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Online publication date: 29 June 2010

To cite this Article Jakli, A. and Saupe, A.(1997) 'Indication of ferroelectricity in columnar mesophases of pyramidic molecules', Liquid Crystals, 22: 3, 309 — 316
To link to this Article: DOI: 10.1080/026782997209379
URL: http://dx.doi.org/10.1080/026782997209379

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LIQUID CRYSTALS, 1997, VOL. 22, NO. 3, 309–316

Indication of ferroelectricity in columnar mesophases of pyramidic molecules§

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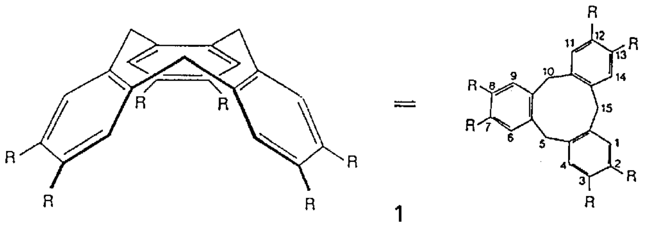
(*Received 29 September 1996; accepted 28 October 1996*)

We have synthesized and studied trisbenzocyclononenes carrying six chiral side chains. They are pyramidic shaped molecules exhibiting columnar mesophases. The optical and electro-optical effects of this chiral pyramidic compound have been studied. A homeotropic alignment of the columnar phase was achieved by cooling the film between plates treated with octadecyltriethoxysilane in the presence of a d.c. field. A transient optical effect was observed with these films on electric field reversal. Simultaneously there was a peak in the time dependence of the electric current flowing through the sample. The observations indicate that the columnar phase is ferroelectric with the polarization parallel to the optical axis. A few degrees below the clearing point, the time for polarization reversal is in the range of seconds and the magnitude of the polarization is $10\,\mathrm{mC\,m^{-2}}$. An electroclinic effect was observed for films with fan textures.

1. Introduction

The occurrence of ferroelectricity in columnar phases of disc-shaped mesogens was predicted by Prost [1]. As a prerequisite for this phenomenon the disc-like molecules have to be chiral and lie tilted with respect to the column axis. The first experimental verification of ferroelectricity in a columnar phase was made in 1992 by Bock *et al.* [2] on a dibenzopyrene with eight chiral side chains. Ferroelectric behaviour was also proved recently with smaller molecules consisting of phenanthrene cores with six chiral side chains [3]. In these tilted columnar phases, the spontaneous polarization is parallel to the C_2 symmetry axis, i.e. perpendicular to the column axis and the tilt plane. A ferroelectric polarization along the column axis was also predicted for pyramidic or bowl shaped mesogens [4]. The bowl shaped molecules may stack in pyramidic columns with a net electric polarization parallel to the column axis [5]. Both ferroelectric and antiferroelectric arrangements of the columns are compatible with rectangular lattices; for hexagonal lattices the antiferroelectric order is not possible [4].



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§Presented in part at the 5th International Conference on Ferroelectric Liquid Crystals, 23–27 July 1995, Cambridge, UK.

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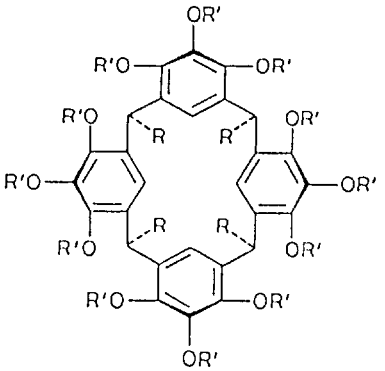
At present only a few types of bowl shaped mesogens are known: trisbenzocyclononenes **1** [5–9], metacyclophanes **2** [10] and metallomesogenic vanadyl Schiff's base complexes **3** [11,12]. In principle they all satisfy the structural requirement to generate a hexagonal columnar superstructure with axial polarity, but so far the existence of any spontaneous polarization has not been demonstrated.

We have synthesized derivatives of trisbenzocyclononenes with six chiral side chains (**6c**,**d**). We chose this core because an 'umbrella-like' conformational inversion of the nine membered ring system (**4**) has been reported in columnar phase by Malthete and Collett [7]. We made optical and electro-optical studies on samples with fan shaped and homeotropic textures, and found evidence that the material has a spontaneous polarization along the optical axis.



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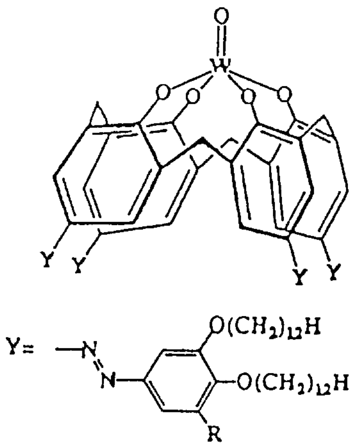

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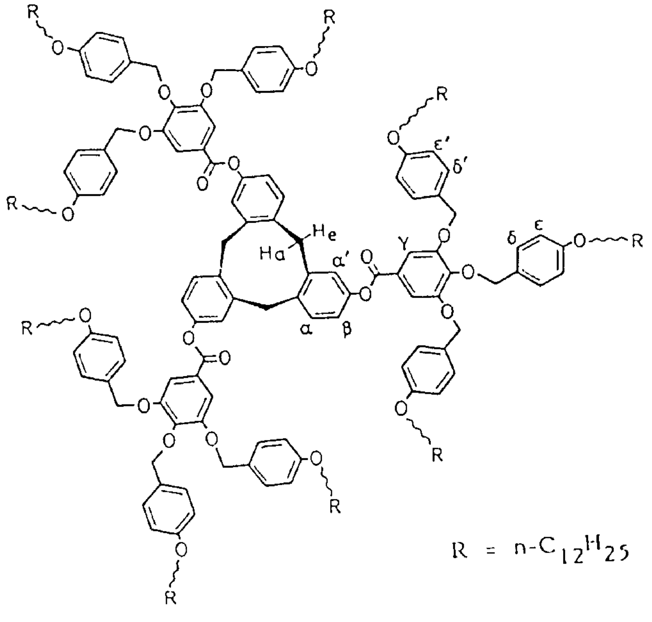

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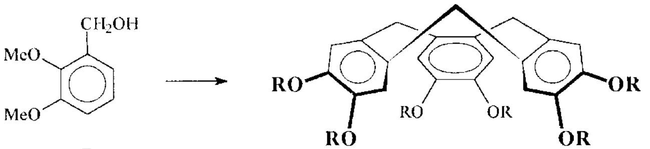
2. Experimental

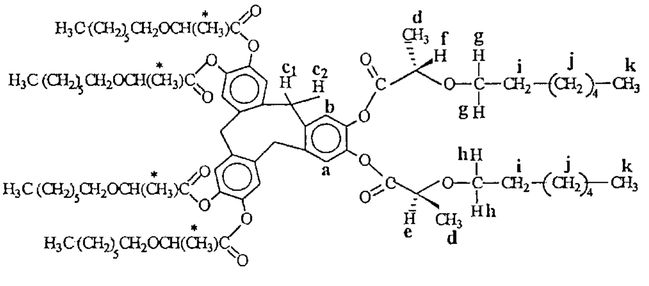
2.1. *Synthesis*

The starting compound for the synthesis of **6c**,**d** was 2,3-dimethoxybenzyl alcohol **5**, which was submitted to Friedel Crafts alkylation to afford the tris(4,5-dimethoxybenzo)cyclononene **6a**. Demethylation using BBr_3 in CH_2Cl_2 yielded the hexahydroxy compound **6b**, which on reaction with the appropriate acids under mild Steglich esterification conditions gave the hexaesters **6c**,**d**.

Both compounds exhibit broad range enantiotropic mesophases from below room temperature up to 113°C and 172°C, respectively (see the table). Only one type of columnar phase showing a pseudo-focal-conic fan texture was observed under the microscope.

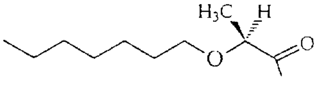
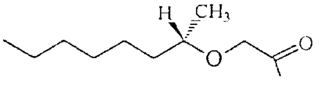


5 **6 a-d**



6c

Table 1. Transition temperatures for the compounds **6a–d**.

Compound	*R*	Phase trans./°C
6a	$-CH_3$	Cr 231–232·7 I
6b	H	
6c		$\mathrm{Col}\underset{98\cdot6}{\overset{113}{\rightleftharpoons}}\mathrm{I}$
6d		$\mathrm{Col}\underset{150}{\overset{172}{\rightleftharpoons}}\mathrm{I}$

2.2. *Analytical data*

The ^1H NMR spectra of compounds **6c** and **6d** show some interesting features. Whereas in compound **6a** one singlet is observed for all six methoxy groups and one singlet for the aromatic protons, in **6c** and **6d** the aromatic protons are no longer equivalent (H_a and H_b in **6c**). Furthermore, there are two quartets for the single proton at the chiral centre of the side chains (H_e and H_f). For one of the non-equivalent methylene protons α to the ether linkage (H_g and H_h), two signals (dt) with different chemical shifts also occur. To prove whether steric hindrance involving the adjacent side chains, due to their chiral branching, might be the reason for the doubling of the signals, we recorded temperature dependent NMR spectra using C_6D_6 and $(D_3C)_2SO$. In both cases, no coalescence was observed up to 350 K using C_6D_6 and up to 393 K using D_6-DMSO. Accordingly, we interpret the phenomenon as a diastereotopic effect. Each chiral side chain has a different environment as compared with its adjacent side chain.

2.2.1. *(S)-Tris[4,5-di-(2-methyl-3-oxadecanoyloxy)benzo]cyclononene* (**6c**)

^1H NMR ($CDCl_3$) d=0·87 (t, J=6·8 Hz, 18 H_k), 1·22–1·40 (m, 48 H_j), 1·53 (d, J=6·8 Hz, 18 H_d), 1·61 (quint, J=7·2 Hz, 12 H_i), 3·41/3·67 (ABt, J=8·8 u. 6·5 Hz, 3 H_g u. 3 H_h), 3·42/3·67 (ABt, J=8·8, 11·7 Hz, 3 H_g u. 3 H_n), 3·72/4·27 (AM, J=14 Hz, 3H_{C1} u. 3H_{C2}), 4·09 (q, J=6·8 Hz, 3 H_e), 4·14 (q, J=6·8 Hz, 3H_f), 7·17 (s, 3H_b), 7·24 (s, 3H_a). IR ($CHCl_3$) ν/cm^{-1}: 2988, 2956, 2930, 2872, 2558 (–C–H), 1782, 1775 (C=O), 1502 (Ar), 1120 (–C–O–C); $[\alpha]_D = -77{\cdot}2°$ (1 mg ml^{-1} $CHCl_3$). See the table for phase transition data.

2.2.2. *(R)-Tris[4,5-di(4-methyl-3-oxadecanoyloxy)benzo]cyclononene* (**6d**)

^1H NMR ($CDCl_3$) d=0·9 (m, 18H), 1·18 (d, J=6 Hz, 9H), 1·19 (d, J=6 Hz, 9H), 1·20–1·44 (m, 48H), 1·6–1·85 (m, 12H), 3·65 (m, 6H), 4·24/4·50 (AB, J=15·8 Hz, 12H), 3·70/4·76 (AB, J=14 Hz, 6H), 7·18 (s, 3H), 7·20 (s, 3H). IR ($CHCl_3$) ν/cm^{-1}: 2980, 2932, 2872, 2857 (–C–H), 1792 (C=O), 1653, 1520 (Ar), 1190 (–C–O–C); $[\alpha]^{23}_D = -9{\cdot}8°$ (1 mg ml^{-1} $CHCl_3$). See the table for phase transition data.

2.3. *Physical properties*

We have studied the textures and electro-optical properties of the columnar phase of compound **6c**. Samples were prepared as 6 µm and 8 µm thick films between glasses coated on their inner surfaces with transparent indium tin oxide (ITO). For some experiments the surfaces were coated in addition with octadecyltriethoxysilane (ODS) which with calamitic phases encourages the director to align normal to the plates.

On cooling a typical fan-like texture appeared in the columnar phase for samples between ITO coated glasses. In the nearly circular fan-like domains, the columns are in the plane of the film [13] and the optical axis has a tangential distribution. In samples, where the inner surfaces were coated also with ODS, in addition to the fan-like domains, spindle like *bâtonnets* formed with straight defect lines in the centre (figure 1). Figure 2 shows part of a *bâtonnet* with a defect line. The whole domain is black between crossed polarizers when the centre line is parallel to the polarizers. With increasing distance from the centre line the alignment turns homeotropic.

The fan textures showed weak switching under fields of 10 V $\mu\mathrm{m}^{-1}$ but only near the clearing temperature. The black crosses in the fans rotated back and forth by less than ±5° following the polarity of the applied field. The effect is much weaker than that observed in other ferroelectric columnar phases [2, 3]. In the temperature region where the columnar and isotropic phases coexisted, fans of different sizes floated in the isotropic regions. Under strong fields, the structure of such fans

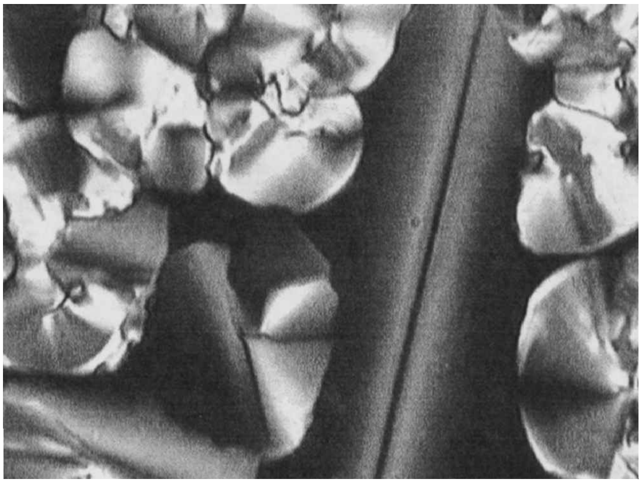


Figure 1. Typical texture between crossed polarizers after cooling without a field; grey spindle-like *bâtonnets* with dark straight central lines and fan shaped domains coexist. $T=23°\mathrm{C}$, $d=8\,\mu\mathrm{m}$, substrates are coated with octadecyltriethoxysilane; the picture represents $0{\cdot}5\,\mathrm{mm}\times 0{\cdot}3\,\mathrm{mm}$ area.

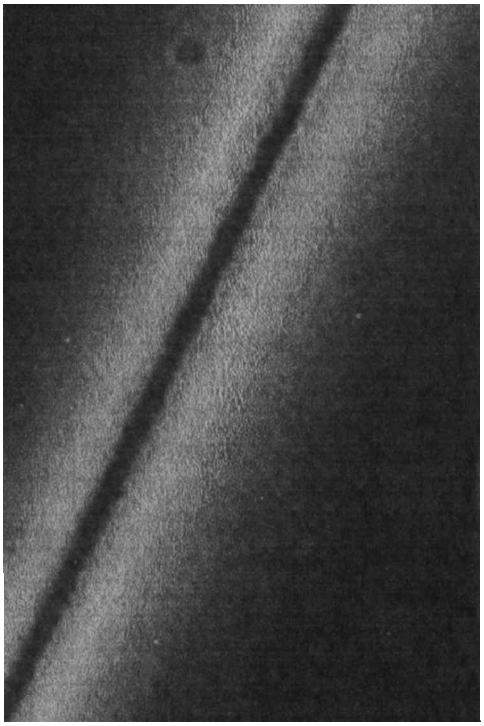


Figure 2. Photomicrograph of one single *bâtonnet*; the crossed polarizers are parallel to the edges of the picture. Area is $150\,\mu\mathrm{m}\times 100\,\mu\mathrm{m}$, $T=23°\mathrm{C}$, $d=8\,\mu\mathrm{m}$, substrates are coated with octadecyltriethoxysilane.

became deformed; typically the smaller fans responded more strongly. Domains with diameter comparable to the sample thickness periodically changed their appearance between fan and *bâtonnet* like textures. The fan like domains have a circular shape, whereas the bâtonnets are elongated; the texture change is accompanied by flow. The turning around of the small liquid crystal domains and their positions is slightly irregular, but strongly correlated to the field reversals. We observed that the fans deformed and gradually became homeotropic in the frequency range between 2 and 5 Hz and above $10\,\mathrm{V}\,\mu\mathrm{m}^{-1}$.

The ODS coated samples could be aligned to give an almost perfect homeotropic texture (see figure 3 (*a*)) when a DC field larger than $10\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ was applied on cooling slowly to the columnar phase ($<0{\cdot}5\,°\mathrm{C}\,\mathrm{min}^{-1}$). Cooling further to room temperature without a field gave a slightly birefringent domain texture with irregular shaped domains of typically $10\,\mu\mathrm{m}$ size (see figure 3 (*b*)). Even at elevated temperatures, the homeotropic texture relaxed slowly (within 24 h) to a slightly birefringent domain texture, but this reformed when the field was reapplied. Within a few hours after field removal, no optical effect is observed in a homeotropic texture when a field of the same direction is reapplied. With a field of reverse polarity, a transient birefringent texture appears in a few seconds and disappears in tens of seconds. The transient, weakly birefringent domain texture is shown in figure 3 (*c*). The time dependence of the transmittance at 93°C under $\pm 75\,\mathrm{V}$ is shown in figure 4. The time to reach maximum intensity (rise time) depends on the applied voltage and temperature. Figure 5 shows the voltage dependence of the rise time at $T=94°\mathrm{C}$. Below 50 V, the contrast is too low and the rise time is too large to measure accurately. The temperature dependence of the rise time is shown in figure 6, where $\ln(\tau)$ is plotted against $1/T$. From the curve, the apparent activation energy is estimated to be $3{\cdot}8\times 10^{-19}\,\mathrm{J}$ ($48{\cdot}7\,\mathrm{kcal\,mol}^{-1}$). This value is comparable to that observed by Malthete and Collett for optically active trisbenzocyclononene structures [7].

In the homeotropic texture a transient electric current peak, with relaxation time of the order of the rise time of the transient optical effect, was observed upon field reversal. The time dependence of the applied voltage and the electric current flowing through the sample are

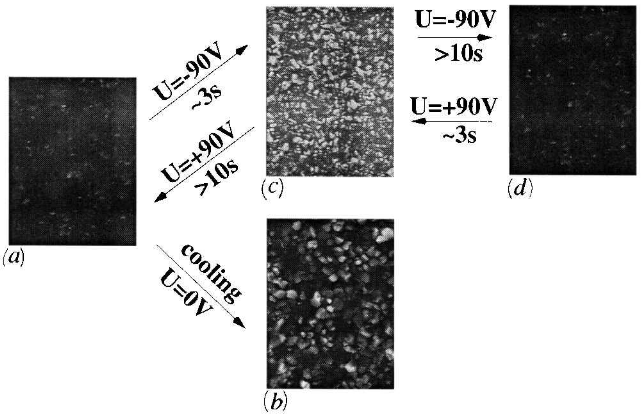


Figure 3. Polarizing photomicrographs of textures; $d = 8\,\mu$m, substrates are coated with ODS. (*a*) $T = 94°$C, obtained on cooling at 0·5°C min^{-1} from the isotropic phase while a d.c. field of 90 V was applied; (*b*) after field removal and cooling to room temperature; (*c*) transient texture at $T = 94°$C, 3 s after the polarity of the d.c. field of 90 V is reversed; (*d*) homeotropic texture relaxed (>10 s) from texture (*c*). Starting from texture (*d*) (which is the same as texture (*a*)), texture (*c*) appears 3 s after $U = +90$ V is applied and relaxes to texture (*a*) after more than 10 s.

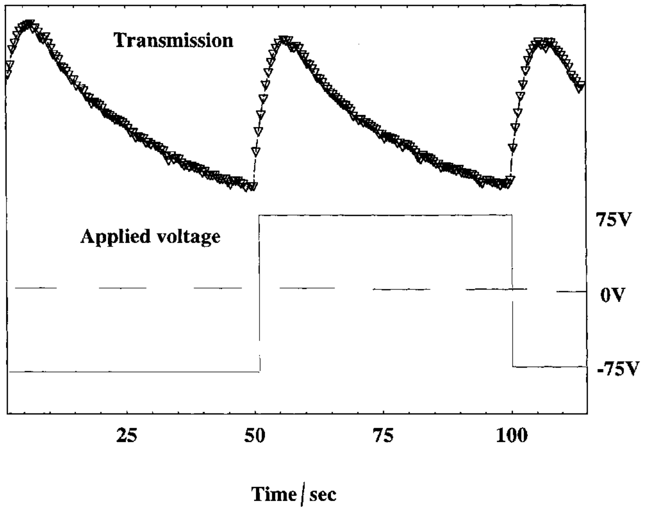


Figure 4. Time dependence of the transmittance at 93°C under applied rectangular voltages of 75 V ($d = 8\,\mu$m).

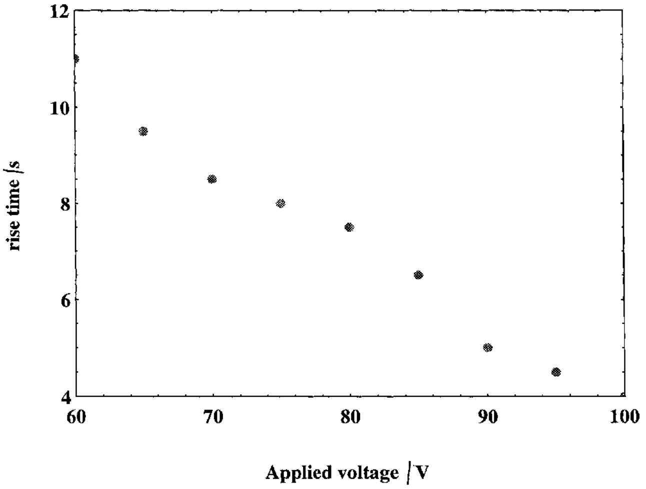


Figure 5. Voltage dependence of the rise time at $T = 94°$C, defined as the time between field reversal and maximum transmittance ($d = 8\,\mu$m).

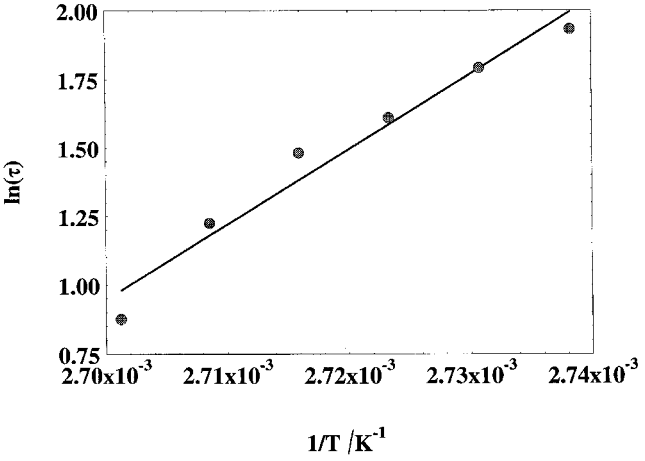


Figure 6. Temperature dependence of the switching time; $\ln(\tau)$ plotted against $1/T$, $U=90$ V. From the slope of the linear fit, the apparent activation energy is $3{\cdot}8\times10^{-19}$ J.

shown in figure 7; the constant background current is due to the conductivity. Deducting this background, we calculated the surface charge per unit area by time integration of the current peak; the charge per unit area as a function of temperature is shown in figure 8. During variation of the temperature, the amplitude of the voltage step was kept constant. Above 90°C, the measured charge per unit area was independent of the voltage above 70 V. A current peak was observed with much smaller decay times and with time integral values an order of magnitude smaller even in the isotropic phase. Of course, here no texture could be observed under the

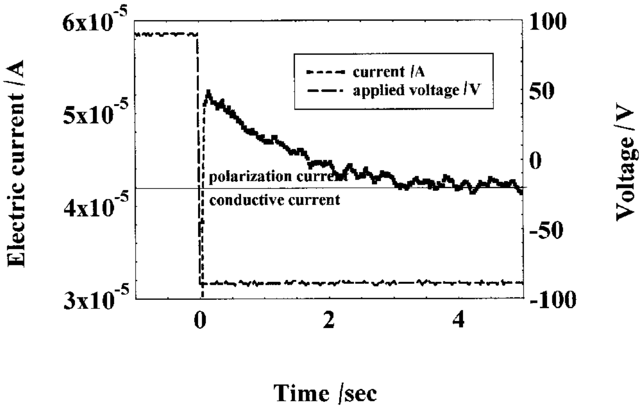


Figure 7. Time dependence of the electric current after field reversal. Sample area is 5 cm^2, $d=8\,\mu$m, $T=99$°C. The background value, $I(\infty)$ is due to the conductivity; in the present case it is 7×10^{-9} $(\Omega\text{m})^{-1}$. The signal is obtained after averaging 8 cycles with a digitizing scope.

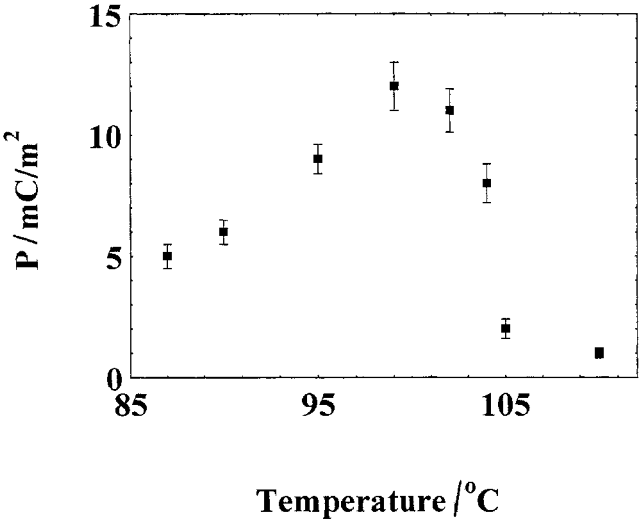


Figure 8. Temperature dependence of the charge per unit area (P) deduced from the electric current $I(t)$ flowing through the sample after reversing the polarity of $U=90$ V. The charge per unit area is calculated as $P=(2A)^{-1}\int_0^\infty (I(t)-I(\infty))\mathrm{d}t$.

polarizing microscope. There was no measurable current peak under unipolar driving conditions (voltage is varied between zero and $U \sim 70$–120 V periodically and stepwise). The current peak appeared only when the polarity of the field was reversed. There was also no current peak observed in samples with fan shaped textures up to 110 V. In this case the value of the constant current was about three times smaller than the background current in the homeotropic texture.

3. Discussion

At the transition from the isotropic phase on cooling, *bâtonnets* form which presumably have a spindle-like structure in that the columns form parallel circles centred on a straight singular line which forms the axis of the *bâtonnet*. Fan textures have a similar basic structure with the defect at the origin perpendicular to the film. Figure 1 shows domains with fan textures and a section with a defect line parallel to the plane of the film. As the distance from the centre line becomes large compared with the film thickness, the texture turns homeotropic (see figure 9).

On cooling a cell with silane coated surfaces, under application of a strong d.c. field ($> 10\ \mathrm{V\,\mu m^{-1}}$), a uniform homeotropic texture is obtained. No uniform homeotropic texture can be obtained under application of a.c. fields. This indicates that the electrically polarized columns are aligned parallel to the field, as expected for a uniaxial ferroelectric material with a spontaneous polarization parallel to the column axes. This structure is similar to the structure proposed for the columnar phase of non-chiral derivatives [4].

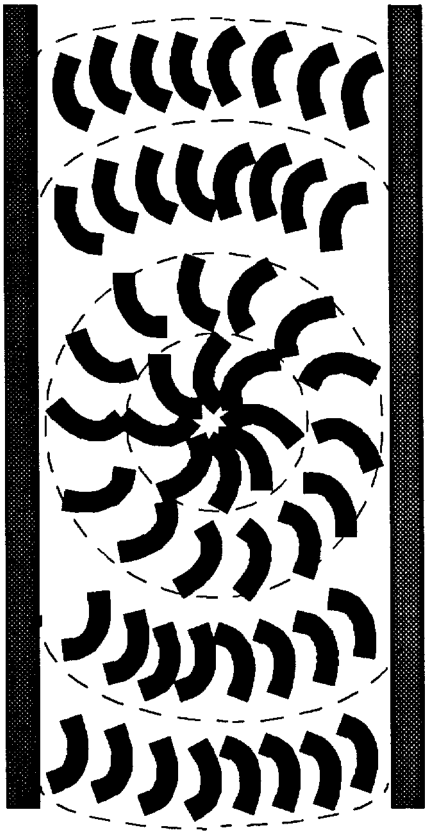


Figure 9. Proposed column structure of the *bâtonnets*, cut perpendicular to the central defect line.

The observation of a weak linear electro-optical effect observed with fan textures can be understood as an electroclinic effect. Due to the presence of chirality, the field induces a tilt of the optical axis, or of the preferred orientation axis of the molecules, against the column axes causing a rotation of the extinction cross. Due to chirality, this tilt induces an electric polarization vertical to the tilt plane and therefore the tilt couples linearly with the field.

Especially interesting is the observation of the transient birefringent structure and the transient electrical current upon field reversal. This indicates that the field can induce a reversal of the polarization and of the columnar structure (<<<<<to>>>>>). It is, however, difficult to propose a plausible mechanism for this reversal of the structure. There can be no collective rotation of the columns, because it would disrupt the structure of the phase. The columns are also too densely packed and too rigid to rotate independently. Although we cannot exclude the 'umbrella-like' conformational inversion [7], we propose another mechanism. We assume that there exists a distribution of domains with a reverse polarization. Reversal could then take place by a shift of domain boundaries. The propagation of the boundaries requires no conformational change of the bowlic molecules, but only a rotation which may take place at a high rate, since the boundary area has more free volume. The appearance of birefringence could be connected with the growth of the different domains, or may be due to some instability that causes an undulation of the columns. The growth rate of the domains determines the polarization current. The experimental results indicate, accordingly, that the growth rate is highest immediately after the field reversal.

Although there are good indications that the phase is ferroelectric there remain doubts, and additional experiments are planned to verify the conclusions. In particular the measurements should be repeated with a material of lower conductivity in order to reduce the background current relative to the polarization current. A more direct determination of the polarization and of the polarization reversal will be attempted by pyroelectric measurements.

The support of this work by the Deutsche Forschungsgemeinschaft (Sfb 335, Anisotrope Fluide) and the help of Dr. I. Jakupovic in interpretation of the NMR spectra are gratefully acknowledged.

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