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Spontaneous chiral domains in the nematic phase of achiral *trans*-4-alkylcyclohexanecarboxylic acids

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Hotel Palatium, Capri, 11–14 September 1996*

We have discovered a spontaneous chiral ordering in thermotropic nematic liquid crystals forming hydrogen bonds, namely in *trans*-4-alkylcyclohexanecarboxylic acids, which do not contain any chiral group in the molecular structure, and have suggested a possible explanation of this phenomenon. The investigation was performed by polarizing light microscopy, using cells with glass substrates treated to give a uniform planar alignment in the nematic phase. On cooling from the isotropic phase, two types of nematic domains with different alignment were found to grow: some possessing a unidirectional planar orientation as expected, and others with a spontaneous twisted molecular arrangement. The appearance of the twisted domains and the sense of their twist were random, i.e. they always emerged in various regions of the cell with different twist sense: thus, they cannot be regarded as induced by stable defects in the surface aligning film. With the coalescence of the nematic droplets, the number of the domains with the spontaneous twist very quickly decreased, since two chiral domains characterized by different handedness transformed into a racemic domain with uniform planar alignment. Here the explanation of the macroscopic texture is given in terms of molecular structure, based upon the ability of the carboxylic acids to organize through hydrogen bonds into not only dimers, but also trimers and oligomers. The microscopic structure influences the macroscopic twisted organization of the director inside the domains, and the surface lies normally to the helix axis. A brief review is given of work done in the fields of hydrogen bonded liquid crystals and of order transitions, together with a Landau–de Gennes model describing the mechanism of the spontaneous chiral ordering.

1. Introduction

Several substances are mesogenic due only to the fact that the monomeric molecules form intermolecular hydrogen bonds in a certain temperature range, thus organizing closed dimers (i.e. cyclic dimers with two hydrogen bonds) characterized by an appropriately elongated shape. Figures 1(a) and 1(b) illustrate this mechanism for the compound *trans*-4-hexylcyclohexanecarboxylic acid. Such dimer molecules have a core rigid enough for the appearance of a mesophase [1]. Among these materials, some organic acids are mesogens particularly suitable for experimental investigation, since their melting point is on average between room temperature and 100°C. Particularly important are the carboxylic acids containing in the core of the

monomeric molecule one benzene ring [2], and the acids containing one cyclohexane ring, first reported by Schubert *et al.* [3], the latter involving compounds in the *trans*-isomeric configuration.

In the 1980s, there were found in the first kind of these substances some interesting features connected with the appearance of order transitions [4], which were described as anchoring transitions driven by temperature [5, 6].

We decided to investigate by means of optical microscopy the *trans*-4-alkylcyclohexanecarboxylic acids. Our aim was to find whether the previously mentioned order transition, on cooling from a uniformly aligned nematic towards a spontaneously twisted nematic structure, appears also in the compounds with a cyclohexane ring, and if so, to clarify whether it is a bulk or a surface property and to develop a model to explain it.

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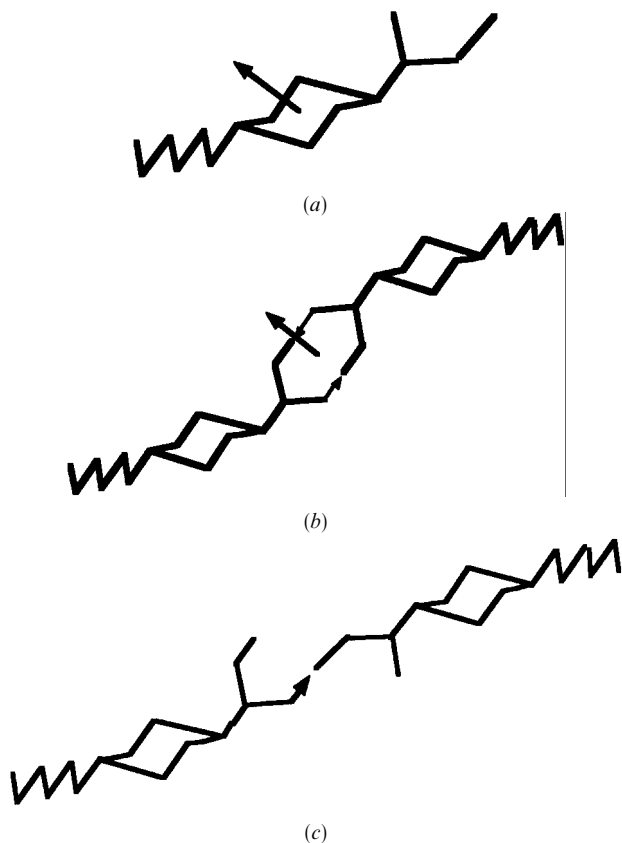


Figure 1. *trans*-4-Hexylcyclohexanecarboxylic acid: scheme of the steric representation of (a) monomer, (b) closed dimer, (c) open dimer.

The present paper is organized in the following way. In § 2 a brief overview on the state-of-the-art is given, in § 3 the experiment is described, and in § 4 the experimental results are discussed, introducing the steric model and its implications. In § 5 the phenomenological model describing the chiral macroscopic structure is presented and its connections with the experiment and with the steric model are stressed. The conclusions are provided in § 6.

2. State-of-the-art

Pioneering work was done by Gray and co-workers on the synthesis of carboxylic acids containing in the core of the monomeric molecule one benzene ring (compounds of the first type [7, 8]) and of the acids containing one cyclohexane ring (compounds of the second type [9, 10]). He focused attention on calorimetric studies of the phase sequences and described the textures. According to the authors, convenient mixtures of new materials of the second type with substances of the first kind can give favourable combinations of physical parameters such as birefringence, dielectric anisotropy,

viscosity, etc. important for optimizing features of electro-optical devices. With the aim of characterizing substances suitable for displays, other researchers measured the dielectric permittivities of both types of materials [11–13]. In the late 1970s, the molecular arrangement of some alkyloxybenzoic acids was investigated by thermal microscopy, dilatometry and X-ray scattering by Blumstein and Patel [14], so obtaining structural parameters such as inter-lamellar distance and molar volume as a function of the number of methylene units of the alkyloxy group. The authors concluded that cohesion in the crystalline state is ensured by dimerized hydrogen bonded molecules, whereas in the smectic phase it is ensured by the attraction between extended aliphatic chains. The effect of intermolecular hydrogen bond formation on the formation of the mesophase was analysed by Volod'ko and Posledovich [15], in the homologous series of *n*-alkyloxybenzoic acids. The authors discovered and reported that the smectic phase of such substances consists not only of dimeric, but also of trimeric and oligomeric species, and that in the smectic phase practically no monomeric molecules are present. Also in cyclohexanol in the solid state, the intermolecular hydrogen bonding was studied by Sciesinska and Sciesinski [16] by analysing the absorption spectra in the far infrared. The latter authors identified several solid phases, characterized by both equatorial and axial conformers, and intermolecular hydrogen bonding. It is noticeable that some of these phases showed closed dimeric configurations, whereas other phases exhibited chain polymeric structures.

The infrared technique was largely applied in studying the dimer concentration in formic acid (deuteriated and not deuteriated) [17], in *p*-heptyloxy- and *p*-octyloxybenzoic acids [18], and in other alkyloxybenzoic acids (e.g. Kirov *et al.* [19]). In reference [17], the difference between the contribution due to hydrogen and deuterium bonds was determined via Raman and IR spectra measurements. In reference [18], the temperature dependence of the infrared spectra was investigated, with reference to the behaviour of the closed dimer contribution. On heating, monomer bands appeared at the smectic–nematic transition. On further heating, bands attributed to open dimers [i.e. dimers with only one hydrogen bond, see figure 1(c) for the same substance as in figures 1(a) and 1(b)] were found in the nematic and in the isotropic phases. Reference [19] was the first attempt to study the concentration of the dimers (both closed and open) as a function of temperature; but measurement uncertainties turned out to be very high with this technique.

We have performed an NMR investigation with the same purpose on *trans*-4-butylcyclohexanecarboxylic acid: the preliminary results are very promising, and

confirm the appearance of open dimers in a narrow temperature range close to the clearing point [20]. We observed also the homologous *trans*-4-hexylcyclohexanecarboxylic acid in another situation: the samples were put into cells with glass plates freshly cleaned and unidirectionally rubbed. If the acids, as in the case of the latter substance, also possessed a smectic phase (in particular, a hexagonal ordered smectic B phase), we observed order transitions. One of them happened on cooling, at a precise temperature ten degrees above the nematic–smectic transition; the unidirectional planar alignment transformed into a multidomain alignment, with the domains twisted with respect to each other [21]. The temperature range of this ordered phase is included in the nematic range, but is contiguous to the smectic range. In this case, we suggested an explanation based on the presence of twisted cybotactic clusters, providing a short range smectic ordering in the nematic phase.

The theoretical problems connected with hydrogen bonds inducing the formation of liquid crystals have been extensively discussed by Sear and Jackson [22], modelling the monomeric molecules as elongated spherocylinders, and taking into account the excluded volume effects and the hydrogen bonding association, with many approximations, having the aim of achieving an analytical theory. Their simplified theory allows the calculation of the phase diagram, which shows very interestingly a re-entrant behaviour. However, it predicts an isotropic–nematic transition for all molecular elongations (monomers included), which is not true for many mesogens, such as several homologues of *p*-alkyloxybenzoic acids and of *trans*-4-alkylcyclohexanecarboxylic acids.

The textural changes of uniformly aligned samples of *p*-alkyloxybenzoic acids were also studied with the infrared technique; see Petrov and Simova [23], and references therein. Some anomalies in the temperature dependence of the elastic constants had already been observed by Rondelez [24] and confirmed in the dielectric and conductivity anisotropies by other researchers [25–27]. Starting from this point, Simova and Petrov [28] found by optical microscopy the existence of a peculiar critical temperature, inside the nematic phase, at which on cooling a well ordered uniform nematic structure changed abruptly into a multidomain texture, exhibiting light scattering of pronounced intensity. Barbero *et al.* [29] showed experimentally that a superimposed twist distortion influences the critical temperature between the two nematic ‘subphases’, and gave a phenomenological model, according to the Landau–de Gennes approach, which describes the observed shift. Such a shift was predicted as due to the variation of the scalar order parameter across the nematic layer

(connected with the presence of cybotactic clusters, not far from the transition smectic C–nematic), and to the fact that a twist deformation is equivalent to a change in the isotropic part of the free energy density.

Later, calorimetric and dielectric investigations also proved in other ways the existence of that critical temperature in some homologous alkyloxybenzoic acids [30]. In other work, Durand and co-workers [31] investigated octyloxybenzoic acid by polarized optical microscopy and X-ray diffraction. They found on cooling the nematic phase, far from the clearing point, the appearance of a spontaneous twisted texture with bifurcation of the surface alignment, and on further cooling a texture instability connected with the formation of elongated smectic A domains at the surfaces. For the existence of such order transitions in the nematic phase, Durand proposed an explanation related to the property of the monomers still present in the mesophase to become bonded to the cell glass surfaces, coated by SiO₂, via hydrogen bonds. Afterwards, Barbero and co-workers [32] discussed, in the spirit of Landau–de Gennes theory, the same experimental results involving two order transitions on cooling, the first from a uniform quasi-homeotropic orientation towards a structure involving twist and tilt, and the second towards a light scattering multidomain texture. More recently, Petrov and Durand [33] studied the mechanism of the spontaneous twist at the surface (covered by SiO₂) observed when cooling samples of heptyloxy- and octyloxy-benzoic acids in the nematic phase. Through the application of an electric field of defined sign parallel to the substrate, the authors biased the twist surface bifurcation, inducing a transition from one to the other bistable state. The explanation was given in terms of order electric polarization close to the surface: the anisotropic depolarizing field due to surface undulations forces the nematic polarization to rotate.

According to the suggestion of these last three studies, the phenomenon of the transition between two nematic ‘subphases’ should be thought of as a particular type of anchoring transition driven by the temperature.

The first observations of surface tilt variations with temperature in a nematic cell were made by Bouchiat and Langevin-Cruchon [34] in the early 1970s: a continuous change was optically detected. Similarly, the surface azimuth variations with temperature as a continuous change were first obtained by Faetti and Fronzoni [35]. Since then, more definite orientation changes have been measured in different geometries and with various substrate treatments; they were recognized as order transitions, i.e. anchoring transitions induced by temperature [36–43]. Phenomenological models have been carried out according to the Landau–de Gennes approach [32, 44–52]. In particular, recently, surface alignment transitions were observed in nematic

liquid crystal cells oriented by means of the SiO evaporation technique, around a two-fold degenerate region [53–58]. In this case both tilt and azimuthal angles undergo a surface transition. Durand and co-workers [53] first described this phenomenon, interpreting it as due to the electrostatic energy related to the order electricity [59, 61]. Such a model was recently used by Petrov and co-workers [31, 33], when dealing with order transitions in alkoxybenzoic acids. In this case, we have to stress that the glass substrate, being covered by a thin layer of SiO, competes with the monomeric molecules still present in the liquid crystal phase in organizing hydrogen bonds with the hydroxyl groups of the monomer itself; hence the monomer density at the surface can be higher than in the bulk, influencing the liquid crystal alignment.

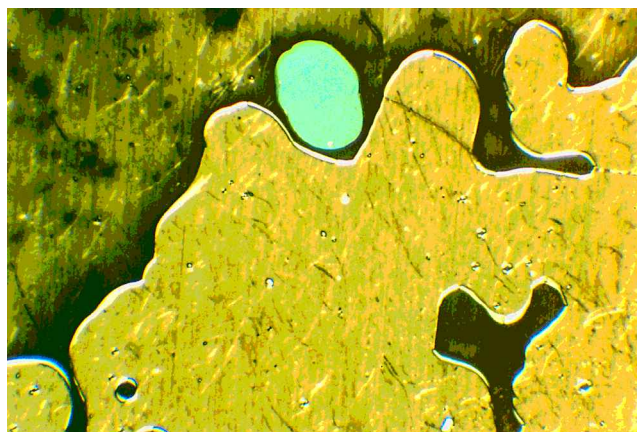
In conclusion, hydrogen bonding and order transitions in liquid crystals are currently a major subject of investigation, from both the fundamental and applied points of view. The study of hydrogen bonding allows researchers to have insight into the molecular steric effect in forming a mesophase, and can be extremely useful for designing new materials for electro-optic devices. The study of order transitions allows us to obtain information on the competition between bulk and surface sources of distortions, and to plan the construction of bi- or multi-stable converters.

3. Experimental

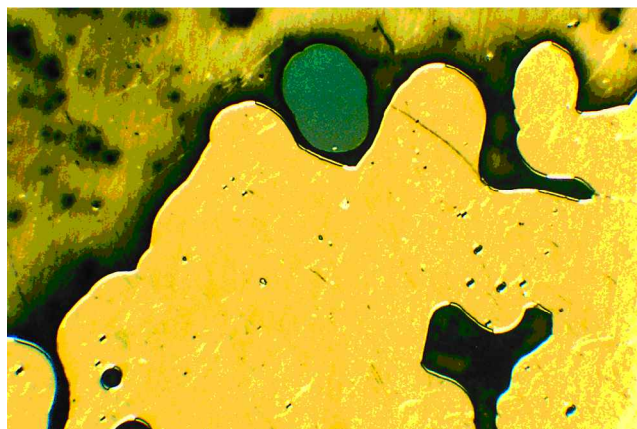
In the experiment, conventional sandwich cells were used. The cells consisted of two parallel glass plates separated by mylar spacers at a distance of about $12\ \mu\text{m}$; cells with a gap of $2\ \mu\text{m}$ were also used. The inner surfaces of the substrates were covered by polyimide and rubbed unidirectionally, in order to obtain a uniform planar alignment. The liquid crystal materials used were *trans*-4-butylcyclohexanecarboxylic acid, *trans*-4-hexylcyclohexanecarboxylic acid, and their eutectic mixture. The monomer structural formulae are $\text{C}_4\text{H}_9\text{C}_6\text{H}_{10}\text{COOH}$ and $\text{C}_6\text{H}_{13}\text{C}_6\text{H}_{10}\text{COOH}$, respectively. The phase sequences of the two compounds and their eutectic mixture were obtained by optical microscopy and DTA observation [1], keeping the materials at a temperature higher than the clearing point for a while before the measurements. For the first substance, the phase sequence was Cr– 36°C –N– 86°C –I; for the second, Cr– 32°C –SmB– 47°C –N– 96°C –I; for the eutectic mixture, it was Cr–(-25°C)–N–(86 – 90°C)–I.

The liquid crystal was introduced into the cell when in the isotropic phase by capillary forces in a vacuum chamber. Then the cell was inserted in a Mettler FP-52 hot stage with temperature control to within 0.1°C . The appearance of the nematic from the isotropic phase, its texture and the local average alignment of the liquid crystal molecules were studied with a polarizing photo-

microscope (Zeiss) and recorded by a digital camera (Sony). The cell was cooled down at the lowest possible rate ($0.2^\circ\text{C}\ \text{min}^{-1}$), to be as close as possible to thermodynamic equilibrium. The nematic phase of the liquid crystal material, on cooling from the isotropic state, first nucleated in small domains which grew in size on decreasing the temperature, and eventually coalesced. We observed that the director alignment in a large part of the domains was unidirectional planar, with a preferred direction coincident with the rubbing direction, as imposed by the pretreatment, whereas in the other parts of domains the alignment was found to be spontaneously twisted. In figures 2(a) and 2(b) is given a



(a)



(b)

Figure 2. Cell, $12\ \mu\text{m}$ thick, viewed between crossed polarizers on cooling from the isotropic phase ($-0.2^\circ\text{C}\ \text{min}^{-1}$), at $\approx 1^\circ\text{C}$ below the clearing point. The yellow region in the centre and lower parts of the picture—(a), shaded yellow, (b) bright yellow—is the main area with unidirectional planar alignment: above, the dark yellow region is the relevant part where nucleation of the nematic phase started from one of the two cell surfaces. The blue domain—(a) bright blue, (b) dark blue/green—is a spontaneous twisted chiral domain. In (a) the sample is rotated by 5° with respect to (b).

sequence of pictures of the sample between crossed polarizers. Each of them corresponds to a certain position of the optic axis in the large planar domain, with respect to the polarizing plane. Complete extinction of the transmitted light can be obtained in that domain, and only in the areas with uniform planar alignment, when the local axis coincides with that of the polarizer (or analyser). On the contrary, there is no position of the cell giving extinction between crossed polarizers of the linearly polarized light transmitted through the domains with a twisted structure. Some domains characterized by a twisted structure appeared and grew in size until they met another domain with uniform planar alignment or a chiral counter-handed domain. Then, the region with the twisted structure quickly collapsed, transforming into a uniformly planar domain. On further cooling, about 2°C below the clearing point, all twisted domains disappeared, and the whole cell exhibited only unidirectional planar oriented areas, with the easy axis more or less coincident with the rubbing direction. Repeating the heating and cooling procedure, we noticed that in all samples the twisted domains appeared only on cooling from the isotropic phase and each time in different places in the cell. Moreover, in the same area of the cell, twisted domains of both handedness were found in different temperature cycles. In conclusion, spontaneous chiral texture arises on cooling, close to the clearing point, in a few small domains, randomly distributed, and with random handedness: such domains vanished some 2°C below the clearing point.

4. Discussion

The main feature of the experiment is the appearance, on cooling from the isotropic phase, below the clearing point but very close to it (within $\approx 1^\circ\text{C}$), of spontaneously twisted domains, whose characteristics are the following:

- (i) they are few in number, occupying a small area, with respect to the more extended regions which are unidirectional planar, according to the polyimide rubbing direction;
- (ii) they occur in random places in different cycles;
- (iii) their handedness is randomly distributed;
- (iv) they survive for only around 2°C below the clearing point, growing and eventually collapsing, due to coalescence;
- (v) they appear only on cooling.

The first feature reflects the fact that the effective local alignment of the liquid crystal is the result of molecular interaction inside the liquid crystal itself and between the liquid crystal and the substrate: in other words, it is the effect of bulk and surface properties of the material. In our cells, both substrates are treated equally,

providing two parallel, in-plane easy axes: hence, if the liquid crystal molecules are not chiral, they have approximately a cylindrical symmetry (as in the case when they are closed dimers), and the resulting alignment in the nematic phase is expected to be unidirectional planar, being dominated by the surface of both substrates, without any competition. However, in the case of chiral molecules, i.e. in the chiral nematic phase, as is well known, such boundary conditions will result in a Grandjean structure (texture with the helix axis perpendicular to the substrates).

In our case, according to experimental observation, in a certain temperature range close to the isotropic–nematic transition, some domains with a chiral macroscopic texture spontaneously appear; in different thermal runs, the domain positions were found to be randomly distributed, and in the same region of the cell twisted domains of both handedness were observed. This means that the formation of the chiral structure is definitely not due to anchoring, not being directly initiated as an effect of the surface treatment. Thus, the chirality origin should be sought in peculiarities of the generation of the nematic phase in the type of compounds under study. In particular, the process of building up intermolecular hydrogen bonds would be expected to play the most important role in the phenomenon.

In fact, hydrogen bonds are involved not only in the formation of dimers from monomers (bulk effect), but also in the formation from monomers of a comb-shaped structure at the interface between liquid crystal and polyimide substrate. The polyimide surface layer indeed competes with the mesogen monomers in attaching to other monomers, preventing or reducing dimer formation at the surface. As a result, the surface is covered by monomers, their aliphatic tails being oriented with a small pretilt with respect to the surface. Thus, the interaction between this monolayer and the remainder of the liquid crystal volume will result in a quasi-planar alignment, with weak azimuthal anchoring, as would be expected. When chirality arises, according to this mechanism, the liquid crystal will adopt the Grandjean texture.

Actually, the observed spontaneously twisted structure is similar to the one very common in cholesterics, i.e. in nematics having a chiral group in the molecule. The same texture for nematics without any chiral group in the molecule was found earlier in alkyloxybenzoic acids [31, 32]; and we were the first to observe it in *trans*-4-alkylcyclohexanecarboxylic acids.

Since all these substances form dimers via hydrogen bonds, we had the idea of interpreting the texture itself as due to features of the dimerization process.

The closed dimer structure is thermodynamically favoured at low temperatures (far from the clearing

point) when, considering two monomeric molecules just about to build up a closed dimer, the rotational kinetic energy of one monomeric molecule with respect to the other, around the axis of one developing hydrogen bond, would be much less than the hydrogen bond energy. However, in the isotropic phase the monomer structure is more favoured for symmetric thermodynamical reasons. As a consequence, to maintain continuity in an intermediate temperature range, namely in our case just below the clearing point, the monomers tend to aggregate on cooling, forming some hydrogen bonds, and then organizing open dimers. Conversely, on heating, in our case from some degrees below the clearing point, the closed dimer structure becomes unstable: some hydrogen bonds break, and a certain concentration of open dimers arises. In another context, we have found, by NMR investigation, direct evidence of the presence of open dimers in *trans*-4-butylcyclohexanecarboxylic acid exactly in the temperature range some degrees below the clearing point; the results will be published elsewhere [20].

The existence and behaviour of the open dimers seem to be the key to the appearance of the chiral macroscopic domains at 'high' temperatures in the nematic phase. The mechanism is now discussed.

On cooling from the isotropic phase, which already contains closed dimers, open dimers and monomers (in amounts sufficient to ensure the absence of any orientational order), the relative concentration of monomers diminishes, crossing the critical value for the appearance of the nematic phase at the clearing point. At the same time, the dimer concentration increases, and the energy of the mutual rotation between two monomeric molecules bonded together in one open dimeric molecule diminishes as well. This enhances the probability of steric interaction between one open dimer and one monomer, or between two open dimers.

At a certain temperature T_2 , on cooling, a small number of open dimers and monomers by mutual interaction form intermolecular hydrogen bonds: in this way they originate oligomers [15, 20] (in particular, trimers and tetramers). Note that, even if the monomer does not contain any chiral group, a trimer is enough to provide a microscopic chirality, either right- or left-handed [see figures 3(a) and (b)]. Moreover, tetramers or other oligomers made with monomers piled one above the other turn out spontaneously to be chiral, of both handednesses; see figures 3(c) and (d). Of course, the probability of forming trimers and tetramers is expected to be greater than for oligomers with a higher number of monomeric constituents. Hence, the oligomers, having a chiral structure of very short pitch (of the order of a hydrogen bond length, 1 Å) play the role of a chiral dopant. The probability of the formation of

left- or right-handed structures is the same. Therefore, the nematic phase of the compounds investigated appears to be in general a racemic mixture (the ground state).

However, in some nematic domains, a fluctuation from the equilibrium distribution of the two chiral species may occur. Therefore, because of the high twisting power of the dopant (consisting of chiral oligomers), a small concentration is enough to create a helical ordering, with short pitch. As a result, several chiral domains are expected to appear in the sample, each of them, with random chirality (pitch of the order of 1–10 μm). The sample as a whole is expected to be mainly a unidirectional planar region containing a racemic set of domains individually of different handedness. On increasing the temperature, the chiral domains vanish, since the oligomers become unstable, due to thermal excitation. On decreasing the temperature, the probability of coalescence of a chiral domain into a unidirectional planar region is high (and the probability of collapse of two differently handed domains increases as well): thus the chiral domains disappear too, at a temperature T_1 . They exist only in a very narrow range T_1 – T_2 (about 2°C) just below the clearing point.

Why do the chiral domains appear only on cooling? The explanation is very simple: on cooling, the rotational kinetic energy in the reference frame of the mass centre of an open dimer decreases, and the probability of matching, between two open dimers which are approaching each other, becomes greater. Conversely, on heating, when the translational movement of the open dimer is increasing, the time when two open dimers are close together and can link is diminished.

5. Theory

Let us consider a cell of thickness d , filled with a *trans*-4-alkylcyclohexanecarboxylic acid in the nematic phase, and consisting for the sake of simplicity of a monodomain, where a chiral Grandjean macroscopic structure, defined by the wave number q , is present in a certain narrow temperature interval T_1 – T_2 (about 2°C) close to the clearing point T_{NI} .

We build up a phenomenological model, in the frame of the Landau–de Gennes approach, assuming as thermodynamical parameters the local azimuth $\phi(z)$ and an oligomer concentration $\rho(z)$ relative to the solution, containing in principle monomers, closed and open dimers, and oligomers. Note that $[x, z]$ is a cartesian frame of reference with the x -axis parallel to the surface buffing direction, and the z -axis normal to the cell plates. In the ideal case, any tilt is supposed to be absent: the cell at room temperature is unidirectional planar, and the planar ordering is kept over all the nematic range and also when some spontaneous twist arises.

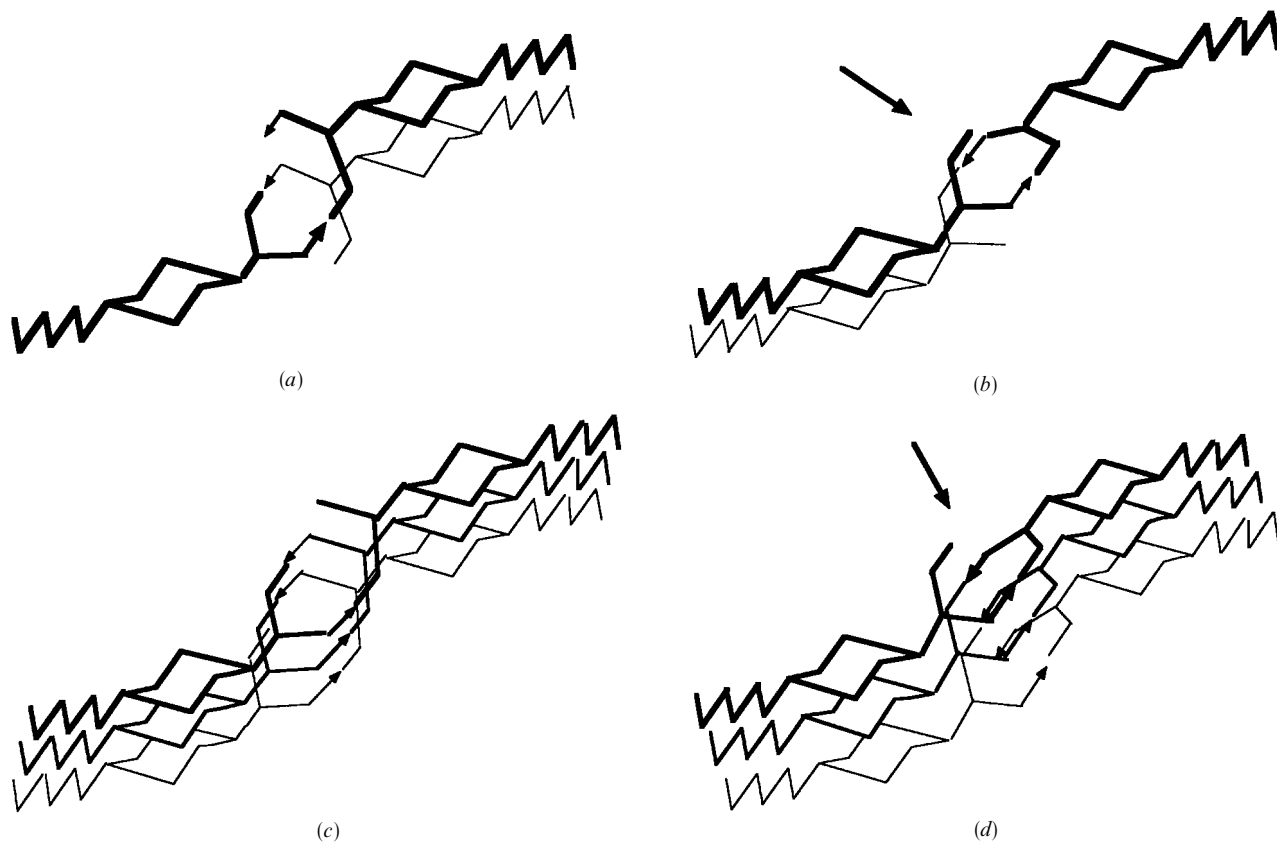


Figure 3. *trans*-4-Hexylcyclohexanecarboxylic acid: steric representation in the case of (a) right-handed trimer, (b) left-handed trimer, (c) right-handed hexamer, (d) left-handed hexamer.

The Landau term in the cell free energy may be written:

$$F_1 = \int_0^d (a_\phi \phi^2 + b_\phi \phi^4 + a_\rho \rho^2 + b_\rho \rho^3 + c_\rho \rho^4 - a_{\phi\rho} \phi^2 \rho^2) dz \quad (1)$$

whereas the elastic term is:

$$F_2 = \int_0^d K_{22}(q - \phi)^2 dz. \quad (2)$$

The integrand of equation (1) represents the free energy density connected to the contribution F_1 , expanded with respect to the local order parameters $\phi(z)$ and $\rho(z)$. In the spirit of the Landau-de Gennes method [62–65], only the coefficients a_ϕ and a_ρ , belonging to the leading terms in the expansion, are dependent on temperature. The coupling coefficient $a_{\phi\rho}$ must be positive, since the presence of oligomers ($\rho > 0$) is the condition for the appearance of chiral domains.

In the simple case of strong planar-anchoring and very weak azimuth-anchoring, the surface energy F_w vanishes, and the cell free energy reduces to [65]

$$F = F_1 + F_2. \quad (3)$$

The minimization of F implies the separate minimization of the elastic term which, due to the form of equation (2), provides:

$$\phi = qz \quad (4)$$

putting $\phi(0) = 0$, according to the rubbing direction, without any loss of generality.

Let us neglect the variation of the oligomer concentration at the surfaces, due to absorption: ρ is assumed to be independent of z , and equation (3) reads

$$F = F_2 = \int_0^d \{a_\phi q^2 z^2 + c_\phi q^4 z^4 + a_\rho \rho^2 + b_\rho \rho^3 + c_\rho \rho^4 - a_{\phi\rho} q^2 \rho^2 z^2\} dz \quad (5)$$

and finally

$$F = \frac{1}{2} A_Q Q^2 + \frac{1}{4} C_Q Q^4 + \frac{1}{2} A_\rho \rho^2 + \frac{1}{3} B_\rho \rho^3 + \frac{1}{4} C_\rho \rho^4 - \frac{1}{2} \alpha Q^2 \rho^2 \quad (6)$$

where the phenomenological coefficients, linear with the

cell thickness, are given by:

$$\begin{aligned} A_Q &= \frac{2}{3} a_\phi d \\ C_Q &= \frac{4}{5} c_\phi d \\ A_\rho &= 2a_\rho d \\ B_\rho &= 3b_\rho d \\ C_\rho &= 4c_\rho d \\ \alpha &= \frac{2}{3} a_\phi \rho d \end{aligned} \quad (7)$$

and the adimensional parameter

$$Q = qd \quad (8)$$

is the reduced helix wavenumber. Hence, Q and ρ characterize the ‘chiral’ macroscopic structure of the nematic liquid crystal and can be regarded as reduced thermodynamical order parameters.

In equation (6), only even powers of Q are present: when $Q > 0$ is a solution of (6), then $Q < 0$ is a solution as well. This describes the random character of the chirality handedness. Furthermore, note that ρ is not subjected to the constraint of parity, and thus odd powers of ρ must also appear in the expansion: only the linear term is always absent, since $\rho = 0$ can describe, in certain temperature intervals, an equilibrium condition.

By minimizing the cell free energy with respect to the reduced order parameters, we obtain:

$$\frac{\partial F}{\partial Q} = Q(A_Q + C_Q Q^2 - \alpha \rho^2) = 0 \quad (9)$$

$$\frac{\partial F}{\partial \rho} = \rho(A_\rho + B_\rho \rho + C_\rho \rho^2 - \alpha Q^2) = 0. \quad (10)$$

These equations show immediately that the unidirectional planar alignment ($Q = 0$) is a solution when the oligomers’ relative concentration vanishes ($\rho = 0$).

For the stability of the alignment equilibrium configuration, the zero-th and first rank quadratic forms of second order derivatives must be positive [67], for example:

$$\frac{\partial^2 F}{\partial Q^2} = A_Q + 3C_Q Q^2 - \alpha \rho^2 > 0 \quad (11)$$

$$\frac{\partial^2 F}{\partial \rho^2} = A_\rho + 2B_\rho \rho + 3C_\rho \rho^2 - \alpha Q^2 > 0 \quad (12)$$

$$H \equiv \frac{\partial^2 F}{\partial Q^2} \frac{\partial^2 F}{\partial \rho^2} - \left(\frac{\partial^2 F}{\partial Q \partial \rho} \right)^2 > 0. \quad (13)$$

Let us analyse what happens to the sample in the nematic range. Outside the narrow interval T_1 – T_2 close to

the clearing point, equations (9) and (10) must provide $Q = 0$ as a stable solution, since no chiral structure was observed there. Moreover, the presence of open dimers was detected by NMR investigation [20] only in that interval T_1 – T_2 : hence the oligomer’s relative concentration ρ must also vanish outside it.

For the stability of this ‘null’ solution, the conditions (11) and (12) have to be verified, which implies as a consequence the validity of inequality (13).

This means that

$$A_Q > 0 \quad (14)$$

$$A_\rho > 0 \quad (15)$$

with A_Q and A_ρ dependent on temperature. When ρ is different (or equal) to zero, Q also behaves in the same manner: both parameters are simultaneously different from zero in the narrow range T_1 – T_2 , vanishing on both sides of T_1 – T_2 . The easiest way to describe such a behaviour is to refer to a conventional thickness $d = 1 \mu\text{m}$: in this case, it is possible to assume $A_Q = A_\rho \equiv A$ [68]. In this way, the direct transition from the nematic ‘disordered’ state [$Q = 0, \rho = 0$] to the ‘bi-ordered’ state [$Q \neq 0, \rho \neq 0$] takes place via a second order transition, as recognized in another context by Benguigui [69]. It is convenient to set up A as a parabolic function of the temperature, based on a reference temperature T^* taken in the nematic phase near to the clearing point:

$$A_Q = A_\rho \equiv A = a \left(\frac{T}{T^*} - 1 \right) + b \left(\frac{T}{T^*} - 1 \right)^2 \quad (16)$$

with $a > 0, b > 0$ and $a/b = 10\%$. The ‘null’ solution [$Q = 0, \rho = 0$] turns out to be stable when

$$\left. \begin{aligned} T < T^* \left(1 - \frac{a}{b} \right) &\equiv T_1 \\ T > T^* &\equiv T_2 \end{aligned} \right\} \quad (17)$$

and the minimum value of the leading parameter A , reached at a temperature $T_m = (T_1 + T_2)/2$, is given by

$$A_m = -\frac{a^2}{4b} < 0. \quad (18)$$

On the other hand, since inside the range T_1 – T_2 both ρ and Q are different from zero, the relations (9) and (10) provide, in this temperature interval:

$$A + C_Q Q^2 - \alpha \rho^2 = 0 \quad (19)$$

$$A + B_\rho \rho + C_\rho \rho^2 - \alpha Q^2 = 0 \quad (20)$$

and for the configuration stability, conditions (11) and

(12) are

$$C_Q > 0 \quad (21)$$

$$C_\rho > 0, \quad B_\rho > 0 \quad (22)$$

giving C_Q , C_ρ and B_ρ positive. Moreover, from the condition concerning the positivity of the quadratic form (13), the inequality

$$B_\rho C_Q + 2(C_Q C_\rho - \alpha^2)\rho > 0 \quad (23)$$

is obtained. By simple inspection, equation (23) is always satisfied if α obeys the constraint

$$\alpha \leq (C_Q C_\rho)^{1/2}. \quad (24)$$

Subtracting equation (19) from (20) we get

$$B_\rho \rho + (\alpha + C_\rho)\rho^2 - (\alpha + C_Q)Q^2 = 0. \quad (25)$$

On the other hand, equation (19) gives:

$$Q^2 = \frac{\alpha \rho^2 - A}{C_Q}. \quad (26)$$

At this point, putting equation (26) into (25), the following second degree characteristic equation is deduced

$$(C_Q C_\rho - \alpha^2)\rho^2 + B_\rho C_Q \rho + A(\alpha + C_Q) = 0 \quad (27)$$

giving only one positive solution for the relative concentration of the oligomers ρ , provided inequality (24) is strictly satisfied:

$$\rho = \frac{-B_\rho C_Q + [(B_\rho C_Q)^2 - 4(C_Q C_\rho - \alpha^2)A(\alpha + C_Q)]^{1/2}}{2(C_Q C_\rho - \alpha^2)}. \quad (28)$$

Afterwards, substituting equation (28) into (26), the reduced wavenumber Q is obtained. We stress the fact that the inequality $A(T) < 0$ is always satisfied inside the interval T_1-T_2 , while the leading parameter $|A(T)|$ vanishes at $T-T_1$, and T_2-T at the left- and right- extremes of the same interval, respectively.

In order to evaluate reliable estimates of Q and ρ , let us assume, as allowable ratios of the phenomenological parameters: $B_\rho/a = 10^{-1}$, $C_Q \sim C_\rho$, $C_\rho/B_\rho = 10^{-1}$. We will distinguish two limiting cases, having different values of the coupling factor: $\alpha = 0$ and $\alpha = (C_Q C_\rho)^{1/2}$.

First case: $\alpha = 0$. In this situation, equation (28) reduces to

$$\rho = \frac{B_\rho}{2C_\rho} \left[-1 + \left(1 - \frac{4AC_\rho}{B_\rho^2} \right)^{1/2} \right] \quad (29)$$

and since, due to the assumptions made about the expansion parameters, the second term under the square root is much smaller than one, the approximate value of the relative concentration of oligomers can be derived

as:

$$\rho \cong -\frac{A}{B_\rho}. \quad (30)$$

From equation (26) it is possible to obtain the value of the reduced wavenumber Q , which turns out to be uncoupled with respect to ρ , and is:

$$Q = \pm \left(\frac{-A}{C_Q} \right)^{1/2}. \quad (31)$$

In the range T_1-T_2 , $A(T) < 0$ has a parabolic behaviour (16), vanishing at $T = T_1$, $T = T_2$: its minimum value is given by relation (18). Correspondingly, the two order parameters reach their maximum values, which read:

$$\rho_M = \frac{a^2}{4bB_\rho} \cong 0.25\% \quad (32)$$

$$Q_M = \pm \frac{a}{2(bC_Q)^{1/2}} = \pm 1.6 \quad (33)$$

giving a minimum pitch $p_m = (\pi/Q_M) \mu\text{m} \cong \pm 2.0 \mu\text{m}$.

Second case: $\alpha = (C_Q C_\rho)^{1/2}$. When condition (24) transforms into the equality $\alpha = (C_Q C_\rho)^{1/2}$ as a limit, the relation (28) is no longer valid, and equation (27) degenerates into a linear equation, giving simply:

$$\rho = -\frac{A}{B_\rho} \left[\left(\frac{C_\rho}{C_Q} \right)^{1/2} + 1 \right]. \quad (34)$$

From equation (26) it is possible to obtain the value of Q , which in this case turns out to be coupled to ρ . We eventually get for Q^2 the following square dependence on A :

$$Q^2 = \left(\frac{C_\rho}{C_Q} \right)^{1/2} \left[\left(\frac{C_\rho}{C_Q} \right)^{1/2} + 1 \right]^2 \left(\frac{A}{B_\rho} \right)^2 - \frac{A}{C_Q}. \quad (35)$$

The parameter maxima are calculated as $\rho_M = 0.5\%$, $|Q_M| = 1.7$. The minimum pitch resulting is $p_m = (\pi/Q) \mu\text{m} \cong \pm 1.8 \mu\text{m}$; the order of magnitude is the same as in the previous case.

What happens in both cases to the reduced wave number, when the temperature is approaching the extremes of the interval T_1-T_2 ? The parameter $|Q|$ goes to zero with the square root of $(T-T_1)$, (T_2-T) , as usually occurs when the transition is of second order.

6. Conclusions

In the framework of the investigations carried out on two main subjects: *liquid crystals exhibiting mesophases due to hydrogen bonds* and *order transitions in liquid crystals*, we have shown that spontaneous chiral domains appear close to the clearing point in the N phase on cooling in non-chiral *trans*-4-alkylcyclohexanecarboxylic acids. The effect is discussed in term of the formation of

ordered helix-like oligomeric structures, left- or right-handed, built up from open dimers by means of intermolecular hydrogen bonds. The polyimide coating, covering the glass substrates, gives indirectly a weak planar alignment to the liquid crystal molecules, forming hydrogen bonds with the monomers; this mechanism simply orients the helix axis of the chiral domain perpendicularly to the cell plates. The chiral domains are stable only over a narrow temperature range: on further cooling they coalesce into unidirectional planar aligned regions. We have provided a phenomenological model, describing the experimental features. By this model an estimate of the helix wavenumber and the oligomers' concentration is obtained, and the second order character of the transitions investigated is recognized.

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