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INDUCTION OF TILTED CHOLESTERIC STRUCTURES IN MICROCONFINED LIQUID CRYSTALS

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Abstract

^{13}C -NMR measurements of the chiral mesogen cholesteryl-undecylcarbonate (CHUC) adsorbed in Anopore membranes with cylindrical pores of $0.2\mu\text{m}$ diameter are presented. The pitch of CHUC in the cholesteric phase is of order of the pore diameter, and in view of the planar axial anchoring a strong influence of the walls on the director field can be expected.

Simulation of the angular dependence of ^{13}C -NMR line shape allows to determine a mean tilt angle of 60° of the director with respect to the helical axes which are oriented along the channels. Furthermore, at $T=341\text{K}$ a correlation time of $130\mu\text{s}$ for reorientational motions could be obtained which is connected with molecular diffusion along the pores. Optical and NMR-measurements are compatible with a tilted helical director field for the cholesteric LC material within the pores.

INTRODUCTION

Orientational order of liquid crystal molecules near solid surfaces is of considerable academic and practical interest [1].

Anopore membranes [2] are systems with an extremely high inner surface to volume ratio. Therefore, they provide an ideal system for the investigation of surface interactions and anchoring properties at solid-liquid crystal interfaces.

The director field of microconfined liquid crystals (LC) is governed by the anchoring properties at the surface and Frank's elastic energy in the LC volume.

Untreated Anopore membranes of $60\mu\text{m}$ thickness which contain nearly cylindrical pores of diameter $0.2\mu\text{m}$ normal to the membrane, orient the director of the adsorbed nematic (N) or smectic-A (S_A) phases parallel axial to the walls of the channels. With lecithin surface treatment a homeotropic alignment can be achieved [3]. In case of

chiral LC phases in cylindrical pores, both planar and homeotropic orientations at the walls are in contradiction with an undisturbed helicoidal director field inside the channels. Hence, a number of possible structures with bulk and surface disclination lines have been predicted and observed in cylindrical capillaries [4, 5].

In a previous paper [6] we studied optical activity and birefringence of chiral LC material adsorbed in untreated Anopore membranes. In case of adsorbed twisted nematic (N^*) phases where the pitch p is large with respect to the pore diameter we observed uniaxial positive birefringence, a reversal of the sign and a strong decrease of the rotary power in comparison to the bulk material. Upon adsorption of the LC material, the membranes were transparent in the isotropic (I) and liquid crystalline phases of the adsorbates but strongly scattered light in the crystalline phase. These optical properties support the assumption of a relatively small number of surface and bulk defects and a long range orientational order in the director field of the liquid crystalline phases confined to the $0.2\mu\text{m}$ pores of Anopore membranes. Combining results of ^{13}C - and ^1H -NMR measurements of adsorbed N^* phases with the optical data, a tilted helicoidal director field inside the Anopore channels has been suggested [6].

This paper is concerned with the orientational order of adsorbed cholesteric (Ch) phases where the pitch is of the same order as the diameter of the pores. It will be shown by means of ^{13}C -NMR that in this case the orientational distribution function $g(\Theta)$ (Θ being the angle between local director and external magnetic field \vec{B}_0) again can be interpreted in the picture of a tilted cholesteric phase with its helical axis along the channel. Furthermore, studies of ^{13}C -NMR line shapes for different orientations of the membrane normal with respect to \vec{B}_0 will be presented, giving evidence of molecular diffusion along the pores.

THEORY

From symmetry considerations, the distribution of the director \vec{n} (polar angles ϑ, φ) in the Anopore membranes must be axially symmetric around the normal (z) to the membrane (Fig. 1). Φ is the angle between the external magnetic induction \vec{B}_0 and the pore axes (along z). The proton decoupled ^{13}C NMR spectra are governed by chemical shift interactions. For uniaxial LC-phases, the chemical shift tensor of all ^{13}C -sites ($k=1,2,\dots,N$) in mesogenic molecules are motionally averaged to axial symmetry around the (local) director \vec{n} . The resonance frequency ν_k of the k -th ^{13}C -

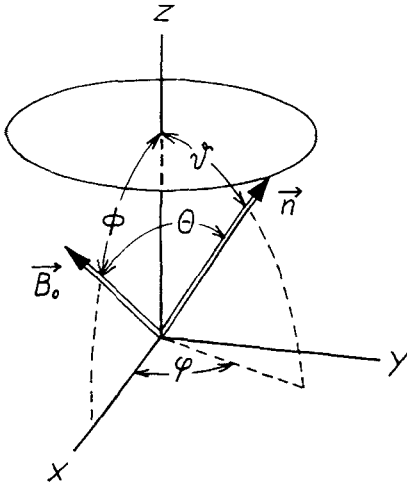


Figure 1: Sample geometry and definition of the angles between pore axes \vec{z} , director \vec{n} and NMR magnetic field \vec{B}_0 . The director is tilted at an angle ϑ with respect to the normal z of the membranes. The z -direction coincides with the pore axes. The external field \vec{B}_0 in the x, z -plane forms an angle Φ with the z axis. The NMR frequency is determined by the angle θ between \vec{B}_0 and \vec{n} .

nucleus is then given by

$$\nu_k = \nu_{0k} + \frac{1}{2} \Delta\nu_k (3 \cos^2 \Theta - 1) \quad (1)$$

where ν_{0k} is the isotropic frequency and $\Delta\nu_k = \nu_{||k} - \nu_{0k}$, $\nu_{||k}$ being the resonance frequency if \vec{B}_0 is oriented parallel to \vec{n} . Θ is the angle between \vec{B}_0 and the director \vec{n} and $\cos \Theta = \cos \Phi \cos \vartheta + \sin \Phi \sin \vartheta \cos \varphi$. For any given value of ϑ , the azimuthal angle φ is equally distributed in the xy -plane, and the corresponding directors form a cone with the polar angle ϑ .

Assuming slow diffusion (i.e. individual molecules do not change their angle Θ during the NMR-measurement) we obtain for the contribution $p[\nu, \vartheta, \Phi]$ of the cone ϑ to the ^{13}C -NMR line shape of one carbon site

$$p[\nu, \vartheta, \Phi] = \frac{1}{\pi |\Delta\nu| \sqrt{3}} \frac{1}{\sqrt{1 + 2(\nu - \nu_0)/\Delta\nu}} \times \left\{ \frac{1}{\sqrt{\sin^2 \Phi \sin^2 \vartheta - [\cos \Phi \cos \vartheta - \sqrt{1 + 2(\nu - \nu_0)/\Delta\nu}/\sqrt{3}]^2}} + \frac{1}{\sqrt{\sin^2 \Phi \sin^2 \vartheta - [\cos \Phi \cos \vartheta \mp \sqrt{1 + 2(\nu - \nu_0)/\Delta\nu}/\sqrt{3}]^2}} \right\} \quad (2)$$

In the last term of Eq.(2), the upper and lower signs refer to the cases $\Phi + \vartheta < \pi/2$ and $\Phi + \vartheta > \pi/2$, resp. From Eq. (2), singularities occur at $\nu_{\pm} = \nu_0 + \frac{\Delta\nu}{2} [3 \cos^2(\Phi \pm \vartheta) - 1]$ (case $\Phi + \vartheta < \pi/2$) and at $\nu = \nu_0 - \Delta\nu/2$ and ν_{\pm} (case $\Phi + \vartheta \geq \pi/2$).

If we denote the distribution density of the polar angle ϑ in the sample by $g(\vartheta)$, the ^{13}C -NMR line shape will be given by

$$f(\nu, \Phi) = \sum_{k=1}^N \int_0^{\pi/2} g(\vartheta) p(\nu_k, \vartheta, \Phi) d\vartheta \quad (3)$$

where the sum is taken over all ^{13}C -sites in the molecules. For known values of ν_{0k} and $\Delta\nu_k$ and given ^{13}C -NMR line shape $f(\nu, \Phi)$, the distribution density $g(\vartheta)$ of the cone angles ϑ should be determined solving the inverse problem in Eq. (3). This can be done using a straightforward regularization method described by Schäfer and Stannarius [7]. Regarding the case when the magnetic coherence length is larger than the diameter of the pores, the corresponding distribution function $g(\vartheta)$ should be independent of the angle Φ between \vec{B}_0 and the pore axes provided there is no diffusion.

Now let us assume, that the width of $g(\vartheta)$ is small (i.e. the tilt angle ϑ of the director is nearly the same for all molecules) and the azimuthal angle φ is screwing long z according to $\varphi(z) = 2\pi z/p$. Here p is the pitch of the resulting conic helical structure of the director field. In that case, translational diffusion of molecules along the pores (i.e. along the helical axis) will infer a time dependence of the azimuthal angle $\varphi = \varphi(t)$.

Rewriting Eq. (1) we obtain (dropping the index k for convenience)

$$\nu[\varphi(t)] = \nu_{00} + \frac{3\Delta\nu}{4} [\sin^2 \Phi \sin^2 \vartheta \cos 2\varphi(t) + \sin 2\Phi \sin 2\vartheta \cos \varphi(t)] \quad (4)$$

where $\nu_{00} = \nu_0 + \frac{\Delta\nu}{4}(3\cos^2 \Phi - 1)(3\cos^2 \vartheta - 1)$ is the resonance frequency in the fast diffusion limit. It can be seen from Eq.(4) that the ^{13}C -NMR line shape will be affected by z -diffusion only in the case $\Phi \neq 0$ (magnetic field \vec{B}_0 inclined to the pore axes). Assuming a Markovian diffusion process along the helical axes with correlation time τ_c , the probability density for stochastic motion from the starting angle φ_0 (at time $t=0$) to the new position φ at time t is given by

$$p(\varphi_1|\varphi_0, t) = \sqrt{\frac{\tau_c}{\pi t}} \exp[-(\varphi_1 - \varphi_0)^2 \tau_c / t] \quad (5)$$

where τ_c is related to the diffusion constant D by $\tau_c = p^2/16\pi^2 D$. To calculate the free induction decay (FID), $G(t, \vartheta)$, in case of director reorientation on the tilt cone ϑ (i.e. z -diffusion in our simple model) we follow the reasoning made in an earlier

paper [8] on self-diffusion in cholesteric LC's by means of ^{13}C -NMR. Thus, the FID is given by

$$G(t, \vartheta) = \frac{1}{\pi} \int_0^\pi d\varphi_0 \int_{-\infty}^{+\infty} \exp[i\Psi(\varphi_0, t)] P[\Psi(\varphi_0, t)] d\Psi(\varphi_0, t) \quad (6)$$

where $\Psi(\varphi_0, t) = 2\pi \int_0^t \nu[\varphi(t')] dt'$ is the phase at time t of the FID of a nucleus, which was situated at angular position φ_0 at time $t=0$. The probability density $P[\Psi(\varphi_0, t)]$, in rather successful approximation [9], can be described by the Gaussian function

$$P[\Psi(\varphi_0, t)] = (2\pi\Delta^2(\varphi_0, t))^{-1/2} \exp \left\{ - \left[\Psi(\varphi_0, t) - \overline{\Psi(\varphi_0, t)} \right]^2 / 2\Delta^2(\varphi_0, t) \right\} \quad (7)$$

$$\begin{aligned} \text{with the mean value} \quad \overline{\Psi(\varphi_0, t)} &= 2\pi \int_0^t dt_1 \int_{-\infty}^{+\infty} d\varphi_1 p(\varphi_1 | \varphi_0, t_1) \nu(\varphi_1) \\ \text{and the variance} \quad \Delta^2(\varphi_0, t) &= \overline{\Psi^2(\varphi_0, t)} - \overline{\Psi(\varphi_0, t)}^2. \end{aligned} \quad (8)$$

Both the mean value $\overline{\Psi(\varphi_0, t)}$ and the averaged square

$$\overline{\Psi^2(\varphi_0, t)} = 2(2\pi)^2 \int_0^t dt_2 \int_0^{t_2} dt_1 \int_{-\infty}^{+\infty} d\varphi_2 \int_{-\infty}^{+\infty} d\varphi_1 p(\varphi_2 | \varphi_1, t_2 - t_1) p(\varphi_1 | \varphi_0, t_1) \nu(\varphi_2) \nu(\varphi_1) \quad (9)$$

can be calculated analytically, using the propagator Eq. (5) and $\nu(\varphi)$ in Eq. (4). We obtain

$$\begin{aligned} \overline{\Psi(\varphi_0, t)} / 2\pi t &\equiv \bar{\nu}(\varphi_0, t) \\ &= \nu_{00} + \frac{3\Delta\nu}{4} \left[\sin^2 \Phi \sin^2 \vartheta \cos 2\varphi_0 \cdot h_7(x) + \sin 2\Phi \sin 2\vartheta \cos \varphi_0 \cdot h_8(x) \right] \end{aligned} \quad (10)$$

and

$$\begin{aligned} \Delta^2(\varphi_0, t) / (2\pi \cdot t)^2 &\equiv \overline{\nu^2}(\varphi_0, t) \\ &= \left(\frac{3}{4} \Delta\nu \right)^2 \left\{ \sin^4 \Phi \sin^4 \vartheta [h_1(x) + h_2(x) \cos 4\varphi_0] + \right. \\ &\quad + \sin^2 \Phi \sin^2 \vartheta \sin 2\Phi \sin 2\vartheta [h_3(x) \cos \varphi_0 + h_4(x) \cos 3\varphi_0] + \\ &\quad \left. + \sin^2 2\Phi \sin^2 2\vartheta [h_5(x) + h_6(x) \cos 2\varphi_0] \right\} \end{aligned} \quad (11)$$

with $x = t/\tau_c$. The relaxation functions $h_1(x) \dots h_8(x)$ are given in Table 1. Using

Eq.(7), the FID in Eq. (6) can be written in the form

$$G(t, \vartheta) = \frac{1}{\pi} \int_0^\pi d\varphi_0 e^{-i\bar{\Psi}(\varphi_0, t)} e^{-\Delta^2(\varphi_0, t)/2}. \quad (12)$$

Putting $\Phi = \vartheta = \pi/2$, Eq.(10)...(12) simplify to the expressions given by Stannarius [8], describing diffusion effects in the cylindrical powder pattern of cholesterics when the helical axes are ordered perpendicularly to \vec{B}_0 . We shall now consider the physical

Table 1: Relaxation functions in the FID ($q \equiv \exp(-x)$, $x \equiv t/\tau_c$)

h_1	$= x^{-1} - (1 - q)x^{-2} - (1 - q)^2x^{-2}/2$
h_2	$= (1 - q)x^{-2}/3 - (1 - q^4)x^{-2}/12 - (1 - q)^2x^{-2}/2$
h_3	$= 64(1 - q^{1/4})x^{-2}/3 - 4(1 - q)x^{-2}/3 - 4q^{1/4}/x - 4(1 - q)(1 - q^{1/4})x^{-2}$
h_4	$= 4(1 - q)x^{-2}/5 - 26(1 - q^{9/4})x^{-2}/45 + 2(1 - q^{1/4})x^{-2} - 4(1 - q)(1 - q^{1/4})x^{-2}$
h_5	$= 4x^{-1} - 16(1 - q^{1/4})x^{-2} - 8(1 - q^{1/4})x^{-2}$
h_6	$= 16(1 - q^{1/4})x^{-2}/3 - 4(1 - q)x^{-2}/3 - 8(1 - q^{1/4})^3x^{-2}$
h_7	$= (1 - q)x^{-1}$
h_8	$= 4(1 - q^{1/4})x^{-1}$

meaning of $\bar{\nu}$ and $\bar{\nu}^2$ defined in Eq.(10) and (11). $\bar{\nu}(\varphi_0, t)$ is a mean frequency and $\bar{\nu}^2(\varphi_0, t)$ a mean variance at time t for spins which started molecular diffusion at $t=0$ with azimuthal position $\varphi = \varphi_0$. For qualitative statements let us assume both quantities $\bar{\nu}(\varphi_0, t) = \bar{\nu}(\varphi_0, T)$ and $\bar{\nu}^2(\varphi_0, t) = \bar{\nu}^2(\varphi_0, T)$ to be constant and equal to their values at time $t=T$ where T is a time interval within the time domain of the NMR-measurement. In that case the NMR-line shape $F(\nu, \vartheta)$, which is the Fourier transform of $G(t, \vartheta)$ in Eq.(12), is simply given by a superposition of Gaussian lines centered at $\bar{\nu}(\varphi_0, T)$ with variances $\bar{\nu}^2(\varphi_0, T)$, i.e.

$$F(\nu, \vartheta) = \frac{1}{\pi} \int_0^\pi d\varphi_0 [2\pi\bar{\nu}^2(\varphi_0, T)]^{-1/2} \exp \left\{ -[\nu - \bar{\nu}(\varphi_0, T)]^2 / 2\bar{\nu}^2(\varphi_0, T) \right\} \quad (13)$$

In the fast diffusion limit ($\tau_c \ll T$), all relaxation functions $h_1 \dots h_8$ vanish (c.f. Table 1 for $x \rightarrow \infty$) and the line shape for each carbon site is a δ -function centered at ν_{00} . In case of slow diffusion ($\tau_c \gg T$), $h_1 \dots h_6 \rightarrow 0$, $h_7, h_8 \rightarrow 1$, and the evaluation of Eq.(13) leads to the line shape given by Eq(2).

To demonstrate the influence of thermal motion on the ^{13}C -NMR line shape within the frame of the cone model, in Fig. 2 the case $\Phi = 54.7^\circ$, $\vartheta = 60^\circ$ is shown according to Eq.(13). In view of the crudeness of the approximation made, only qualitative conclusions can be made. To be more realistic, Eq.(12) has to be evaluated, using the correct expressions for $\overline{\nu}(\varphi_0, t)$ and $\overline{\nu^2}(\varphi_0, t)$ given in Eq.(10) and (11). Nevertheless,

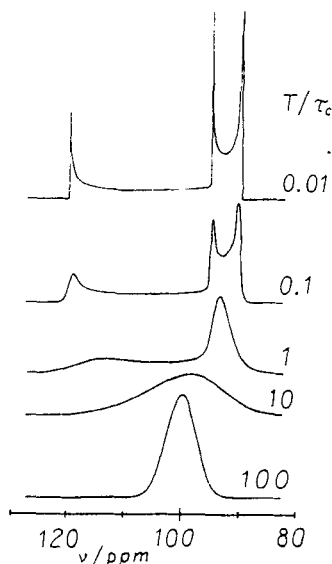


Figure 2: Calculated ^{13}C NMR line shapes according to Eq. (13) for a single carbon site with $\nu_0=100\text{ppm}$ and $\Delta\nu=20\text{ppm}$. $\vartheta = 60^\circ$, $\Phi = 54.7^\circ$. In the slow motion case ($T/\tau_c \ll 1$), singularities appear at $\nu = \nu_{\pm}$ and $\nu = \nu_0 - \Delta\nu/2$. With increasing molecular motion (top to bottom) the lineshape smoothes until in the fast diffusion limit a single line at $\nu = \nu_0$ remains.

the general features of the motional line narrowing process are adequately described by the simple Eq.(13). This can be proved, e.g., by comparison of the correct line shape in the case $\Phi = \vartheta = \pi/2$ [8] with the approximation given by Eq.(13). For fixed value of $\Delta\nu$, the best fit to the correct line shape is achieved at a definite value of T/τ_c and an estimate value of the correlation time τ_c can be obtained.

EXPERIMENTAL AND DISCUSSION

The LC material used in our experiments was cholesteryl-undecylcarbonate (CHUC). Its optical properties have been studied extensively by the Halle LC-group [10]. The high-frequency part of the ^1H -decoupled ^{13}C -NMR spectrum at 75MHz of the bulk material CHUC is shown in Fig. 3 for the isotropic phase (350K) and in the Ch phase (341K). The assignment of the peaks to the ^{13}C -atoms in the molecule has been performed following Freeman and Morris [11]. The pitch of the left-handed helical director field of CHUC at $T=341\text{K}$ in bulk material is $0.22\mu\text{m}$ [12], i.e. nearly equal to the diameter of the Anopore channels. The simulated spectrum in Fig. 3

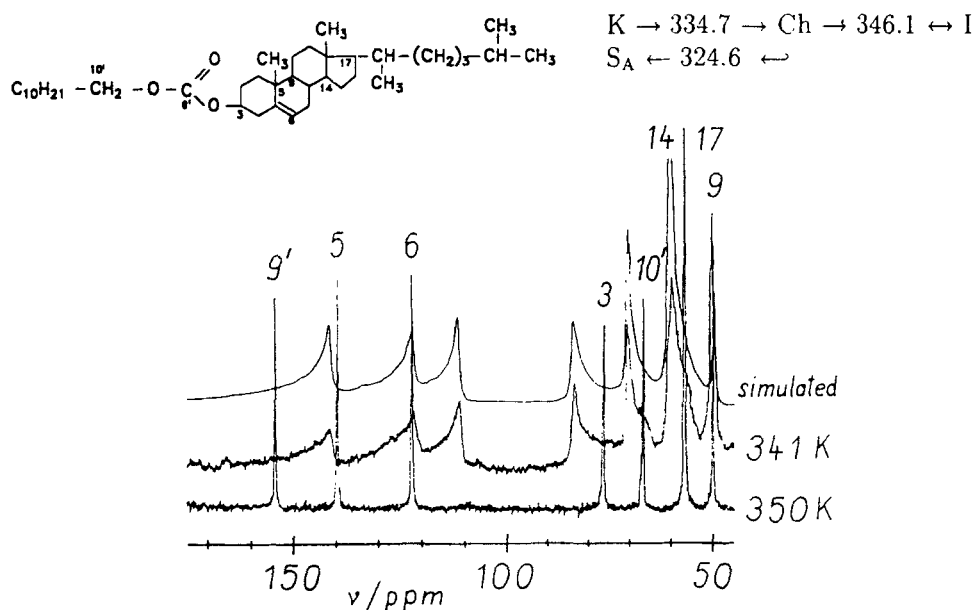


Figure 3: Proton decoupled ^{13}C NMR spectra of a CHUC bulk sample at 75 MHz in the isotropic ($T=350\text{K}$) and cholesteric (341K) phases. Chemical shifts are in ppm with respect to TMS, *Top*: simulated spectrum with an assumed random distribution of the helical axes around the direction of \vec{B}_0 .

has been obtained assuming a Gaussian distribution (standard deviation 30°) of the helical axes around \vec{B}_0 . This distribution indicates that $\vec{B}_0 \approx 7T$ is insufficient to completely orient the sample which has a small negative anisotropy of diamagnetic susceptibility.

Furthermore, the experimental spectra allow for the determination of the values ν_{0k} and $\Delta\nu_k$ (c.f. Eq.(1)). As can be seen from Fig. 3, at $T=341\text{K}$ the $\Delta\nu_k$ are positive for carbon atoms $9'$ ($\Delta\nu_{9'} = 26\text{ppm}$), 5 ($\Delta\nu_5 = 36\text{ppm}$), 6 ($\Delta\nu_6 = 22\text{ppm}$) and negative for atoms 3 ($\Delta\nu_3 = -15\text{ppm}$), $10'$, 14 , 17 ($\Delta\nu_{10'} = \Delta\nu_{14} \approx \Delta\nu_{17} \approx -8\text{ppm}$), whereas $\Delta\nu_9$ is nearly zero.

Anopore membranes filled with CHUC in the Ch phase have negative birefringence and are optically active [6], indicating a long range orientational order of the director field inside the channels. In Figs. 4 and 5 ^{13}C -NMR spectra of CHUC adsorbed in Anopore membranes are shown. In the isotropic phase, all ^{13}C -NMR lines are broadened to about 3ppm in Anopore membranes which we explain mainly by \vec{B}_0 -

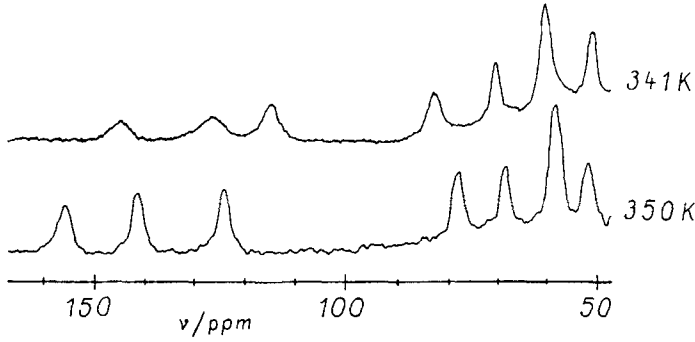


Figure 4: Proton-decoupled ^{13}C -NMR spectra of CHUC in Anopore $0.2\mu\text{m}$, Resonance frequency 74.5MHz, $\Phi = 0$

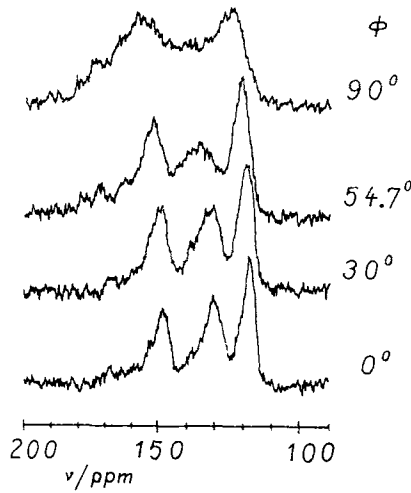


Figure 5: Angular dependence of ^{13}C -NMR line shape of lines 9',5,6 in Anopore $0.2\mu\text{m}$ at $T=341\text{K}$

inhomogeneities due to demagnetization effects in the NMR-sample consisting of 50 stacked membrane-platelets (length 15mm, width 3..5mm). For $\Phi = 0$, the ^{13}C -peak positions at $T=341\text{K}$ are nearly unchanged in Anopore with respect to the bulk (c.f. Figs. 3 and 4), whereas the line shape becomes more smooth. Therefore, we assume the helical axes being oriented along the channels and look for the distribution function $g(\vartheta)$ defined in Eq.(3). In Fig. 6, the result of the fitting procedure [7] is shown. As can be seen, the average tilt angle is about 60° and the relatively small half-width of about 15° seems to allow the application of the cone model presented in the previous section. We will now discuss the angular dependence shown in Fig.5. With increasing angle Φ , a line broadening together with higher values of the chemical shifts are observed. If $g(\vartheta)$ from Fig. 6 and Eq.(3) are used to simulate the line shape, this cannot be explained. Therefore, we take into account *molecular diffusion along*

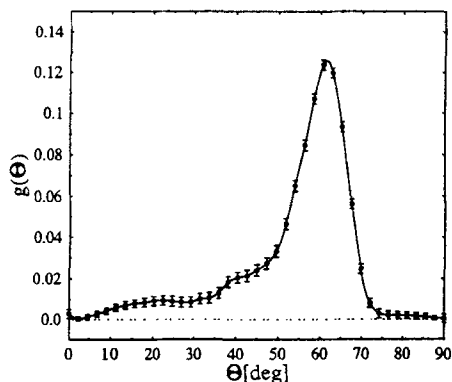
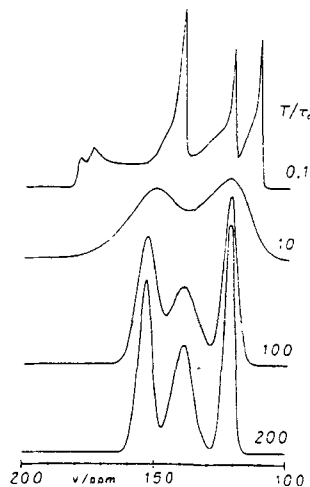


Figure 6: Calculated director distribution density $g(\vartheta)$ for CHUC adsorbed in Anopore $0.2\mu\text{m}$ at $T=341\text{K}$ (Cholesteric phase)

the pores. To illustrate the fitting procedure for the angular dependence of the line shapes, in Fig. 7 the $\Phi = 54.7^\circ$ spectrum is presented. Using the director distribution density $g(\vartheta)$ obtained from the fit of the $\Phi = 0^\circ$ -spectrum (c.f. Fig.6), the line shape at an arbitrary angle Φ is approximated by a superposition of functions $F(\nu, \vartheta)$ given by Eq.(13), where the averaging time T (FID acquisition time) is the fitting parameter. It can be seen, that the best fit to the experimental spectrum for $\Phi = 54.7^\circ$ in Fig. 5 is

Figure 7: Calculated influence of z -diffusion on the ^{13}C NMR line shape of carbons 9',5 and 6 at $\Phi = 54.7^\circ$ with $g(\vartheta)$ from Fig. 6. The optimum fit is achieved for $T/\tau_c=100$



obtained for fast diffusion ($T/\tau_c=100$), whereas the line shape in the slow motion case ($T/\tau_c=0.1$, Eq.(2)) differs significantly from the experiment. The value of $T/\tau_c=100$ gives an adequate fit to the complete angular dependence of the spectra in Fig. 5.

Following the method described in the previous section we obtain for the correlation time (at $T=341$ K) the value $\tau_c \approx 130\mu\text{s}$. Assuming the pitch of CHUC to remain unchanged upon adsorption ($p \approx 0.22\mu\text{m}$), a diffusion coefficient $D = p^2/16\pi^2\tau_c \approx 2.4 \cdot 10^{-12}\text{m}^2/\text{s}$ would result. This value of D seems to be reasonable, but in view of the increased optical rotary power of adsorbed CHUC with respect to the bulk material, the pitch might be increased in the pores, which would also increase the diffusion coefficient D .

CONCLUSION

From ^{13}C -NMR measurements it seems to be evident that upon adsorption in Anopore channels of $0.2\mu\text{m}$ diameter the cholesteric LC-material CHUC (pitch $0.22\mu\text{m}$ at $T=341\text{K}$) with its helical axes is oriented along the cylindrical pores. Furthermore, the average tilt angle of the long molecular axes with respect to the helices is about 60° , which is comparable to a S_C^* -like director field. With growing inclination of the external magnetic field \vec{B}_0 with respect to the pore axes, there can be observed an increasing influence of molecular diffusion on ^{13}C -NMR line shape of the sample. However, the correlation time obtained from ^{13}C -NMR line shape simulations is insufficient to determine the translational diffusion coefficient as long as the pitch of the LC material confined to the pores is unknown.

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