Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Schmiedel, H. , Stannariu, R. , Feller, G. and Cramer, Ch.(1994) 'Experimental evidence of a conic helical liquid crystalline structure in cylindrical microcavities', Liquid Crystals, 17: 3, 323 — 332
To link to this Article: DOI: 10.1080/02678299408036573
URL: http://dx.doi.org/10.1080/02678299408036573

LIQUID CRYSTALS, 1994, VOL. 17, NO. 3, 323–332

Experimental evidence of a conic helical liquid crystalline structure in cylindrical microcavities

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(*Received 12 October 1993; accepted 23 November 1993*)

Optical activity has been measured for cholesteric (Ch), twisted nematic (N*) and ferroelectric (S_C^*) substances confined in cylindrical channels of anodic oxidized aluminium (*Anopore* membranes). ^{1}H and ^{13}C NMR studies of the adsorbed N* phase in combination with measurements of the rotary power suggest a conic helical director field in the pores, as in a common S_C^* structure, with the helical axes oriented along the cylindrical channels and the helicoidally ordered local directors on average being inclined at an angle $\theta < 90°$ to the cylinder axes. Supposing the validity of the de Vries formula, the sign and magnitude of the optical activity in Anopore indicate a change in birefringence and pitch with respect to the bulk sample.

1. Introduction

The anchoring properties of liquid crystals on amorphous surfaces [1] are of considerable practical and academic interest. They determine, in combination with the liquid crystal elastic energy, the structure of the director field in microconfined liquid crystalline droplets [2] and cylinders [3]. Crawford *et al.* [4, 5], and Vrbančič *et al.* [6], studied the molecular order and dynamics in the isotropic and nematic phases of nematic substances adsorbed in the cylindrical channels of inorganic Anopore membranes [7] (see figure 1). The non-treated Al_2O_3 walls orient the nematic director along the axes of the cylindrical pores, whereas lecithin coated channels induce a homeotropic orientation of the director at the wall [4, 6, 8], leading to three basic types of nematic director field configurations, i.e. the planar-radial, planar-polar and escaped radial configurations [9]. In future liquid crystal device applications, the confinement of liquid crystals in inorganic networks might prove to be as successful as the polymer dispersed liquid crystal display (PDLC) [10]. A crucial problem here is the fabrication of suitable inorganic pore systems with appropriate surface anchoring conditions allowing for external switching of the director field and controlling the optical properties.

In this paper, we study the behaviour of *chiral* liquid crystalline phases in non-treated inorganic micropores (Anopore membranes). For such phases, both planar and homeotropic orientations of the director at the surfaces of the channels would be in frustration with the formation of an undisturbed helicoidal structure of the director field within the pores. The experiments described in this paper were performed with

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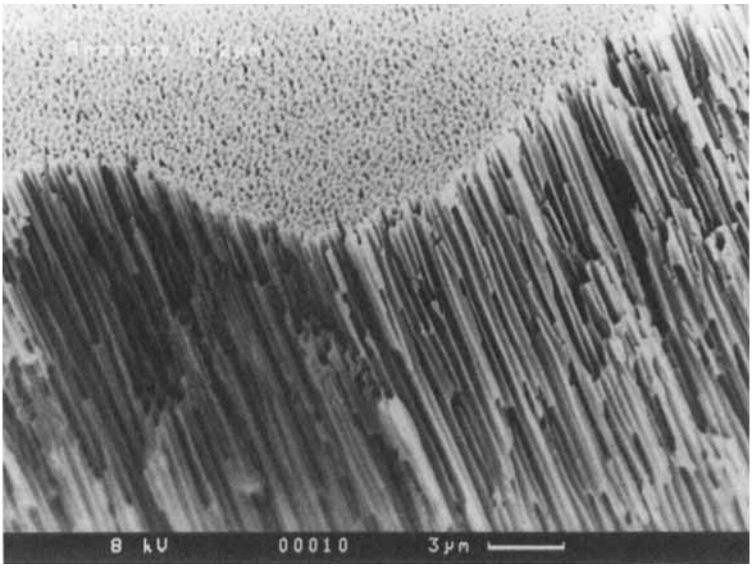


Figure 1. Scanning electron microscope photograph of an Anopore membrane (WHATMAN International Ltd.) with pore diameter 0·2 μm. The cylindrical channels within the Al_2O_3 network are perpendicular to the surface of the membrane, with a thickness 60 μm, and exhibit a narrow pore size distribution.

pure cholesteric (Ch), pure ferroelectric (S_C^*) and mixtures of nematic and cholesteric (twisted nematic, N*) materials.

In the case of N*, the present study will give evidence for the existence of a S_C^*-like tilted helicoidal director field inside the Anopore channels. Furthermore, the experimental data indicate that either the pitch of the helix for the confined phase becomes much smaller than in the bulk, or the rotary sense of the helix inside the channels is reversed with respect to the free phase.

2. Materials and sample preparation

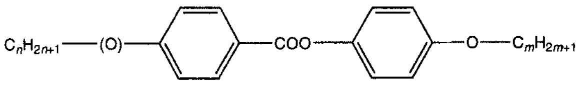
The liquid crystal materials used in our experiments are summarized in the table, together with references for the LC bulk properties. The pitch (periodicity of the helicoidal structure) of ChUC changes from $p_0 = -217\,\mathrm{nm}$ at the phase transition ($\mathrm{Ch} \leftrightarrow \mathrm{I}$) to $p_0 = -439\,\mathrm{nm}$ measured near the ($\mathrm{Ch} \leftrightarrow \mathrm{S_A}$) transition [11]. The negative value of p_0 indicates a left-handed helicoidal director field [12]. N* phases were induced by addition of small amounts of the chiral dopant ChUC to the nematic mixture M5 [13, 14]. The pitch of the ferroelectric smectogen DOBAMBC in the S_C^* phase varies in the range between $p_0 = 0{\cdot}9\,\mu\mathrm{m}$ to $2{\cdot}8\,\mu\mathrm{m}$ [15]. Anopore membranes were filled with the LC materials given in the table in the isotropic phase and slowly cooled into the LC mesophases using a Mettler hot stage. The samples remained optically transparent, so that measurements of birefringence and optical activity by means of polarizing optical microscopy (Jenapol-d) could be performed.

NMR samples consisted of about 50 slices of Anopore membranes stacked inside a 7·5 mm glass tube, with their pore axes uniformly directed normal to the rotation axis of the tube. The angular dependence of the NMR spectra was obtained by rotating the NMR glass tube around its axis.

Chemical structures of the investigated substances.

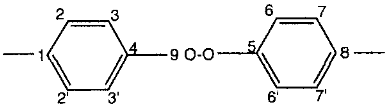
M5 (Halle) [26, 27]
1O–O6: 24·8 mol %
5O–O8: 27·2 mol %
6O–O7: 12·0 mol %
6–O4: 36·0 mol %

*n*O–O*m*:

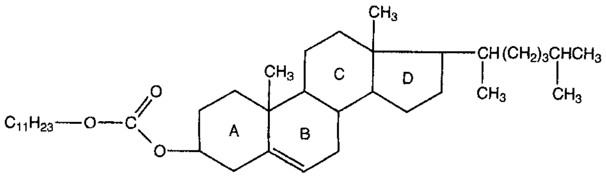


$N \leftrightarrow 70{\cdot}5^\circ \leftrightarrow I$

Numbering of the carbon positions in the *n*O–O*m* aromatic rings:

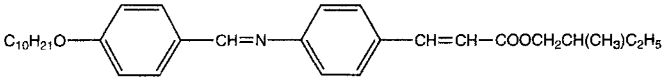


Cholesteryl undecyl carbonate ChUC [27, 28, 13]



$C \rightarrow 61{\cdot}6^\circ C \rightarrow Ch \leftrightarrow 73{\cdot}0^\circ C \leftrightarrow I$
$S_A \leftarrow 51{\cdot}5^\circ$

DOBAMBC [29, 15]



$C \rightarrow 76^\circ C \rightarrow S_C^* \leftrightarrow 93^\circ C \leftrightarrow S_A \leftrightarrow 113^\circ C \leftrightarrow I$
$S_H^* \leftarrow 60^\circ$

3. Experimental results

The optical activity ψ/d (rotation angle ψ of the polarization plane of the linearly polarized light per path d) for light propagating along the helical axis is shown in figure 2 in case of sandwich cells of ChUC (see figure 2 (*a*)), M5 + 4 wt % ChUC (see figure 2 (*b*)) and DOBAMBC (see figure 2 (*c*)), together with the ψ/d data for the adsorbed LC materials in Anopore (0·2 μm pore diameter), for light propagating along the direction of the channel axes, i.e. normal to the membrane.

In the isotropic phase, both rotary power and birefringence are nearly zero for all samples. The sign of the optical activity for the N* and S_C^* samples is reversed in Anopore with respect to the bulk LC material. Pure ChUC adsorbed in Anopore rotates the plane of polarization to the right ($\psi < 0$) at all temperatures, whereas the optical

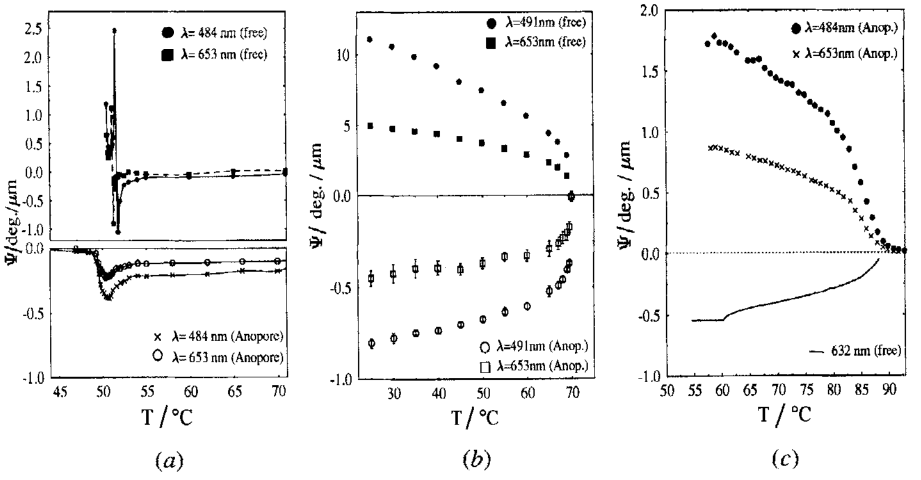


Figure 2. Rotary power of ChUC (*a*), M5 + 4·0 wt %. ChUC (*b*) and DOBAMBC (*c*) as a function of temperature.

activity changes its sign for bulk ChUC samples short above the phase transition temperature (Ch ↔ S_A), where the pitch increases to infinity.

It could be proved by means of conoscopy that Anopore membranes filled with LC materials are optically uniaxial with the optical axis oriented along their channels. Furthermore, using a λ-plate, conoscopic images of the samples allowed the determination of the character of the birefringence, i.e. the sign of $\Delta n = n_e^{\text{eff}} - n_o^{\text{eff}}$ where n_e^{eff} and n_o^{eff} denote the extraordinary and ordinary refractive indices of the LC-filled Anopore samples, respectively. Δn is positive over the whole temperature range for M5 + 4 wt % ChUC (N*) and DOBAMBC (S_A, S_C^*) increasing with decreasing temperature. Anopore samples filled with ChUC are optically negative below T_c and become optically positive for temperatures below 51°C.

For a study of the orientational order of the director field, we measured ^{1}H and ^{13}C NMR spectra of the LC materials adsorbed in Anopore membranes. ^{1}H NMR spectra at 32 MHz and temperature $T = 298$ K of M5 and twisted M5 (M5 + 4 wt % ChUC) are presented in figure 3. The bulk sample of pure M5 exhibits the typical doublet splitting (see figure 3 (*a*)) caused by the magnetic dipole–dipole interactions of the lateral phenyl protons in *n*O–O*m* (cf. the table, protons bound to the carbon positions 2, 2′, 3, 3′, 6, 6′, 7, 7′) indicating the homogeneous alignment of the director along the external magnetic field $\mathbf{B}_0$ [16]. As the nematic always aligns parallel to the $\mathbf{B}_0$ field, the line shape is independent of rotation of the sample tube. In the bulk sample of M5 + 4 wt % ChUC, the helical axes are arranged perpendicular to $\mathbf{B}_0$ [14], leading to the typical 'cylindrical powder pattern' of figure 3 (*e*).

In figure 3 (*b*)–(*d*) and (*f*)–(*h*), ^{1}H NMR spectra of adsorbed pure M5 and twisted M5 are presented for $\mathbf{B}_0$ parallel ($\Phi = 0$) and perpendicular ($\Phi = 90°$) to the channels and for the magic angle orientation ($\Phi = 54{\cdot}7°$). It is obvious that for the twisted nematic mixture, after adsorption in Anopore channels of 0·2 μm diameter, the ^{1}H NMR line shape changes dramatically from the cylindrical powder pattern (see figure 3 (*e*)) to an almost ordered spectrum in figure 3 (*f*)–(*h*).

Comparing figure 3 (*b*), (*f*) for $\Phi = 0$ and 3 (*c*), (*g*) for $\Phi = 90°$, one finds that the doublet splitting in Anopore is larger for pure M5 than for twisted M5, indicating the perfect alignment of the pure M5 with the pore axes, in contrast to a deviation of the

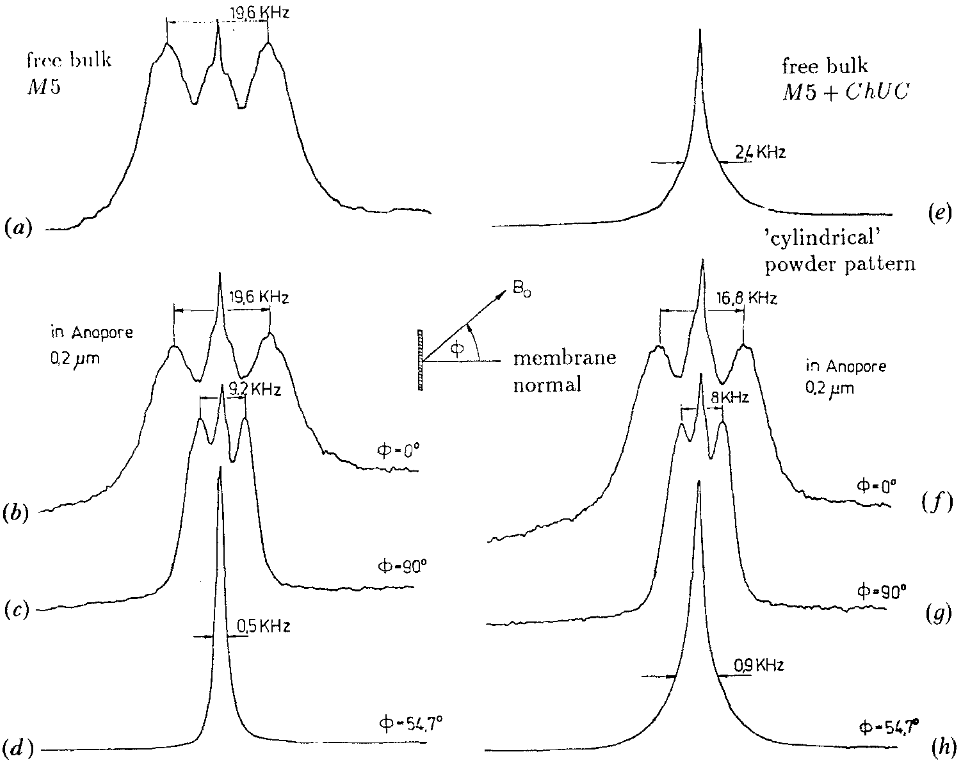


Figure 3. Proton NMR spectra of M5 at 32 MHz and $T = 298$ K. (*a*) bulk sample M5, (*b*)–(*d*) M5 in Anopore 0·2 µm, (*e*) bulk sample M5 + 4·0 wt% ChUC, (*f*)–(*h*) M5 + 4·0 wt% ChUC in Anopore 0·2 µm.

director from the orientation of the pore axes in the latter sample. In the magic angle orientation, the line width is smaller in the case of pure M5, giving evidence of a narrower angular distribution of the directors (better alignment) for the pure substance in Anopore.

A more detailed determination of the orientational order of the samples may be obtained from ^{13}C NMR. In figure 4, the experimental ^{13}C NMR spectra are presented for twisted M5 (4 wt% ChUC) in Anopore 0·2 µm at 314 K. The ^{13}C resonance frequency was 74·5 MHz. Indexing of the peaks in the spectra in correspondence with the individual aromatic carbon sites (cf. the table) was performed according to the previous work of Oehler [13]. Previous ^{13}C NMR studies of the bulk nematic and isotropic phases of M5 and its components allowed the determination of the chemical shift tensors for the aromatic carbon sites of M5 involved [17].

As can be seen from the figure, the angular dependence of the ^{13}C lines is pronounced for the aromatic carbons and weak for the alkyl chains. This is explained by the small chemical shift anisotropy of the alkyl carbons. As any individual carbon resonance line in a spectrum provides the same information on the director order and orientation, we have restricted the line shape fitting to the aromatic part of the spectrum, which is completely separated from the aliphatic part.

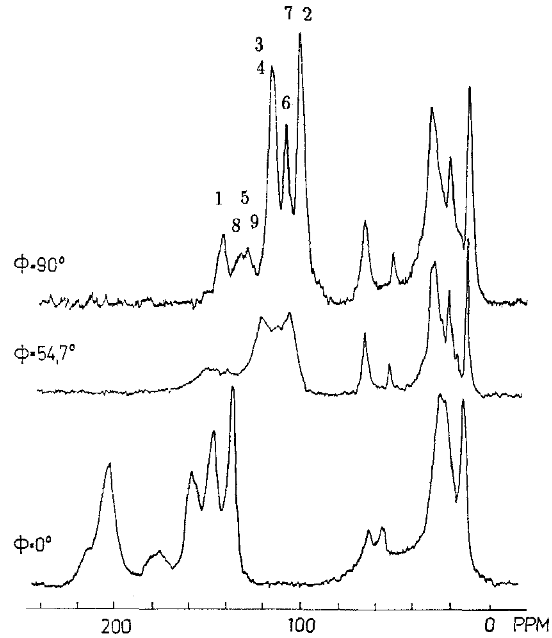


Figure 4. ^{13}C NMR spectra of M5 twisted by addition of 4·0 wt% ChUC in 0·2 μm Anopore membranes. Resonance frequency 74·5 MHz, $T = 314$ K. Chemical shift in ppm with respect to TMS. Peak indices correspond to the numbering of the carbon positions in the table.

4. Discussion

2.1. *Optical measurements*

The optical activity of a conic helical structure for light propagating along the helix axis away from the waveguide regime [12] is approximately given by the modified de Vries formula [18]

$$\frac{\psi}{d} = 45^\circ \frac{p^3(n^2 - n_o^2)^2}{2\lambda_V^2[2\lambda_V^2 - (n^2 + n_o^2)\cdot p^2]}, \tag{1}$$

where p is the pitch, λ_V is the vacuum wave length of light and n_o is the ordinary refractive index of the corresponding unwound LC structure. The index of refraction n in equation (1) is

$$n = \frac{n_e n_o}{\sqrt{(n_e^2 \cos^2\theta + n_o^2 \sin^2\theta)}}, \tag{2}$$

where the tilt angle is θ, and n_e denotes the extraordinary index of refraction of the untwisted and non-tilted LC structure. For $\theta = 90°$, we obtain $n = n_e$, and in this case, equation (1) reduces to the well-known de Vries formula [19] for the rotary power of common cholesteric phases. A possible local biaxiality [20, 21] has been neglected in view of its smallness [22]. Equation (1) can be used to determine the pitch of the chiral phase. Thus, using the ψ/d data for the bulk sample M5 + 4·0 wt% ChUC (cf. figure 2) and the refractive indices $n_e(\lambda, T)$, $n_o(\lambda, T)$ of M5 [23], we obtain the value for the pitch p by solving the cubic equation (1) for p for given temperatures T and wavelengths λ_V. We find $p = (2{\cdot}44 \pm 0{\cdot}03)$ μm over the whole temperature range of the

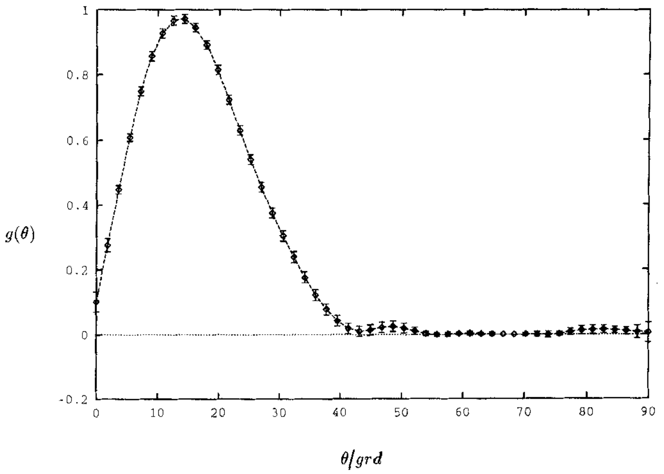


Figure 5. Director distribution density $g(\theta)$ with respect to the Anopore channel axes in 0·2 μm pore filters for M5 + 4·0 wt% ChUC at $T = 314$ K, as determined from the 0° spectrum of figure 4 by a deconvolution method.

N* phase of the twisted nematic mixture, which is in good agreement with values measured with the Cano wedge method.

The validity of the modified de Vries formula for the homogeneously tilted helicoidal structure was proved by Seppen *et al.* [15]. By means of equation (1), they determined the tilt angle θ of the undistorted S_C^* helix of DOBAMBC using the previously determined values of the pitch and the refractive indices n_e and n_o. The tilt angles obtained were in good agreement with those obtained by unwinding the helix.

However, a straightforward application of the de Vries formula to chiral phases adsorbed in the microchannels of Anopore membranes is not possible for several reasons. The main problem consists in the fact that filled Anopore membranes are microheterogeneous in the plane perpendicular to the direction of light propagation (for normal incidence). This means that the electric permittivity (or the indices of refraction which enter the de Vries formula) will be a certain average involving the permittivities of the liquid crystal and of the porous anodic aluminium oxide membrane in a complicated manner. Nevertheless, the high optical activity of the adsorbed chiral materials in Anopore (cf. figure 2) suggests a long range helicoidal orientational order of the director field inside the pores.

4.2. *NMR experiments*

For more detailed information about the chiral liquid crystal orientational order in the microcavities, we calculated the orientational distribution function $g(\theta)$ by fitting the ^{13}C NMR spectra of the twisted nematic mixture. The numerical procedure is based on a straightforward regularization method [24] which gives an excellent fit of the experimental pattern, with the distribution function $g(\theta)$ being the sole fitting parameter. The contributions of the ChUC carbons to the spectrum have not been taken into consideration, because of the low amount of ChUC involved. They may lead to small deviations between the experimental and simulated line shapes which can be neglected. As seen from figure 5, the director distribution function computed from the ^{13}C 0° spectrum exhibits a maximum near $\theta = 20°$. $g(\theta) = W(\theta)\sin(\theta)$ is proportional to the distribution density of the directors with respect to the pore axes, which are equivalent

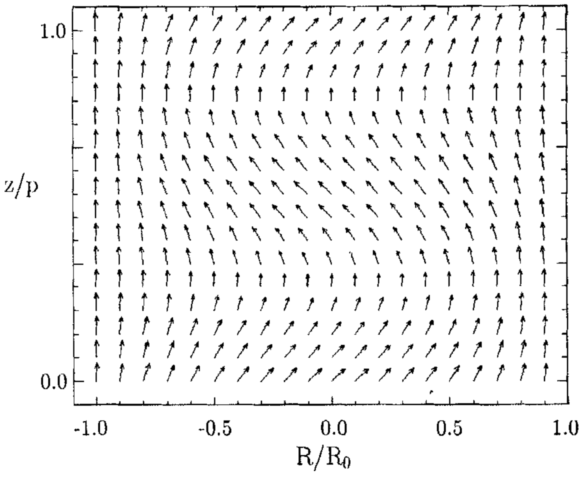


Figure 6. Suggested structure of the helical order of twisted nematic M5 + ChUC inside cylindrical channels (non-treated Anopore filters). The alignment is planar axial at the walls and the tilt is a maximum in the pore centre. The tilt is screwed along the z axis, similarly to the well known S_C^* structure.

to the direction of light propagation in the optical experiments. The macroscopic azimuthal distribution of the directors should be isotropic by symmetry considerations. The factor $\sin(\theta)$ accounts for the summation over all azimuthal orientations. A complete spherically isotropic director field distribution would correspond to $W(\theta) = 1$, yielding $g(\theta) = \sin(\theta)$; the common cholesteric structure with the helices parallel to the pore axes would give $p(\theta) = \delta(\theta - \pi/2)$ (with sharp peaks at the 90° positions in the 0° spectrum).

There is evidence that the actual director distribution function $g(\theta)$ may be somewhat broader than the function shown in figure 5, because diffusion of the M5 molecules during the NMR time τ might tend to narrow the resonance spectrum by partial averaging over the orientations $\theta(r)$ in the pore cross-sections with radii r comparable to $\sqrt{(2D\tau)}$ (D being the mean diffusion coefficient). Thus, the director field inside the channels is distributed on a cone around the pore axes, with an aperture of approximately 40° and a distribution width of at least 20°.

4.3. *Comparison of NMR and optical data*

The distribution function $g(\theta)$ obtained from NMR should be compatible with a long range helicoidal structure of the director field, in order to explain the optically measured rotary power of the sample. Therefore we propose the model of a conic helical nematic director field for the adsorbed N* phase in Anopore filters as depicted in figure 6.

Assuming the validity of a de Vries-like expression for the rotary power in such a structure, we have to conclude that the sign of the rotary power can only be changed either by reversing the rotary sense of the helix (i.e. changing the sign of p) or by changing the denominator $[2\lambda_V^2 - (n^2 + n_o^2)\cdot p^2]$ in equation (1). The latter occurs, for example, in free bulk ChUC near the (Ch $\leftrightarrow$ S$_A$) transition where the helix length passes the optical wavelength range in the sample. It seems reasonable that such changes in the denominator will occur mainly as a result of a changed pitch, since the averaged indices of refraction cannot differ significantly from the bulk values. Therefore, the change in the optical activity in Anopore with respect to the free substance for the N* and S_C^* phases studied, where the pitch in the bulk is larger than λ_V, could be explained either by a significant reduction of the pitch of the adsorbed chiral phases or by a reversal of the rotary sense of the helical structure. In the case of ChUC (see figure 2), the pitch in the free phase is shorter than λ_V (expect near the phase transition to S_A) and in the adsorbed cholesteric phase a reversal in the sign of the rotary power occurs just near the transition to the S_A phase where, even in the bulk, the de Vries formula is no longer valid.

The change in the sign of the birefringence for adsorbed ChUC in Anopore may be an indication of a change in the preferred orientation of the director from a more radial alignment relative to the pores ($\Delta n < 0$ for T between $\approx 51°C$ and 73°C) to a more axial alignment ($\Delta n > 0$ for $T < 51°C$), with the appearance of the smectic A phase. This should be proved by NMR measurements in forthcoming investigations.

5. Summary and conclusions

From the NMR and optical studies presented in this paper, it seems reasonable to assume the existence of a conic helicoidal structure of the director field for twisted nematic materials microconfined in cylindrical pores with planar surface anchoring. The existence of such structures in bulk cholesterics has been discussed, for example, by Pleiner and Brand [25].

Based on the de Vries formula, we have considered two possible explanations for the surprising reversal of the sign of optical activity for N* and S_C^* samples by adsorption in Anopore membranes. A profound interpretation of the optical data, however, requires the solution of Maxwell's equations for microheterogeneous systems, which exceeds the scope of this paper.

This work has been supported by the Deutsche Forschungsgemeinschaft with grant Schm 902/1. The authors gratefully acknowledge valuable discussions with Professor G. Pelzl and Professor A. Saupe from Halle. We would like to thank Dr U. Boehnke for the electron microscope photographs, and Dr H. E. Müller and Dr H. Ernst for assistance in the NMR measurements.

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