordings No.1,2,3, ... in the S_C phase for suitable chosen time intervals $t_{\mathrm{rec},1}$, $t_{\mathrm{rec},2}$, $t_{\mathrm{rec},3}$ ... separated by short-time thermocycling $S_C \rightarrow N \rightarrow S_C$, it could be possible to store several pictures simultaneously in one and the same LCC in the form of a very complex combination, which is visible in the N phase. Perhaps if the temperature increases monotonically in the N and I phases it would be possible thermally to erase these pictures selectively according to their different recording times and their different stability, respectively.

The precise examination of such phenomena is very difficult, because the quantitative estimation of the status of two or more mutually mixed different mosaic images is much more complex than the estimation of the contrast in one and the same image. In order to analyse this situation, one could try to simplify it by means of a more effective control over the texture growing in the S_C phase. Such control would allow the production of only a few singly shaped and easily distinguishable domains, and in this manner it would facilitate their identification as a particular image (texture).

3. Discussion

3.1. *Molecular structure and two nematic subphases for OOBA*

In order to understand the SME in nematics with short range smectic C order and dimerized molecules, we have to take into account the structure of the molecules of *p*-*n*-alkyloxybenzoic acids and especially OOBA. It is important also to present some of the most typical macroscopic characteristics of its nematic phase. The SME [8, 9] and the electro-optical memory effect [3, 5, 6] are observed in nematics with short range smectic A or C order, when the structural unit forming the nematic phase is a supramolecular complex. In nematics with short range smectic order, such complexes are cybotactic groups [19]. In these cases, the memorization is provoked by plastic deformation possible in the quasi-smectic complexes. This is an important place for us to look for the mechanism of the SME, taking into



(*a*) (*b*)

(*c*) (*d*)

(*e*) (*f*)

(*g*)

Figure 3. Surface memory effect with two textures (No.1 and No.2) in one and the same cell. The cell walls are covered with ITO; the recording times of the textures at 105°C are 1·25 h and 10 min, respectively; magnification 450 × ; the cell is placed between two crossed polarizers. (*a*) Texture No.1 in the S_C phase at 105°C. (*b*) Schematic view of texture No.1. (*c*) Texture No.1 in the N phase at 120°C. (*d*) Texture No.2 in the S_C phase at 105°C. (*e*) Schematic view of the texture No.2. (*f*) Mixed textures No.1 and No.2 in the N phase at 125°C. (*g*) Schematic view of the mixed textures No.1 and No.2. Full line = contours from texture No.1; dashed line = contours from texture No.2.

account the nematic structure of OOBA, as well as the other homologues of the *p*-*n*-alkyloxybenzoic acids displaying nematic and smectic C phases: *p*-*n*-heptyl- and -nonyl-oxybenzoic acids, HOBA and NOBA. For substances displaying only the nematic phase, the 'flow alignment effect' [11] is in many respects similar to the SME and its mechanism is presumably the same.

The molecules of *p*-*n*-alkyloxybenzoic acids tend to associate in dimers with hydrogen bonds connecting their respective acid groups [20]. The hydrogen bonds in the benzoic acids [21] are strong ($\approx 5\,\mathrm{kcal\,mol^{-1}}$ or $21\,\mathrm{kJ\,mol^{-1}}$ or $0{\cdot}22\,\mathrm{eV}$) and as a result, the relative concentration of non-associated molecules is small. Using high resolution IR techniques [22], we examined the concentration of the three kinds of molecular forms (cyclic dimers, open dimers and monomers) depending on the temperature. We found that on cooling below a temperature (T^*) approximately in the middle of the nematic phase interval (e.g. around 120°C for OOBA), the monomers disappear and only cyclic and open dimers remain, the cyclic predominating. In a set of articles [23–26] we have demonstrated very sharp anomalies exhibited by the temperature dependences of some typical liquid crystal constants at $T = T^*$. We also found that this temperature divides the nematic phase interval for OOBA into two subphases: a high-temperature one N_1 with the properties of a conventional nematic and a low-temperature one N_2 with markedly quasi-smectic character. The transition $N_1 \leftrightarrow N_2$ is accompanied by a strong texture transformation [25]. Above T^* the coexistence of the dimers and monomers having different molecular lengths is not favourable for smectic-like fluctuations and, as a result, a classic nematic is established, while below T^*, the monomers disappear [22], the dimers are more compact molecular forms and this stimulates the smectic order fluctuations as well as the formation of quasi-smectic complexes. We accept that at T^* (which is critical [27]) a transition from classic to quasi-smectic nematic occurs. The correlation length ξ, describing the growth of the cybotactic groups, is macroscopic at T^* and, as we have demonstrated, $\xi \approx 0{\cdot}1d$ [27, 28]. This result confirms the shift of T^* by the boundary conditions [26] and bulk deformations [27]. The boundaries can also change the local monomer/dimer concentration [29]. Both the temperature and the surface-induced monomer/dimer concentration changes could be two important parameters in dimerized nematics with short range smectic order oriented by SiO oblique evaporation.

3.2. *Anchoring of OOBA molecules on glass plates covered with SiO or with ITO*

The nematic liquid crystal orientation can be characterized in principle by the polar angle θ (between the director $\vec{n}$ and the substrate's normal $\vec{S}$) and by the azimuthal angle ϕ (between the director and the plane of evaporation). Three surface anchoring states of OOBA molecules on a SiO layer are possible [15]: (a) planar anchoring (characterized by $\theta = \pi/2$ and $\phi = \pi/2$ and realized when $\alpha < 60°$); (b) tilted anchoring (characterized by $0 < \theta < \pi/2$ and $\phi = 0$ and realized when $\alpha > 72°$); (c) intermediate anchoring (characterized by $0 < \theta < \pi/2$ and $0 < \phi < \pi/2$ and realized when $60° < \alpha < 72°$). In the intermediate case, one can induce simultaneously two easy directions ($+\phi$ and $-\phi$) at one and the same point of the cell wall—bifurcation of the tilted orientation and bistable anchoring.

Our experimental results are the first concerning the SME of nematics with short range smectic C order, provoked by exposing SiO or ITO layers deposited on glass substrates to a S_C phase. We are not sure that anchoring exhausts the memorization mechanism, because anchoring exists even in situations without any recorded image. Nevertheless we have estimated the anchoring characteristics for the different walls of our cells. At first we used the following formula for the anchoring energy W_S [30]: $W_S = (\pi^2/2)K_{\mathrm{eff}}d\,l^{-2}$, where d is the cell thickness ($20\,\mu\mathrm{m}$ in our case), K_{eff} is the effective elastic constant ($10^{-6}\,\mathrm{erg\,cm^{-1}}$ or $10^{-11}\,\mathrm{J\,m^{-1}}$ [31]) and l is the thickness of the surface induced walls in the N state. Then using these values of W_S and another formula [32] $W_S = K_{\mathrm{eff}}(\vec{n}.\vec{n}_0)^2\,L^{-1}$, where L is the extrapolation length [31], and assuming that $(\vec{n}.\vec{n}_0) \approx 1$, we calculated L. The results are presented in table 2.

Finally, we compared the L values with the N–I correlation length ξ which is already known [31]: $\xi \approx 0{\cdot}1\,\mu\mathrm{m}$. It turned out that $L \sim \xi$, which means strong anchoring. If we take the correlation length according to [27], $\xi = 0{\cdot}1d$, we have $\xi = 2\,\mu\mathrm{m}$ in our case. And lastly, if we take ξ from [28], we obtain $\xi = 2{\cdot}2$ to $2{\cdot}3\,\mu\mathrm{m}$. In the last two situations we have $L \ll \xi$, which means very strong anchoring.

It is interesting to compare now the data from table 2 with the conclusions about the stability of the recording which can be drawn from figure 2. Figure 2 convinces us that the strength of the memorization decreases from the case of SiO($\alpha = 60°$) walls, through the cases of SiO($\alpha = 66°$) and ITO walls and finishing in the case of SiO($\alpha = 86°$). One should note the very impressive fact that the anchoring energy decreases in the same sequence. Obviously a higher anchoring energy stimulates stronger memorization.

3.3. *The SME considered from the viewpoint of energy*

The analysis of SME in our case is difficult for at least two reasons. First, recording is a complex two stage process. Second, the N phase of OOBA is not an ordinary one, but splits into two subphases N_1 and N_2.

Table 2. Data on anchoring energy and on extrapolation and correlation length in different liquid crystal cells filled with OOBA.

Cell wall covering	Width of disinclination line in nematic /μm	Anchoring energy /J m^2	Extrapolation length /μm	Extrapolation to correlation length ratio /%
SiO($\alpha = 60°$)	2·5	16×10^{-5}	0·06	2·8
SiO($\alpha = 66°$)	5	4×10^{-5}	0·25	12
ITO	5	4×10^{-5}	0·25	12
SiO($\alpha = 86°$)	7·5	$1·8 \times 10^{-5}$	0·55	26

The static erasure procedure was studied by us systematically only in the interval $T^* < T < T_{N-I}$ and only there did we succeed in obtaining the value of the activation energy $U = 4$ eV or 385 kJ mol^{-1} or 90 kcal mol^{-1}. In the I phase, we did one experiment, which demonstrated the possibility of static erasure, but did not allow us to determine U in an analogous way. In the interval $T_{SC-N} < T < T^*$ we could not practically achieve an erasure effect at all. Therefore we may not overestimate the value 4 eV when discussing here the nature and the stability of the SME.

There is a natural tendency to use the value of U when defining the strength of the SME [10]. This is possible in our opinion only if an exact microscopic model of the SME exists and demonstrates clearly the physical meaning of U as some kind of intramolecular bonding energy or as a potential wall fixing the director of a single molecule in a certain direction. Unfortunately, (i) such a theory does not exist now, and moreover, (ii) the values of U given by different authors (see table 1) and by us (4 eV) are so high, that they do not permit such a straightforward interpretation. The values mentioned are of the order of the strongest chemical bonds which combine single atoms into molecules [33]. Thus, if we consider U as a simple barrier energy which has to be surpassed by thermal activation in order to provoke the erasure by rotational diffusion, we would obviously destroy the liquid crystal molecules or at least initiate a fast sublimation of the liquid crystal (the intramolecular forces typically correspond to energy values of the order 1–5 eV [33]. These are the reasons why we do not accept U as a direct measure for the strength of the SME effect and prefer to consider U carefully as a phenomenological parameter describing the experiments on static thermal erasure in an LCC. Now we have two goals: (a) to propose a useful phenomenological interpretation of the quantity U and (b) to propose another definition for the strength (stability) of the SME, which does not depend so straightforwardly on U.

We could connect U directly with τ: when $k_BT = U$ we have $t_{er} = \tau$. However, we have already demonstrated that the extrapolation parameter τ has no reasonable physical meaning in our system. Therefore, it is more useful to differentiate the equation, which introduces U. Then we obtain: $U = (1/t_{er})[dt_{er}/d(1/k_BT)]$, i.e. U is the relative change of t_{er} for unit change of the reciprocal temperature $(1/k_BT)$. Since t_{er} is a measure for the stability of the recorded image, U simply indicates the thermal sensitivity of the erasure process or of the SME. Accepting such a definition, we can imagine four typical situations: (1) stable recording with high thermal sensitivity; (2) stable recording with low thermal sensitivity; (3) unstable recording with high thermal sensitivity and (4) unstable recording with low thermal sensitivity.

It is the right place here to introduce a useful criterion about the stability or the strength of the SME. We propose to consider the SME as stable (strong) in a certain temperature interval if $t_{er} > t_{rec}$ for the entire interval and, on the contrary, that the SME is unstable (weak) if $t_{er} < t_{rec}$. The temperature at which the recording has been carried out is assumed to be fixed here. In this sense our results on static erasure indicate a rather stable (strong) SME ($t_{er} \gg t_{rec}$ for T in the interval from $T^* = 120$°C to $T_{N-I} = 148$°C), which is thermally very sensitive in comparison with other cells (our value $U = 4$ eV is greater than all other data in the table 1). We cannot classify in a similar manner our SME in the intervals $T_{SC-N} < T_{er} < T^*$ and $T_{er} > T_{N-I}$ due to the lack of experimental data.

We suppose that the N phase, after erasure and before going into the S_C phase is an initial unexcited state with an initial energy W_0 reflecting the thermodynamic equilibrium. Going into the S_C phase we go practically into the state where the action of the boundary forces (anchoring) provoking the initial nematic state (for example planar orientation with $\theta_0 = 0$ and $\phi_0 = 0$) starts to become weaker. And this will be a stronger effect when the phase transition energy h is greater than the thermal activation, i.e. $hN_A^{-1} \gg k_BT$ or $h(k_BTN_A)^{-1} \gg 1$. N_A is the Avogadro constant and k_B is the Boltzmann constant. In our case (for OOBA) $h \approx 0·3$ kcal mol^{-1} or $hN_A^{-1} = 0·013$ eV while $k_BT = 0·033$ eV for $T = 108$°C = 381 K. Thus $h(k_BTN_A)^{-1} < 1$ and we expect that the bulk forces are not as strong as the surface forces. This means that the boundary forces keep on acting even in the S_C phase. However, since the director $\vec{n}$ in this phase is constrained to rotate in two cones simultaneously [34], it is forced by torsion to change its orientation from (θ_0, ϕ_0) to (θ_c, ϕ_c). The initial nematic state is characterized by the energy $W_0(\theta_0, \phi_0)$, and the state, which is induced by the boundaries, in S_C phase is described by the energy $W_c(\theta_c, \phi_c)$. The transition $W_0 \rightarrow W_c$ on the recording process is actually a transition from an unexcited to an excited state.

At the transition back from S_C to N (figures 1(*a*) and 1(*b*) or 3(*a*) and 3(*c*)) the texture which has been formed and recorded in the S_C state is preserved (memorized) in the N state as a demonstration of the SME. When the LCC as a whole is in the nematic state, it has actually the following complex structure: immediately at the surface there is a thin smectic layer, while the bulk liquid crystal is nematic with quasi-smectic ordering. This situation is described by the energy $W_c(\theta_c, \phi_c)$ of the memorized texture. It means that the imposed local director distortion which has been generated in the S_C phase is retained in the N phase as an excited non-equilibrium state in the form of a plastic deformation in the frame of a thin layer at the LCC surface. Increasing the temperature causes relaxation of the director from the excited W_c to the equilibrium W_0 state. This is the essence of the thermal erasure process. Its rate depends strongly on the temperature (figure 2).

In our case (for OOBA), the nematic interval is divided by the temperature T^* into two subphases: a quasi-smectic one N_2 for $T < T^*$ and an ordinary nematic one for N_1 for $T > T^*$. We succeeded in erasing the recorded texture in the ordinary nematic phase N_1 only as a result of breaking the dimer molecules into monomers after the transition from N_2 to N_1. The induction by the surface of a smectic A-like structure [29, 35] far above the nematic–smectic C transition temperature, and especially the smectic layer generation below T^* could be important in the interpretation of the SME. According to this argument, the SME is connected with surface smectic layering and the full erasure is a full destruction of the pre-surface smectic layer. We assume that the formation of a smectic surface layer of a density markedly higher than that of the nematic bulk is a process analogous to adsorption, where an anomaly of the molecular density is realized near to the surface (the adsorbent).

We observed thermal erasure in the N_1 phase only when t_{rec} is very short (2 min). In the case when $t_{rec} > 20$ min (figure 2) dynamic erasure occurs just in the I phase. In this case, we observed (figures 1(*c*), 1(*d*) and 1(*e*)) that the N→I phase transition front with a horizontal temperature gradient does not destroy the SME. We interpret this effect as a preservation (due to the long recording time) of the smectic layer in the I phase (but now not so thick as it was in the N_2 phase below T^*). It is difficult, however, to determine exactly the temperature in the I phase where the memorizing nucleus completely disappears.

4. Conclusions

(1) We have examined for the first time the surface memory effect in OOBA, in a cell whose walls had been covered with SiO or ITO.
(2) We have tried for the first time to study the recording process, by means of dynamic erasure experiments.
(3) We succeeded in erasing the memorized image in the nematic phase, above the temperature T*.
(4) We observed for the first time the recording of several images in one and the same cell, where they exist simultaneously.
(5) We proved that in our cell (for the combination of liquid crystal substance OOBA and cell wall covering, SiO or ITO) there is a strong anchoring, which raises the stability of the recorded textural image.
(6) Analysing the recording process (by dynamic erasure) and the erasure process in the high temperature nematic subphase (by static erasure), we have concluded that the surface memory effect in our case is a strong, stable one and has a large thermal sensitivity.

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References

[1] Heilmeir, H., and Goldmacher, E., 1968, *Appl. Phys. Lett.*, **13**, 132.
[2] (*a*)Tani, C., 1971, *Appl. Phys. Lett.*, **19**, 241; (*b*) Hareng, M., Le Berre, S., and Thirant, L., 1974, *Appl. Phys. Lett.*, **25**, 683.
[3] Soref, R. A., 1970, *J. Appl. Phys.*, **41**, 3022.
[4] Kahn, J., 1973, *Appl. Phys. Lett.*, **22**, 111.
[5] Petrov, M., Petroff, B., and Simova, P., 1978, *C. R. Acad. Bulg. Sci.*, **31**, 647.
[6] Simova, P., Petrov, M., 1981, *Mol. Cryst. liq. Cryst.*, **74**, 275.
[7] Friedel, G., 1922, *Ann. Phys. (Paris)*, **18**, 273.
[8] Clark, N. A., 1985, *Phys. Rev. Lett.*, **55**, 292.
[9] Ouchi, Y., Feller, M. B., Moses, T., and Shen, Y. R., 1992, *Phys. Rev. Lett.*, **68**, 3040.
[10] Myrvold, B., 1995, *Liq. Cryst.*, **18**, 287.
[11] Yokoyama, H., Kobayashi, S., and Kamei, H., 1984, *J. Appl. Phys.*, **56**, 2645.
[12] Guyon, E., Pieranski, P., and Boix, M., 1973, *Lett. Appl. Eng. Sci.*, **1**, 19.
[13] Urbach, W., Boix, M., and Guyon, E., 1976, *Appl. Phys. Lett.*, **25**, 479.

[14] Monkade, M., Boix, M., and Durand, G., 1988, *Europhys. Lett.*, **5**, 697.

[15] Jerome, B., Pieranski, P., and Boix, M., 1988, *Europhys. Lett.*, **5**, 693.

[16] Pieranski, P., and Jerome, B., 1991, *Mol. Cryst. liq. Cryst.*, **199**, 167.

[17] Adamson, A. W., 1976, *Physical Chemistry of Surfaces*, 3rd edition (Wiley and Sons), Chap. 14.

[18] Herbert, A. J., 1967, *Trans. Faraday Soc.*, **63**, 555.

[19] De Vries, A., 1970, *Mol. Cryst. liq. Cryst.*, **10**, 31.

[20] Corsar, R. D., and Atkinson, G., 1971, *J. Chem. Phys.*, **54**, 4090.

[21] Deloche, B., and Cabane, B., 1971, *Mol. Cryst. liq. Cryst.*, **19**, 25.

[22] Petrov, M., Anachkova, E., Kirov, N., Ratajczak, H., and Baran, J., 1994, *J. mol. Liq.*, **61**, 221.

[23] Simova, P., and Petrov, M., 1981, *J. Phys. D*, **14**, 1.

[24] Simova, P., and Petrov, M., 1983, *Phys. Stat. Solidi*, **A80**, K153.

[25] Petrov, M., and Simova, P., 1985, *J. Phys. D*, **18**, 239.

[26] Petrov, M., and Simova, P., 1986, *Phys. Stat. Solidi*, **A95**, K165.

[27] Barbero, G., Komitov, L, Petrov, M., and Strigazzi, A., 1991, *Int. J. Mod. Phys.*, **B5**, 2229.

[28] Petrov, M., Antonova, K., Kirov, N., Tenev, T., and Ratajczak, H., 1994, *J. Mol. Struct.*, **327**, 265.

[29] Petrov, M., Braslau, A., Levelut, A. M., and Durand, G., 1992, *J. Phys. II*, **2**, 1159.

[30] Williams, C. E., and Kleman, M., 1974, *J. Phys. Lett. (Fr)*, **35**, L-33.

[31] De Gennes, P. G., 1974, *The Physics of Liquid Crystals* (Oxford: Clarendon Press).

[32] Rapini, A., and Papoular, M., 1969, *J. Phys. (Fr)*, 30 Coll., **4**, C4–54.

[33] Ficini, J., Lumbroso-Bader, N., and Depezay, J.-C., 1968–1969, *Elements de Chimie-Physique* (Paris: Hermann), Chap. 5.

[34] Clark, N. A., and Lagerwall, S. T., 1984, *Ferroelectrics*, **59**, 25.

[35] Ivanov, N. B., and Petrov, M., 1992, *Liq. Cryst.*, **11**, 953.