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Textures of homologous 4-*n*-alkyloxybenzoic acids: spontaneous chirality and surface memory

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By using polarizing microscopy analysis we have found that several achiral homologues of the 4-*n*-alkyloxybenzoic acids, displaying only the nematic phase, exhibit the optical properties of a chiral liquid crystal system. These acids possess a mesophase due to the formation of dimers via hydrogen bonding. The microtextural analysis was carried out in the temperature ranges of the isotropic, nematic and crystal phases. The nucleation of a chiral texture in small domains emerging on cooling in the isotropic phase was observed. These small domains are characterized by a conoscopic cross which presents an azimuth of 45° with respect to the polarizer axis, contrary to the usual nematic drops, for which the conoscopic cross is not rotated. On further cooling, these domains coalesce in the nematic phase close to the clearing point, thus building large chiral monodomains. Such coalesced droplets exhibit very thin stripe lines, as in the case of pure cholesterics with a tilted helix axis. Moreover, left- and right-handed chiral domains were observed, combined in regions partially separated by 'oily streaks', also typical of pure cholesterics. On cooling, the chiral nematic (N*) phase transformed through a pronounced texture transition into a normal nematic phase. However, the small chiral grains that formed from the isotropic phase are retained close to the surface, acting as 'memorizing centres'. With suitable boundary conditions, they can provide a macroscopic twist driven by the surface. Moreover, a twisted smectic B not present in the bulk phase diagram was found and interpreted as induced by the surface. Also in the crystal phase a strong memorization of the chiral N* texture was observed.

1. Introduction

Usually the molecules of liquid crystals are approximated as rigid rods. Together with Maier–Saupe [1] mean-field analysis, this approximation was used [2] for the description of the nematic phase of conventional liquid crystals like MBBA and PAA. These classical theories [1, 2] neglect the internal degrees of freedom of each liquid crystal molecule, i.e. the variation of the molecular structure with temperature and due to surface effects, taking into account only the interaction among rigid rods, by expanding the free energy of the liquid crystal system to the second or fourth power of the scalar order parameter. However, some investigations [3–10] of 4-*n*-alkyloxybenzoic acids which display nematic (N) and smectic C (SmC) phases, such as heptyl-,

octyl- and nonyl-oxybenzoic acids (usually referred to as HOBA, OOBA and NOBA), indicated anomalies in the temperature dependence of the elastic constants, the electroconductivity and the dielectric permittivity. The temperature trends of these constants strongly deviate from those of classical nematics. The experimental results demonstrated an evident texture transition and a dramatic increase of the depolarized Rayleigh scattering intensity [7] at a certain temperature T^* in the nematic range.

Using FTIR spectroscopy [11–13], three states of the molecules of HOBA, OOBA and NOBA were detected, viz. closed dimers, open dimers and monomers, with a different distribution at different temperature, demonstrating the dependence of the molecular structure on temperature. The temperature induced variations of the molecular shape, due to the effect of the thermal activation energy $K_B T$ (where K_B is the Boltzmann constant)

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on the hydrogen bonds (linking up the monomers in closed or open dimers), together with the temperature anomalies of characteristic liquid crystal constants, indicate that the rigid rod approximation cannot be used for a description of the nematic state organized from dimer molecules, like those of the 4-*n*-alkyloxybenzoic acids.

A further development of the classical theories is necessary, keeping the mean field approximation and taking into account the internal degrees of freedom of the molecules arising from the variation amongst the above-mentioned three molecular states: closed dimers, open dimers and monomers. Recently, a model in this direction was presented by Barbero *et al.* [14]. In this model the energy of hydrogen bonding was expressed as being connected with the influence of the dimerization process on the macroscopic properties, so giving a possible explanation of some temperature anomalies of the scalar order parameter, as well as of the equilibrium relative concentrations of closed dimers, open dimers and monomers. The problem of considering the short range forces and fluctuations that characterize nematics with short range smectic order, like the 4-*n*-alkyloxybenzoic acids, as well as the coexistence of this smectic order with the nematic long range order, which is necessary to describe nematics with internal degrees of freedom of the molecules, is still open for debate.

In order to make a first contribution to solving this problem, a wide range of homologues of the 4-*n*-alkyloxybenzoic acids displaying only the nematic phase (i.e. the homologues with $i = 2$–6 C atoms in the alkyl chain) and those displaying nematic and smectic C phases (the homologues with $i = 7$–12) have to be investigated. In the present work we have dealt with the first homologues range, exhibiting only the nematic phase, whereas the second homologues range will be the subject of future work. In the first group, the homologues with $i = 3$–6 are particularly interesting, and especially one with $i = 6$, because it neighbours the 7th homologue, displaying a smectic C phase below the nematic phase, where the smectic order fluctuations are very pronounced. By varying the homologue number i from 2 to 6, we may deduce some information concerning the nucleation and frustration of the smectic ordering.

The spontaneous chirality which was discovered in the nematic phases of the achiral *trans*-4-alkylcyclohexane-carboxylic acids and explained by the formation of chiral oligomers [15] could also be achieved in 4-*n*-alkyloxybenzoic acids, since both acid types form hydrogen bonds. This phenomenon, together with the development of smectic order fluctuations, can dramatically influence the order parameter of nematic phases organized by flexible molecules and preceding a smectic C phase on cooling.

The subjects of our investigation are two-fold: spontaneous chirality and surface memory (comprising anchoring transitions). The mechanisms involved are hydrogen bonding and smectic order fluctuations.

The theory, which must be modified in order to describe the nematic phase characterized by molecules with internal degrees of freedom, has also to take into account variation in the state of the molecules (which promotes or retards the mesophase), achieved as a consequence of surface action. It was demonstrated [9] that the formation of strong hydrogen bonding of monomers with orienting solid surfaces could induce various types of surface transition. That is why the interface between liquid crystals made up from dimers and a solid plate could be decisive in the formation of the nematic phase and induce some connected surface phenomena, such as anchoring transitions, or surface instabilities, and surface memory effects as well [16].

A full understanding of the phenomenon is yet to be reached, since the problem is complicated and requires a wide set of substances and several surface conditions to be analysed. In this first state, we restrict our investigation to homologues of the 4-*n*-alkyloxybenzoic acids displaying only the nematic phase ($2 \leqslant i \leqslant 6$), filling cells made from solid plates with two types of boundary conditions: just glass plates cleaned without any other treatment (dielectric surfaces), and rubbed ITO plates (conducting surfaces).

2. Experimental results and discussion
2.1. *Liquid crystalline materials*

We have investigated the 2nd, 3rd, 4th, 5th and 6th homologues of the 4-*n*-alkyloxybenzoic acids, which are achiral materials. The phase transition temperatures are as follows:

C-2: (I–N) 165.0°C monotropic;   (N–Cr) 136.0°C
C-3: (I–N) 157.0°C;   (N–Cr) 137.0°C
C-4: (I–N) 160.0°C;   (N–Cr) 145.0°C
C-5: (I–N) 158.0°C;   (N–Cr) 116.0°C
C-6: (I–N) 153.0°C;   (N–Cr) 107.0°C.

The 2nd homologue displays a monotropic nematic phase only formed during cooling from the isotropic liquid.

2.2. *Solid plate treatment and surface conditions*

For liquid crystal cell (LCC) preparation we used: (a) glass plates cleaned by acetone and alcohol and thoroughly dried, without any other treatment; (b) ITO coated glass plates, rubbed in one direction.

The LCC were prepared without spacers; the cell thickness was only about 2–3 μm and the surface contribution enhanced. The liquid crystal was inserted in the cell by capillary forces in the isotropic phase.

Using equal boundary conditions, achieved either with non-treated or rubbed ITO treated glass plates, we investigated the above-mentioned substances in their nematic and crystal phases on heating and on cooling. In order to detect the texture transitions expected, a thermal microtextural analysis was carried out with very slow heating and cooling rates ($0.1°C\,min^{-1}$), using Linkam hot stage equipment and a Leitz polarization microscope, with Sony-Grundig recording apparatus. As a result of careful observation we found some new effects which are very reproducible, using the same substances and applying the same boundary conditions. Most of these effects (like spontaneous chirality, surface induced twist and surface induced smectic B phase) appeared with all the substances investigated; we have concentrated our attention on such effects, assuming that they can be considered typical for those homologues of the 4-*n*-alkyloxybenzoic acids displaying as a mesophase only the nematic phase. Our interpretation will be more definite after investigation of homologues with $i > 7$, displaying both nematic and smectic C phases or only a smectic phase (e.g. the 16th homologue). Such a study is now in progress. Here we would like to introduce some arguments which allow us to anticipate some phenomena due to both structural and macroscopic properties of the 4-*n*-alkyloxybenzoic acids.

2.2.1. *Oligomerization*

The closed dimer molecule, which is stable at low temperature, is built by two monomeric molecules, linked by hydrogen bonds. The energy of the bonding is approximately $5\,kcal\,mol^{-1}$ [17]. The dimer ring can be destroyed at higher temperature: therefore a closed dimer, by stretching and vibrating out from the plane of the two hydrogen bonds, can transform into an open dimer with only one hydrogen bond with rotational deformations around single hydrogen bond $-H\cdots O-$ axis, or into two free monomers. The energy for full decomposition (an equilibrium reaction between closed dimer and two monomers) is higher order than that for partial decomposition (closed–open dimer). Formation of new hydrogen bonds is also possible by twisting around the $-H\cdots O-$ axes of open dimers lying near to each other and/or the simultaneous coupling between open dimers and monomers (oligomerization) [15]. This oligomerization process, which is a molecular organization stimulated by temperature variation and/or by surface action, could be the basis for achieving a spontaneous twist in a system of achiral molecules (supramolecular chirality). This phenomenon has already been observed [15], for instance in the case of the *trans*-4-alkylcyclohexanecarboxylic acids.

2.2.2. *Surface coupling*

With regard to coupling with monomers or dimers (open or closed), surfaces can act like hydrophilic (PVA, ITO and SiO treatment) or hydrophobic (polyimide) systems. Hydrophilic surfaces couple by hydrogen bonding with the acidic part of monomers, whereas hydrophobic surfaces favour dielectric coupling with alkyl chains. On the other hand, the closed dimers are attracted only by hydrophobic surfaces. As a result, a hydrophilic surface favours the presence of monomers strongly attached via hydrogen bonds, thus inducing a bidimensional smectic-like monomeric phase in coexistence with the bulk nematic phase, whereas a hydrophobic surface can have both monomers and dimers bonded to it by electric forces, and so with weaker coupling.

This complicated coupling of monomers with the orienting surfaces can provide, in the case of hydrophilic surfaces, the nuclei for oligomerization through hydrogen bonding with other monomers or open dimers coming from the bulk, resulting in chiral oligomeric molecules attached to the surfaces, which can align other chiral oligomeric molecules in the same way, thus penetrating deeply into the bulk.

In the case of hydrophilic attachment, we believe that for hydrogen bonding between one monomer and the surface, the coupling energy involved should be comparable with the energy of coupling between two monomers for dimer formation. Considering the three molecular states—closed dimers, open dimers and monomers—as electrostatic charges, we can imagine them as quadrupoles and dipoles, respectively. The last consideration has important consequences, since it allows us to predict in dimer systems the creation of bulk and surface phenomena, both of a dipolar character like flexoelectricity (connected with the flexibility of the dimeric molecule) or of a quadrupolar character, like a flexoelectricity gradient (connected with the dimer density variation). Moreover, if the orienting surfaces favour monomers, it follows that the order parameter of the nematic state diminishes: this means that a gradient of the scalar order parameter will appear normal to the plates, resulting in an ordoelectric polarization parallel to the orienting surfaces themselves [9]. This polarization is generated as a result of hydrogen bonding between the surface and both monomers and open dimers. Thus a surface torque arises, which can enhance or depress a spontaneous twist of the dimeric nematic phase.

2.2.3. *Smectic fluctuations*

Smectic order fluctuations definitely appear upon cooling in the nematic phase of those homologues which also exhibit the smectic C phase, like 4-*n*-alkyloxybenzoic acids with C-atom number $i > 7$ in the alkyl chain. However, in the homologues with $i = 6$ and $i = 5$, which

exhibit only a nematic phase, such smectic fluctuations can also appear, even though no smectic phase is present in these compounds.

The above three structural and macroscopic mechanisms must be taken into account to understand the behaviour of the substances under investigation. The properties of these mechanisms obviously confirm the necessity to take into account the internal degrees of freedom of the molecules in describing the nematic phase. Also the order–disorder equilibrium transition (between open and closed dimers), due to the variation with temperature of the hydrogen bonding distribution, is driven by the surface action, and overlaps the short and long range order in the dimer system. Moreover, molecules with different shape pack with different probability in quasi-smectic complexes like cybotactic clusters, more easy packing being achieved by closed dimers. In fact, closed dimers are compact elongated molecules, and a packing in supramolecular nematic-like complexes is to be expected, implying an arrangement of the molecular centres of mass in the same plane, thus organizing quasi-layers. Consequently, the longer the molecules, the higher the probability of obtaining short range smectic ordering in coexistence with the nematic long range order. Taking into account this property for the liquid crystals considered here, we expect that on reducing the dimer molecular length when the C-atom number i in the tail diminishes from 6 to 2, the probability of correlated smectic order fluctuations will become negligible and hence the generation of quasi-smectic layers will be suppressed. On the textural level, we expect to observe strong or weak texture transitions in the temperature range of the nematic phase, depending on the molecular length, or, in the present case, on the 'homologue number' i. Such a transition was earlier observed for homologues with $i > 7$, displaying nematic and smectic C phases. It is now important to find the critical homologue length where the texture transition and the smectic order fluctuations are suppressed. This limiting case is interesting in order to understand the nature of the smectic phase nucleation and the possible presence of a smectic frustration.

Finally, due to the structural and macroscopic properties of the mechanisms previously described, a spontaneous twist is expected, due to the effect of temperature change and surface action on the dimer systems. We are looking for optical textures characteristic for such chiral phases, where the nucleation and the evolution of the elementary structures are interesting features. The peculiar strong coupling of the liquid crystal molecules with the surface could transform the mesogen's crystal phase into a smectic phase with pronounced textural characteristics at a temperature below the nematic range. For instance, the twisted smectic B phase can be induced. The

spontaneous twist, generated at a molecular level, can be transformed (by suitable surface conditions) into a macroscopic effect, which is easily observable and can be driven by the surface. This has been proved in the present work.

2.3. *Microtextural thermal analysis*

Investigations are reported on the achiral 2nd (C-2), 3rd (C-3), 4th (C-4), 5th (C-5) and 6th (C-6) homologues of the 4-*n*-alkyloxybenzoic acids.

#### 2.3.1. *Nucleation of chiral texture in the isotropic phase*

The appearance and evolution of this texture as a function of temperature for different surface treatments is now described. In figure 1(*a*), the generation of the elementary texture (grains or domains) is shown in the isotropic phase of C-3. The liquid crystal cell is prepared with ITO rubbed plates without spacers. The temperature is 156.5°C (equal to $T_{NI} - 0.5°C$). Looking from right to left, and because of the horizontal temperature gradient, the grain texture is observed to start as a set of small particles, 1 μm in size. At this stage of the nucleation they do not present a well defined, clear optical shape or texture. They represent one stage of the evolution of chiral structures emerging in the isotropic phase. The stage before the formation of these grains cannot be visualized, since the grain size is very small and the Mauguin adiabatic optical rule is not achieved, meaning that the light electric vector cannot follow the director variation. Looking on the left side of the picture (where the temperature is 0.2°C lower) it is possible to see that these grains coalesce, transforming into larger domains with pronounced conoscopic character. The conoscopic crosses, formed after the coalescence of the grains from the first observable state, are in the plane of the cell plates and form an azimuth equal to 45° with respect to the polarizer. This proves the spontaneous chirality of the droplet structure [18]. On further temperature decrease, further coalescence takes place, but this behaviour remains unchanged. At $T_{NI} - 1°C$ we observed twisted bipolar droplets, which express the spontaneous twist of this achiral system [19].

In figure 1(*b*), the same effect of the generation of twisted grains is shown for C-4 at 159.4°C (equal to $T_{NI} - 0.6°C$). The cell has ITO rubbed plates.

In figure 2(*a*), the transition between a spontaneous twisted nematic texture on the left side, and a partially untwisted nematic texture on the right side, is shown for C-4 in a cell with ITO rubbed plates, on cooling from the I phase. The temperature was $T = 158.3°C$ and the cooling rate 0.1°C min^{-1}. In the spontaneous twisted nematic domain (on the left), there are fine stripe lines with a very small period, as in the case of cholesterics. This means that there is a tilt of the helix axis with
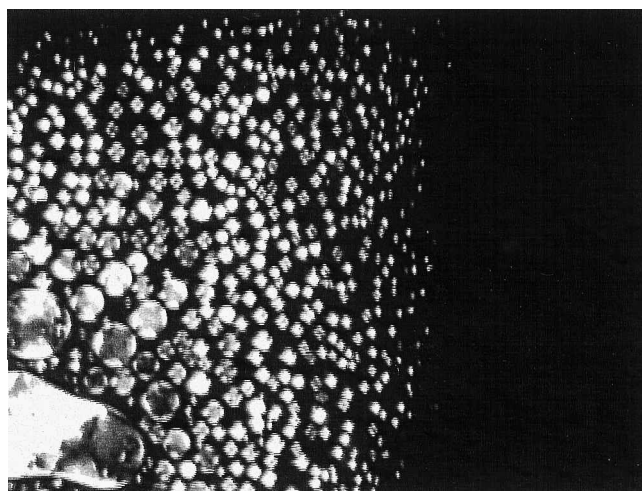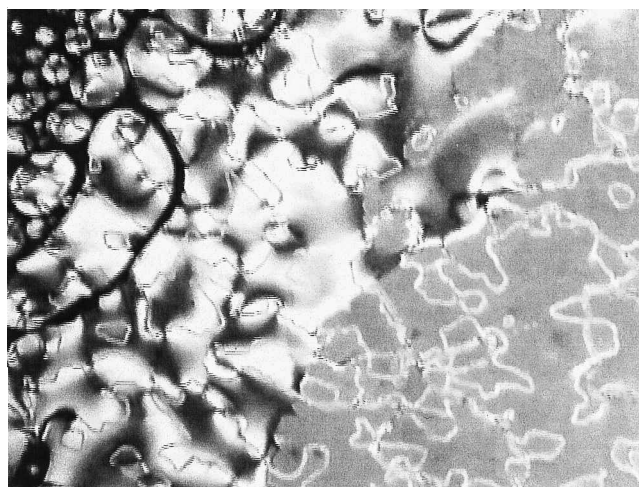
(a)
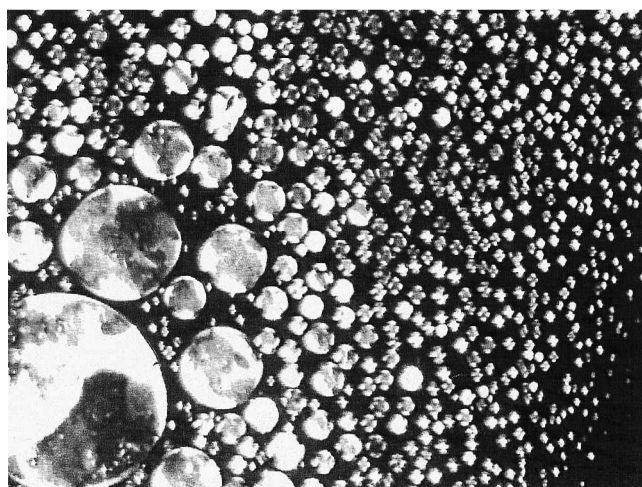
(b)

Figure 1. (a) The generation of elementary grains is shown in the isotropic phase of C-3. Cell prepared with ITO rubbed glass plates without spacers. The temperature is 156.5°C (equal to $T_{NI} - 0.5$°C); crossed polarizers, magnification 250 ×. Note the conoscopic crosses, formed after coalescence of the grains from the first observable stage and their azimuth = 45° with respect to the polarizers. (b) The same occurrence for C-4 at 159.4°C = $T_{NI} - 0.6$°C.


(a)

(b)

Figure 2. (a) The transition between a spontaneous twisted nematic texture (left) and a partially untwisted nematic texture (right) for C-4 in a cell with ITO rubbed plates, on cooling from the I phase. $T = 158.3$°C, cooling rate 0.1°C min^{-1}; crossed polarizers, magnification 250 ×. Note the stripes with very small period in the chiral domain (left), as for the cholesterics (chiral pitch in the range of submicrons). (b) The same transition in C-3, at $T = 155.0$°C, on cooling. Note that the fine stripe texture of the twisted nematic is partially kept in the untwisted nematic phase.

respect to the normal to the cell plates. The chiral pitch of the twisted domain seems to be in the submicron range.

In figure 2(b), the same transition is shown for C-3 between a spontaneous twisted nematic phase and an untwisted one, at $T = 155.0$°C, upon cooling under the same experimental conditions. Moreover, figure 2 demonstrates that the fine stripe texture of the twisted nematic is partially retained in the untwisted nematic phase.

C-6 exhibits the same effect at $T = 152.6$°C, but upon faster cooling (1°C min^{-1}). The small striped domains

appeared preferentially near to the inversion lines in coexistence with the grains which failed to coalesce into bigger chiral structures. The striping appears preferentially near to the defects, probably because in these domains the planar orientation is destroyed, thus provoking tilt. This is one typical cholesteric texture where confocal stripes arise.

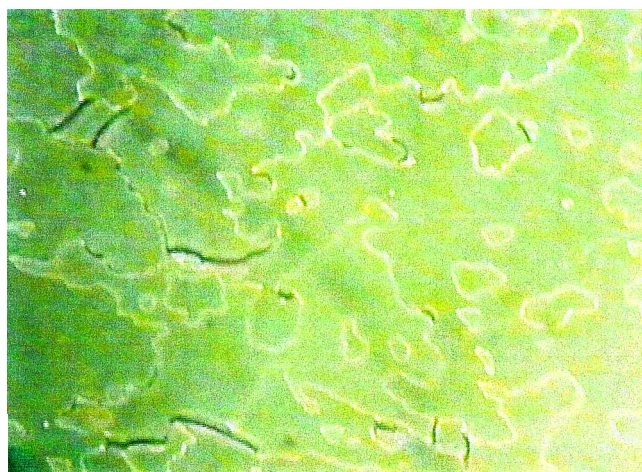The region between the spontaneous twisted N* and the untwisted nematic N phases is presented for C-4

in figure 3(*a*). It is detected upon very slow cooling ($0.1°C$ min^{-1}) during the coalescence process of domains with left and right chiral sense—the small dark and
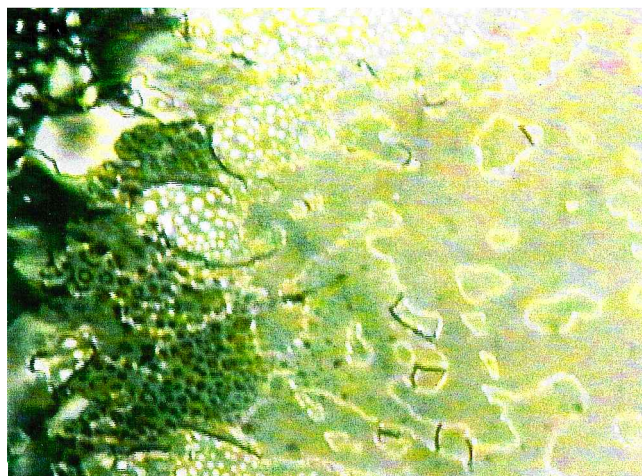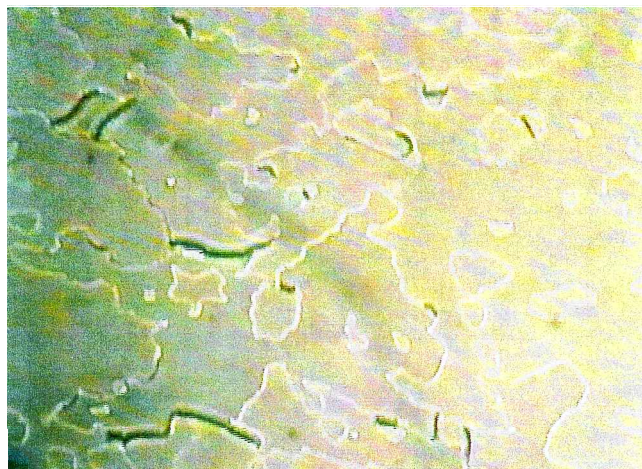
white domains, respectively, according to compensator measurements with crossed polarizers. Between the regions of left chiral sense (the dark domains) and those of right sense (the white domains) one can see thick dark lines, reminiscent of the well known 'oily streaks', typical for the cholesteric phase. Since nematic and cholesteric liquid crystals are miscible in all proportions, any intermediate state between pure nematic and a given cholesteric phase can be achieved. Therefore many similarities emerge between the defects and the textures of nematics and cholesterics. In this sense, the dark thick lines in figure 3(*a*) can be interpreted as lines which are typical for cholesterics, being imposed on the bright inversion lines of an untwisted nematic N. These 'oily streak' lines in our case were partially destroyed and disappeared upon further cooling in the untwisted nematic area (right part of the picture), due to competition between the chiral N* and the usual N phase.

Figure 3(*b*) and 3(*c*) at $T = 156.6°C$ ($T_{NI} - 3.4°C$) show 'oily streaks' partially formed in the same conditions as in figure 3(*a*). The thick 'oily streak' lines diminish with falling temperature (from left to right side). Two analyser positions are presented, which differ by a $\pm 12°$ rotation with respect to the crossed polarizer position. In figure 3(*b*) several greenish thick lines on a brown background are observed, which in figure 3(*c*) transform into brown thick lines on a green background, as can be observed for the 'oily streaks' in pure cholesterics.

Figure 4 shows the spontaneous twist effect at the second state in C-4 oriented by ITO surfaces rubbed in order to achieve a planar unidirectional texture. This twist transition starts in the low temperature range in the nematic phase. In this case, $T = 151.0°C$ ($T_{NI} - 9.0°C$). The border between the two twisted areas lies at about $60°$ with respect to the easy axis (horizontal in the picture) and moves with temperature variation. Each of

(*a*)

(*b*)

(*c*)

Figure 3. (*a*) Region between the spontaneous twisted N* state and the untwisted nematic N for C-4, upon very slow cooling ($0.1°C$ min^{-1}), just below the clearing point, during the coalescence process of domains with left and right chiral sense—the small dark and white domains, respectively: crossed polarizers. Thick dark lines are formed between the region with left chiral sense (the dark domains) and that of right chiral sense (the white domains) and are reminiscent of the 'oily streaks', typical for the cholesteric phase. (*b*) and (*c*) at $T = 156.6°C = T_{NI} - 3.4°C$, show on cooling the evolution of the 'oily streaks'. The number of 'oily streaks' diminishes with decreasing temperature (from left to right). Two analyser positions are presented, which differ by a $\pm 12°$ rotation with respect to the crossed polarizer position. Note several greenish 'oily streaks' on a brown background (*b*), transforming into brown 'oily streaks' on a green background (*c*), as can be observed in the case of pure cholesterics.
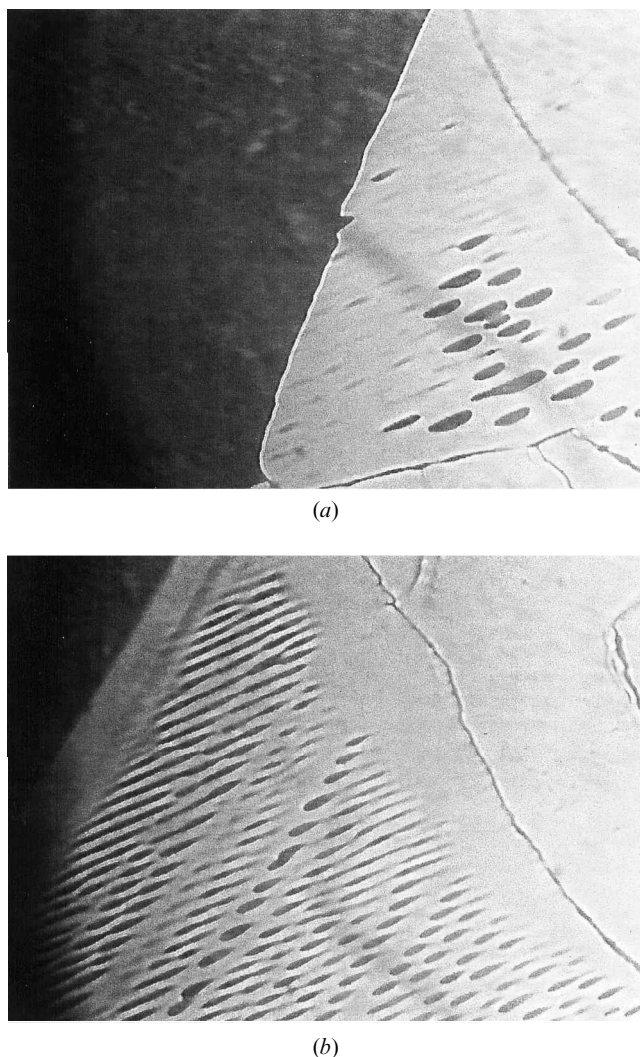
(a)

(b)

Figure 4. Spontaneous macroscopically twisted regions (a), formed at the second stage in C-4 samples oriented by rubbed ITO surfaces. This twist transition starts in the low temperature range in the nematic state. In this case $T = 151°C = T_{NI} - 9°C$. The border between the two twisted areas forms about 60° with respect to the easy axis (horizontal in the picture) and moves (b) with temperature variation. Each of the reversibly twisted monodomains (twins) memorizes the twisting power and the polarization of the other, which is shown by the small domains, with an elliptical form, arrayed with their long axes in a direction forming about 45° with respect to the easy axis.

the reversibly twisted monodomains (twins) memorizes the twisting power and the polarization of the other, as is shown by the small domains, with an elliptical form, arrayed with their long axes in a direction forming about 45° with respect to the easy axis.

This effect demonstrates that the twisting and the untwisting in the first stage (close to T_{NI}) are not well established near to the surface, but only deep in the

bulk. So only at the second stage is the interaction between the ITO rubbed surface and the liquid crystal (probably due to hydrogen bonding of monomers and open dimers with the ITO) a possible reason for the helix aligning effect, which accompanies the small droplets coalescence. This means that the equilibrium N*–N is dependent on the temperature and on the surface action. These two observable parameters can provide the starting for the second twist stage, giving the macroscopic effect, involving a strong texture change.

One important conclusion is that the surface in some sense memorizes on cooling the structure variation that first appeared at a higher temperature in the bulk (before the transition N*–N); subsequently, under suitable experimental conditions, the surface can reproduce the twist in a new bulk configuration aligned by the surface itself. This is consistent with the hypothesis that the surface keeps non-coalesced elementary chiral grains that appeared in the bulk in a temperature range close to the clearing point, where the typical twisted texture cannot be visualized. These elementary chiral grains coexist during cooling in a latent memorization state, whereas in the bulk they coalesce and undergo a textural N*–N transition. These grains can then be considered as 'memorizing centres' of the spontaneous twisted structure.

2.3.2. Surface induced smectic B phase not existing in the bulk phase diagram

We found a surprising result (see figure 5): on heating C-3 in a cell prepared with rubbed ITO glass plates, at 137°C a transition from crystal to nematic phase was expected, but showed a texture fully reminiscent with the mosaic smectic B phase—see Demus and Richter [20]—smectic B-like domains were formed (heating rate 1°C min⁻¹). In figure 5(a) these domains are seen at 3°C below the actual transition to the nematic phase. Then 1°C below the transition to the N phase, oriented elongated nematic 'grooves' appeared, figure 5(b). They are visible in the upper left part of the picture as dark bands. These nematic 'grooves', which appear after heating the smectic B-like mosaic texture, are always oriented parallel to the optic axis of the domains which are surrounded by inversion walls, typical of the mosaic texture in smectic B. Presumably we have detected a twisted smectic B texture, which was predicted by Demus and Richter [20] for chiral systems, but never observed till now. When in the smectic B phase, the sample can exhibit a remarkable optical activity: the domains can be strongly coloured, see figure 6(a). Figure 5(b) and 6(b) show that the transition from the surface induced smectic B to the nematic phase can occur with pronounced pretransitional lines, a typical feature of layered systems. In conclusion, it is more likely that the hydrogen
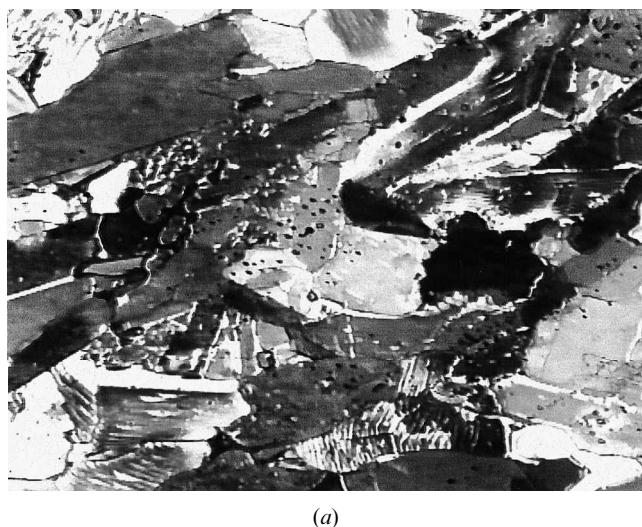
(*a*)

(*b*)

Figure 5.   Formed at 134°C, on heating, C-3 in a cell with rubbed ITO glass plates. Texture fully reminiscent of the mosaic smectic B phase [18] (heating rate 1°C min^{-1}). (*a*) Domains at 3°C below the actual transition to the N state; (*b*) 1°C below the same transition. Note (*b*) the appearance of oriented elongated nematic 'grooves'. They are visible in the upper left part of the picture as dark bands, always oriented parallel to the optic axis of the domains. The domains are surrounded by inversion walls, typical of the mosaic texture in smectic B.

bonding of dimer liquid crystals with the ITO surfaces is reponsible for providing a smectic B-like phase, which is therefore induced by the surface. Note that figure 6 displays the same effect in the same substance (C-3), but at a higher heating rate (5°C min^{-1}).

2.3.3. *Texture transition between two nematic subphases (N$_1$ and N$_2$) due to smectic order fluctuations*

Figure 7 shows a transition N$_1$–N$_2$ in C-6 with ITO treated glass plates. N$_1$ is the higher temperature, normal
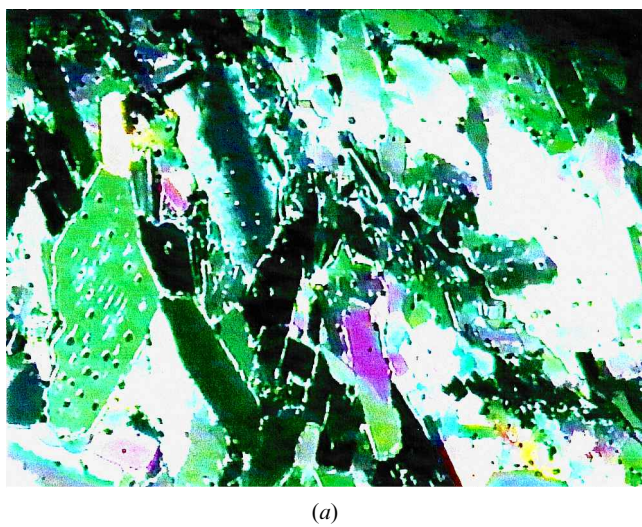
(*a*)
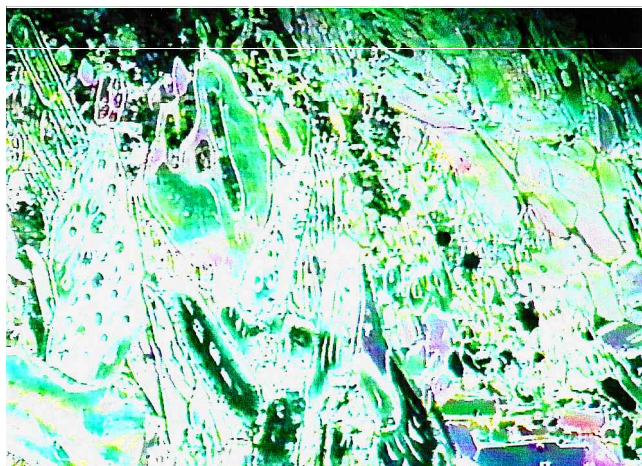
(*b*)

Figure 6.   (*a*) Remarkable optical activity, several domains appearing strongly coloured. (*b*) Pronounced pretransitional lines close to the transition from the surface-induced smectic B to the nematic phase, a typical feature of layered systems. Note that in this figure the same effect as in figure 5 for the same substance (C-3) is presented, but at a higher heating rate (5°C min^{-1}).

nematic subphase, see figure 7 (*a*); whereas in figure 7 (*b*) the lower temperature nematic subphase N$_2$ is presented, which is characterized by a polycrystalline texture made by many small grains about 2 μm in size.

In non-oriented samples, where the cells were prepared with untreated plates, this transition began on heating at 135°C ($T_{NI} - 18$°C), which is just in the middle of the nematic phase. On cooling from the isotropic phase, the transition N$_2$–N$_1$ started at 121°C. The hysteresis is about 14°C, which is typical for phase transitions of weak first order. In cells prepared with rubbed ITO surfaces, the texture transition in C-6 is either not as pronounced as in untreated cells, or is completely

(*a*)

(*b*)

Figure 7. Order transition N_1–N_2 in C-6 with ITO treated glass plates. N_1 is the higher temperature, normal nematic subphase (*a*); N_2 is the lower temperature nematic subphase (*b*) characterized by a polycrystalline texture (small grains, about $2\,\mu$m in size).

depressed. For example at 113.7°C upon cooling, only a weak change in the texture was observed with crossed polarizers. Thus, the conducting ITO surface tends to suppress the texture transition. Also in C-5 an order transition was found, but weaker than that of C-6. For instance, in untreated cells on heating, the weak transition N_2–N_1 starts at 149°C ($T_{NI} - 9$°C). Instead, in rubbed ITO cells, this transition is fully depressed. Consequently, smectic order fluctuations exist in C-6 similarly to C-7, C-8 and C-9, even although C-6 does not exhibit a smectic C phase.

Smectic order fluctuations also exist in C-5, as demonstrated by the appearance of a weak texture transition.

However, in C-4, C-3 and C-2 we did not observe any texture transition for the above mentioned types of surfaces. Hence C-5 is the limiting homologue where smectic order fluctuations disappear. We emphasize that these fluctuations diminish with decreasing of the molecular length, and in C-4 they completely disappear. These fluctuations are very sensitive to surface action: in C-5 for a conducting surface, e.g. ITO, they are fully depressed. The experiment has allowed us to find the critical alkyl chain length, corresponding to C-5, where smectic fluctuations start to appear (for higher length) or are deleted (for lower length), even if the smectic phase is absent in the bulk phase diagram. But there is another critical length, corresponding to the inability to build up a smectic phase in the bulk, corresponding to C-6. In fact, when the smectic order fluctuations are not strong enough, only a transition from nematic to crystal phase can take place, exactly as in the case of C-6. From a more general point of view, it would be interesting to perform an experiment with a material (C-16 for example) exhibiting the formation of smectic C directly from the isotropic phase, in order to describe fully the origin and properties of smectic order fluctuations, not only in the nematic, but also in the isotropic phase.

2.3.4. *Surface memorization in the crystal phase*

It is worth noting that the experiments also showed a memorization of the grain texture in the solid state. The crystal phase strongly memorizes the chirality of the system induced in the first spontaneous twisting stage—chiral nematic phase near to the I–N* transition. This is a consequence of the previously described mechanism which implies that during cooling in the bulk the transition N*–N takes place, the surface retaining the elementary chiral grains created close to the isotropic–nematic transition (see figure 1). After further cooling these 'memorizing centres' are stabilized by the crystal, which behaves as a storage medium.

Furthermore, we succeeded in preparing a thin structured film of C-2 with a selective optical activity, by condensing onto an ITO treated glass plate evaporated material consisting of C-2 in the chiral nematic phase. The result is a very thin (in the nm range) solid glass-like film (see figure 8). This film memorizes the selective reflection properties of the mesophase and can act as a selective circular polarizer. Figure 8(*a*) is taken with crossed polarizers, whereas figure 8(*b*) and 8(*c*) are taken with the analyser rotated by ±45° with respect to the previous position. Such a strong memorization of the chiral N* texture in a crystal could be used as a photo-optical medium for data recording and storage, which in turn is important for the preparation of reliable optical disks. Interestingly, different polarizations are
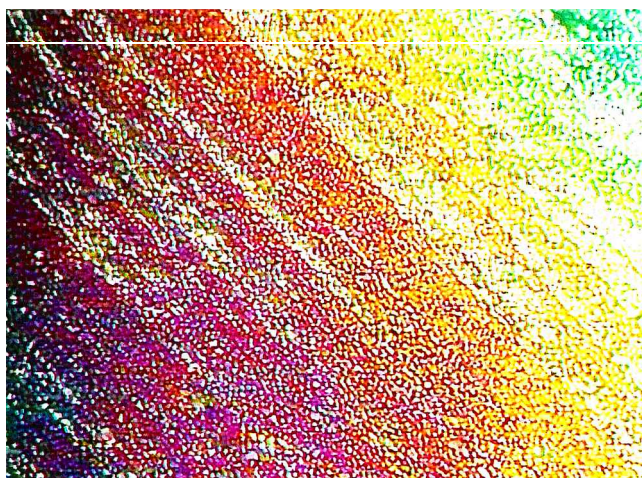
possible. The shape (small ellipsoids) and the size (about 1 μm) of the memorizing grains as nucleation centres are also noticeable.

(*a*)

(*b*)

(*b*)

Also a strong coloured transition (between red and green) induced by temperature has been found, for instance in C-5 oriented by ITO treated plates. This could be explained in terms of macroscopic chirality [21].

3.   Conclusion

Several achiral homologues of the 4-*n*-alkyloxybenzoic acids displaying only the nematic phase were investigated. They were found to exhibit pronounced optical properties of a chiral liquid crystal system. The microtextural analysis indicated that the chiral texture nucleated in small domains or grains in the isotropic phase. The conoscopic cross of these domains was rotated by 45° with respect to the polarizer axis, contrary to the usual nematic drops, whose conoscopic cross is not rotated. Coalescence in the nematic phase close to clearing point gave rise to large chiral monodomains, covered by a very fine stripe texture, as in the case of pure cholesterics with a tilted helix axis. Left- and right-handed chiral domains grouped in regions partially separated by 'oily streaks' are also typical for pure cholesterics. On further cooling, the chiral nematic phase underwent a definite texture transition, becoming a normal nematic. Nevertheless, the small chiral grains formed at the first stage from the isotropic phase are stabilized in a latent state near to the surface, acting as 'memorizing centres'. If the boundaries favour hydrogen bonding, as in the case of hydrophilic surfaces, a twist driven by the surface can then arise in macroscopic regions.

Due to the strong hydrogen bonding with the surface, a twisted smectic B not present in the bulk phase diagram can be generated. We observed this structure for the first time; it was predicted long ago by Demus and Richter, but never found till now.

Figure 8.   Thin (in the nm range) structured film of C-2 with selective optical activity, formed by condensing onto an ITO treated glass plate material evaporated from the chiral nematic phase. This film memorizes the selective reflection properties of the mesomorphic state and could act as a selective circular polarizer. (*a*) Taken with crossed polarizers; (*b*) and (*c*) with the analyser rotated by ±45° with respect to the previous position. Note the shape (small ellipsoids) and size (about 1 μm) of the memorizing grains as nucleation centres.

References

[1] MAIER, W., and SAUPE, A., 1959, *Z. Naturforsch*, **14a,** 889; MAIER, W., and SAUPE, A., 1960, *Z. Naturforsch*, **15a,** 287.

[2] DE GENNES, P. G., 1974, *The Physics of Liquid Crystals* (Oxford: Oxford University Press).

[3] GRULER, H., and MEIER, G., 1973, *Mol. Cryst. liq. Cryst*., **23,** 261.

[4] RONDELEZ, F., 1972, *Solid State Commun*., **11,** 1675.

[5] CARR, E. F., 1972, *Phys. Rev. A*, **12,** 327.

[6] SIMOVA, P. D., and PETROV, M., 1983, *Phys. Stat. Solidi*., **A80,** K 135.

[7] PETROV, M. P., and SIMOVA, P. D., 1985, *J. Phys. D., appl. Phys*., **18,** 293.

[8] BARBERO, G., KOMITOV, L., PETROV, M. P., and STRIGAZZI, A., 1991, *Int. J. mod. Phys. B*, **5,** 2229.

[9] PETROV, M. P., BRASLAU, A., LEVELUT, A. M., and DURAND, G., 1992, *J. Phys. II (Fr.)*, **2,** 1159.

[10] FRUNZA, L., FRUNZA, S., PETROV, M., SPARAVIGNA, A., and TORGOVA, S. I., 1996, *Mol. Mater*., **6,** 215.

[11] PETROV, M. P., ANACHKOVA, E., KIROV, N., RATAIJCZAK, H., and BARAN, J., 1994, *J. mol. Liq*., **61,** 221.

[12] PETROV, M. P., ANTONOVA, K., KIROV, N., RATAIJCZAK, H., and BARAN, J., 1994, *J. mol. Struct*., **327,** 265.

[13] PETROV, M. P., ANTONOVA, K., KIROV, N., RATAIJCZAK, H., and BARAN, J., 1998, *J. mol. Struct*., **444,** 81.

[14] BARBERO, G., EVANGELISTA, L. R., and PETROV, M. P., 1999, *Phys. Lett. A*, **256,** 399.

[15] TORGOVA, S. I., KOMITOV, L., and STRIGAZZI, A., 1998, *Liq. Cryst*., **24,** 131.

[16] PETROV, M. P., and TSONEV, L. V., 1996, *Liq. Cryst*., **21,** 543.

[17] DELOCHE, B., and CABANE, B., 1972, *Mol. Cryst. liq. Cryst*., **19,** 25.

[18] RUEDINGER, A., and STARK, H., 1999, *Liq. Cryst*., **26,** 753.

[19] DRZAIC, P. S., 1999, *Liq. Cryst*., **26,** 623.

[20] DEMUS, D., and RICHTER, D., 1978, *Textures of Liquid Crystals* (Leipzig: V.E.B. Deutscher Verlag für Grundstoffindustrie).

[21] MONTRUCCHIO, B., SPARAVIGNA, A., TORGOVA, S. I., and STRIGAZZI, A., 1998, *Liq. Cryst*., **25,** 613.