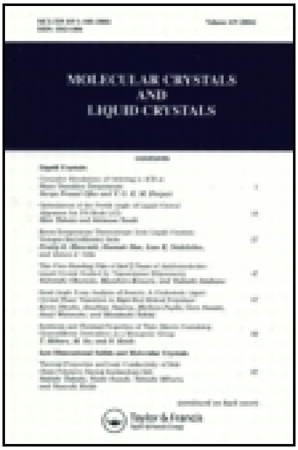

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Optical Properties of Microconfined Liquid Crystals

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OPTICAL PROPERTIES OF MICROCONFINED LIQUID CRYSTALS

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Abstract

This paper is concerned with studies of birefringence and optical activity of the twisted nematic mixture 5CB/CB15 confined to cylindrical pores of ANOPORE (AP) membranes. Both birefringence and optical activity of the liquid crystal (LC) filled membranes exhibit unusual properties. The sign of the optical activity is reversed with respect to the bulk LC phase.

Measurements have been performed using polarizing microscopy and generalized transmission ellipsometry. By means of ^{13}C-NMR and FTIR experiments an increase of the tilt angle between local director and membrane normal with raising chiral dopant concentration could be proved. However, an unambiguous model for the structure of the chiral director field inside the pores could not be established up to now.

INTRODUCTION

The competing influence of bulk elastic energy and surface alignment interaction on the director field of microconfined liquid crystal phases is of great theoretical and practical interest [1]. The untreated ANOPORE membranes [2, 3] have been proved to orient the director of an adsorbed nematic (N) liquid crystal inside the pores parallel to the membrane normal [4]. The formation of a LC-like surface layer in LC-filled ANOPORE membranes in the isotropic phase and the phase transition from uniaxial to planar polar director field by pretreating the membranes with surfactants of increasing chain length have been investigated [5]. In case of an adsorbed twisted nematic (TN) or cholesteric (Ch) or chiral smectic (S_c^*) phase, however, the strong planar axial anchoring at the inner surface of the pores is incompatible with the director field of the corresponding unconfined liquid crystalline phase. Different possible director configurations of chiral liquid crystals in cylindrical cavities can be derived theoretically [6] depending on the anchoring conditions.

R. J. Crawford et al. [7] reported an experimental study of TN LCs confined to submicrometer cylindrical cavities. From their deuterium NMR measurements they concluded that for pitch lengths large to the pore diameter there exists a radially twisted director field which undergoes a phase transition to an axially twisted planar bipolar configuration when the pitch length is diminished below the pore diameter. In previous papers [8, 9] we interpreted our NMR data and measurements of optical activity of TN LC-filled AP-membranes suggesting a conic tilted cholesteric director field.

Here, we have studied the optical properties in more detail. In Sect. 2 we report the birefringence measurements of liquid filled ANOPORE membranes being complex ordered mixtures. In Sect. 3 we explain the experimental setup and sample configuration of optical activity measurements and present the results obtained by Generalized Transmission Ellipsometry. In Sect. 4 FTIR experiments are reported and finally, the results will be summarized.

BIREFRINGENCE

By symmetry reasons, AP-membranes macroscopically should behave as uniaxial crystals, the optical axis being aligned along the membrane normal. As far as the diameter of the pores (d=0.2μm) is small with respect to the wavelength of light (λ), the microscopically heterogeneous membrane can be regarded as a homogeneous medium whose ordinary (n_{oA}) and extraordinary (n_{eA}) indexes of refraction are obtained by appropriate averaging.

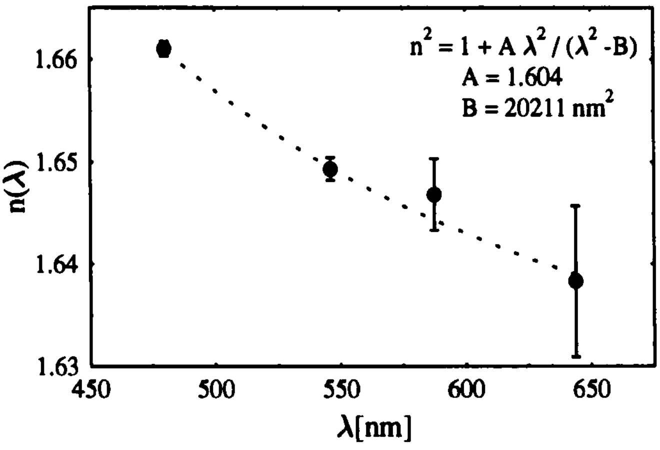

Figure 1
Refraction index of ANOPORE bulk material

Applying classical theory of dielectric permittivity of ordered mixtures [10] we obtain

$$n_{eA}^2 = n_m^2 + \nu\left(n_{pp}^2 - n_m^2\right) \tag{1}$$

$$n_{oA}^2 = n_m^2 - \frac{2\nu \cdot n_m^2\left(n_m^2 - n_{ps}^2\right)}{(1+\nu)n_m^2 + (1-\nu)n_{ps}^2} \tag{2}$$

where $\nu = V_p/(V_p + V_m)$ is the porosity of the membrane, i.e. the relative volume fraction of the pores, and n_{pp}^2 and n_{ps}^2 are the averaged values of the square of the refraction index of the material filled into the pores in case of electric field $\vec{E}$ being aligned parallel (pp) and perpendicular (ps) to the pore axis. n_m is the index of refraction of the isotropic membrane matrix. The refraction index of the porous AP-membrane material (cf. Fig.1) has been determined by imbibing micronized (empty) membranes into immersion liquids with perfect index matching (monitored by vanishing of the Becke line [11]). Eq.(2) corresponds to the case of $\vec{E}$ perpendicular to the membrane normal, where nontrivial depolarization effects have to be taken into account. In the case of planar axial adsorbed (nematic) liquid crystal phases we have

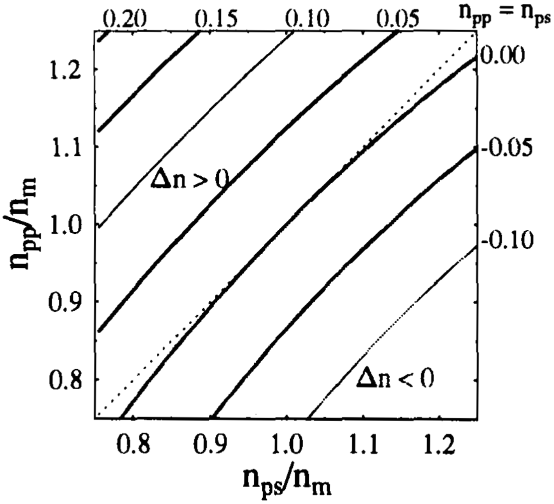

Figure 2
Reduced birefringence $(n_{eA} - n_{oA})/n_m$ of the filled membrane with n_m being the refraction index of the membrane material and n_{pp} and n_{ps} being the refraction indices of the adsorbed material in case of $\vec{E}$ parallel and perpendicular to the pore axes, respectively

$n_{pp} = n_e$ and $n_{ps} = n_o$ with $n_{e,o}$ being the refraction indices of the bulk LC-phase. In Fig. 2 the reduced birefringence $\Delta n_A/n_m = (n_{eA} - n_{oA})/n_m$ of the membrane can be determined for given values of the reduced refraction indices n_{pp}/n_m and n_{ps}/n_m of the material filled into the pores. It can be seen that in case of filling the pores with isotropic liquids ($n_{pp} = n_{ps}$) the membrane will be (weakly) positive birefringent except in the case of perfect index matching ($n_{pp} = n_{ps} = n_m$) where it is isotropic. The

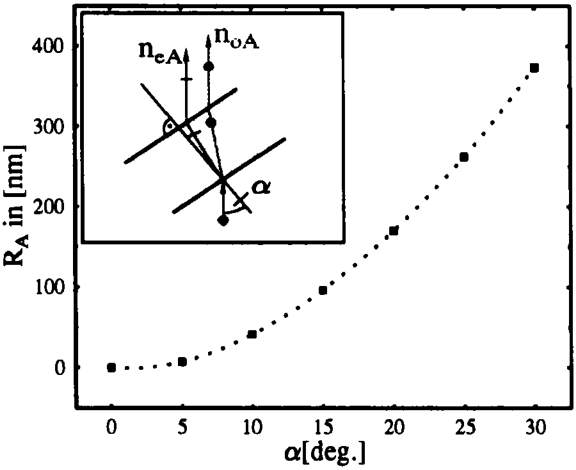

Figure 3
Optical path difference R_A as a function of the inclination angle α for 5CB in AP (d=0.2μm) at t=33.2° and λ=484nm :
n_{eA}=1.700, n_{oA}=1.610 (Wiener, ν=0.48, n_m=1.660)
n_{oA}(fit)=1.633

birefringence of the AP-membranes can be determined, e. g. by measuring the optical path difference $R_A(\alpha)$ between the extraordinary and ordinary waves after traversing the membrane inclined at angle α with respect to the light beam direction (cf. Fig.3). The path difference is given by

$$R_A = n_{oA} d \left[\left(1 - \frac{\sin^2 \alpha}{n_{eA}^2} \right)^{1/2} - \left(1 - \frac{\sin^2 \alpha}{n_{oA}^2} \right)^{1/2} \right] \tag{3}$$

and can be measured by means of a compensator. In Fig.4, the indices of refraction of

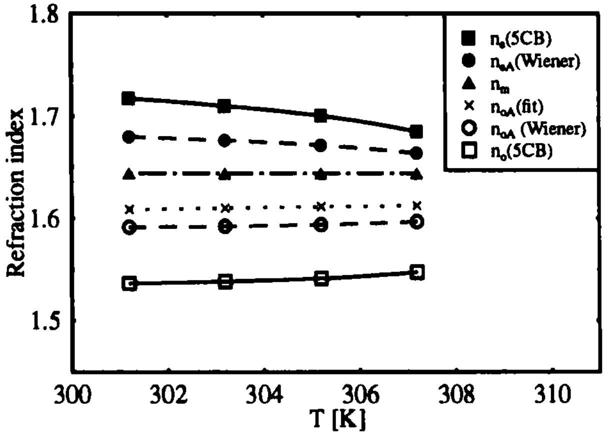

Figure 4
Refraction indices of pure 5CB in bulk and 5CB-filled AP-membranes (λ=591nm)

5CB in bulk and of 5CB-filled AP-membranes are plotted for the wavelength 591nm as a function of the temperature. The fit of the optical path difference data of 5CB-filled AP-membranes has been performed putting n_{eA} according to Wiener's formula Eq. (1). We used $n_{pp} = n_e(5CB)$ and $n_{ps} = n_o(5CB)$ because of the planar axial director field inside the cylindrical pores.

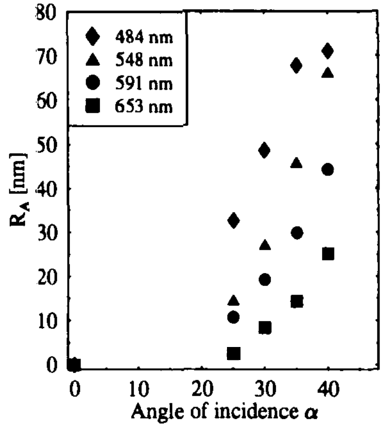

Figure 5
Optical path difference (R_A) between ordinary and extraordinary waves traversing AP-membranes filled with castor oil (n=1.483...1.476). From the data a weak negative birefringence follows.

The value of the porosity ν=0.48 has been determined by weighing the empty and the 5CB-filled membrane. As can be seen from Fig.4, the experimentally determined value of the birefringence of the filled AP-membrane is about 25% smaller than that predicted by Wiener's formula. This disagreement gives some hint to the more complex nature of light propagation in ANOPORE membranes. Furthermore, regarding the filling of the membranes with isotropic liquids, we observe again a violation of Wiener's theory. Whereas the 5CB-filled membrane at temperatures above the clearing temperature $T_c = 35°C$ is nearly isotropic because of nearly perfect index matching, filling with isotropic liquids whose refraction index differs significantly from that of the AP-matrix (e.g. castor oil n=1.48, cf. Fig. 5) results in weakly negative birefringent membranes if the measurement is performed using light propagating at angles $\alpha < 45°$ with respect to the membrane normal. Although this birefringence is small with respect to that measured for LC-filled AP-membranes (cf. Fig.6) it is an indication that the Wiener model can be used only in a first approximation. Furthermore, it is very surprising that the birefringence of these membranes appears to be weakly positive when measured with light propagating perpendicularly to the membrane normal! Therefore, the mechanism of light propagation parallel or perpendicular to the pore axes must be different. Presumably, wave guiding effects influence the light propagating at small angles α in the membrane.

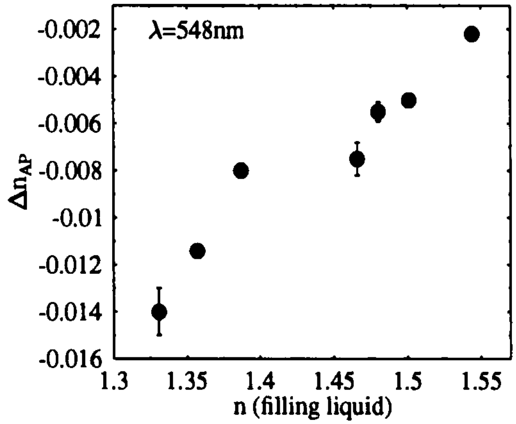

Figure 6
Imbibition curve: Apparent birefringence of AP-membranes filled with isotropic liquids of various indices of refraction. The values of the birefringence have been obtained fitting the optical path differences (cf. Fig.5) to Eq.(3).

OPTICAL ACTIVITY

We investigated ANOPORE membranes filled with twisted nematic mixtures consisting of the nematic liquid crystal 4-cyano-4′-pentylbiphenyl (5CB) and the chiral dopant 4-cyano-4′-(2 methyl)-butylbiphenyl (CB15). The concentration of the dopant CB15 in the liquid crystalline mixture varied from 0.24 wt % to 25 wt % yielding a helicoidal structure of a positive handiness exhibiting a pitch in the range from about 60μm to 600nm.

We have analyzed the anisotropic transmission function of filled, optically active membranes by means of a Rotating Analyzer Ellipsometer (J. A. WOOLLAM CO.) in the Generalized Transmission Mode [12]. The samples were placed in a METTLER hot stage and temperature was stabilized within a range of 0.1K. The spectra have been recorded within a spectral range of 400-1300nm at an angle of incidence Θ_i=0° (c.f. Fig. 7). The anisotropic transmission properties are described by the normalized complex Jones transmission matrix:

$$\begin{pmatrix} B_{\|} \\ B_{\perp} \end{pmatrix} = \begin{pmatrix} T_{pp} & T_{sp} \\ T_{ps} \cdot T_{pp} & 1 \end{pmatrix} \begin{pmatrix} A_{\|} \\ A_{\perp} \end{pmatrix} \qquad (4)$$

where $A_{\|,\perp}$ denote the electrical field components in the plane of incidence and perpendicular to it. The same definition is used for the transmitted light ($B_{\|,\perp}$).

The normalized transmission coefficients are related to the commonly used coeffi-

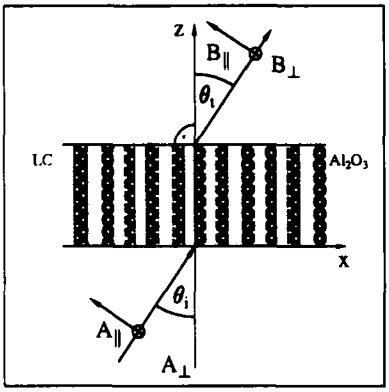

Figure 7
Definition of the directions of the electrical field components

cients of the Jones transfer matrix by:

$$T_{pp} = \frac{t_{pp}}{t_{ss}} = \tan \Psi_{pp} e^{i\Delta_{pp}} \quad (5)$$

$$T_{sp} = \frac{t_{sp}}{t_{ss}} = \tan \Psi_{sp} e^{i\Delta_{sp}} \quad (6)$$

$$T_{ps} = \frac{t_{ps}}{t_{pp}} = \tan \Psi_{ps} e^{i\Delta_{ps}} \quad (7)$$

The phases of the cross-diagonal coefficients provide immediately the sign of the optical rotation of the plane of polarization of linearly polarized light. In case of $\Delta_{sp} \sim 0$ the sign of the rotation angle ψ is positive and in case of $\Delta_{sp} \sim \pi$ it is negative. The value of the rotation angle can be obtained from the three complex transmission coefficients by:

$$\begin{aligned} \psi &= -\frac{1}{2}\frac{Re\left\{B_\parallel^* \cdot B_\perp\right\}}{\left|B_\parallel\right|^2 - |B_\perp|^2} \quad \text{with} \\ B_\parallel &= T_{pp}\cos^2\phi + \sin^2\phi + \frac{1}{2}(T_{sp} + T_{ps}T_{pp})\sin 2\phi \\ B_\perp &= -\frac{1}{2}(T_{pp} - 1)\sin 2\phi - T_{sp}\sin^2\phi + T_{ps}T_{pp}\cos^2\phi \end{aligned}$$

where ϕ is the azimuthal angle of incidence between the electrical field vector and the molecular frame.

In Fig. 8a the rotary power of the adsorbed mixture 5CB + 10% CB15 (pitch $\approx 1.5\mu m$) is compared to that of the bulk. The rotary power of the bulk sample has proved to be an order of magnitude larger than that of the ANOPORE sample whereas the sign of the rotary power is reversed.

In case of AP-samples the rotary power does not depend on the azimuthal angle ϕ

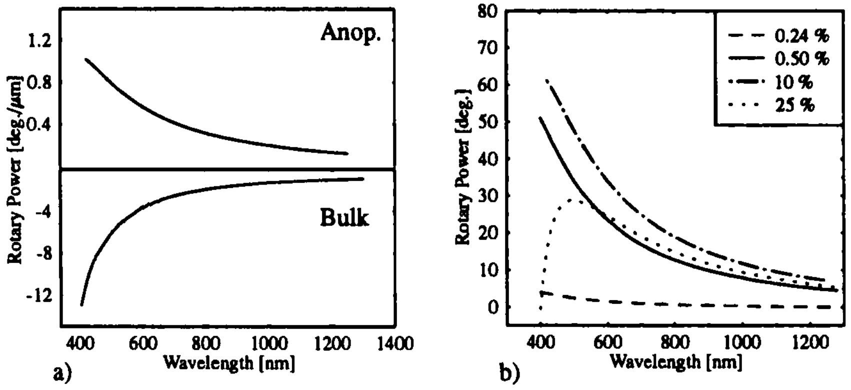

Figure 8
Rotary power of the twisted nematic mixture 5CB/CB15 as a comparison (a) of bulk and ANOPORE-sample and (b) several dopant concentrations at $T_{red} = T/T_c = 0.975$

because of symmetry reasons. Fig. 8b shows the dependence of the rotary power spectra on the concentration of the dopant at a constant reduced temperature $T_{red}=T/T_c = 0.975$.

FTIR-MEASUREMENTS

The infrared absorption dichroism method for determining the molecular order of liquid crystals is reasonable simple and has been widely used [13, 14, 15, 16, 17].

The CN stretching vibration of 5CB and CB15 yields a strong isolated absorption band in the mid infrared spectral region localized around 2227cm^{-1}. The corresponding transition moment points along the C≡N bond and is commonly assumed to be directed parallel to the long molecular axis of 5CB and CB15 [18, 13, 15]. Consequently, the CN stretching band is well suited for the investigation of the arrangement of the LC molecules inside the ANOPORE channels.

AP-membranes of about 10mm×20mm size are assembled between CaF_2 windows (15mm×30mm) and mounted into a home-build goniometer cell thermostated by flowing water. This cell was adjusted into the sample compartment of a BioRad FTS-60a Fourier Transform Infrared spectrometer. A wire grid polarizer with an efficiency of >98% was placed behind the sample cell.

Spectra were recorded by tilting the AP-membrane against the incident IR beam by an angle of $\alpha = 45°$. The dichroitic ratio is defined as

$$R = \frac{A_{\|}}{A_{\perp}}, \tag{8}$$

where $A_{\|}$ and $A_{\perp}$ are the absorbances of the CN stretching vibration band of 5CB corresponding to IR radiation polarized parallel and perpendicular to the incident plane, respectively. Neglecting the local electrical field correction [14, 15, 18, 13] the IR order parameter of 5CB with respect to the cylinder axis is given by [16, 17]

$$S_{IR}(CN) = \frac{R-1}{R-1+3\cdot\sin^2\alpha/n_{eff}^2} \tag{9}$$

with the effective extraordinary refractive index $n_{eff} = n_{oA}\left[1-(n_{eA}^{-2}-n_{oA}^{-2})\sin^2\alpha\right]^{1/2}$ $\approx$1.55, taken in the mid infrared spectral range.

Fig. 9a shows the temperature dependence of the CN order parameter, S_{IR}(CN), of 5CB and different 5CB/CB15 mixtures. It becomes evident that the increase of the weight fraction of 5CB results in a reduction of S_{IR}(CN).

The IR order parameter of an ensemble of LC molecules characterized by a local director field tilted with respect to the cylinder axis by the angle Θ can be written as follows:

$$S_{IR} = S_{mol}\cdot\frac{1}{2}\cdot\left(3\cos^2\Theta-1\right) \tag{10}$$

where we suppose that the distribution of the transition dipole moments around the pore axes are of rotational symmetry and independent from each other. Furthermore, assuming the order parameter of the long molecular axes with respect to the LC director, S_{mol}, to be identical in pure 5CB ($\Theta = 0°$) and in 5CB/CB15 filled AP-samples at the same reduced temperature we calculated the tilt angle (Θ) of the local director with respect to the pore axis.

Fig. 9b shows that by increasing the weight fraction of CB15 up to x_{CB15}=0.25 the tilt angle increases continuously up to $\Theta = 45°$.

SUMMARY

Twisted nematic liquid crystal 5CB/CB15 mixtures adsorbed on ANOPORE membranes have been studied by means of FTIR, Generalized Transmission Ellipsometry and polarizing microscopy.

From FTIR-measurements it becomes evident that upon adsorption of twisted

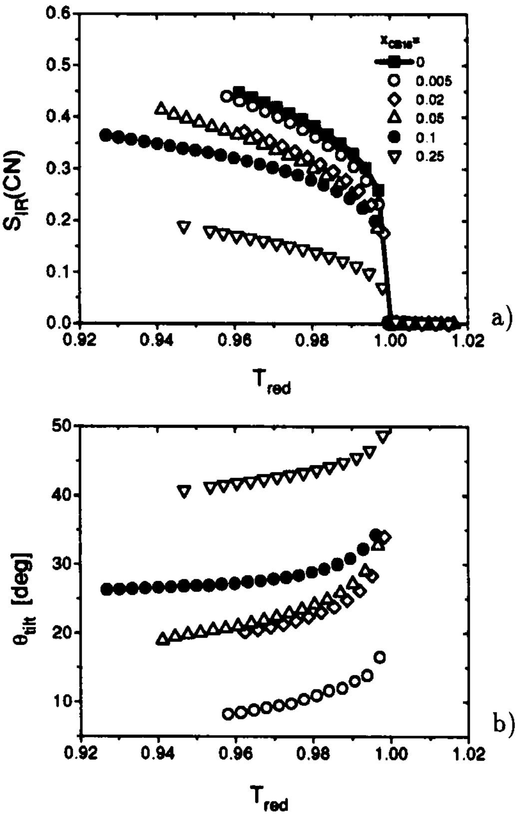

Figure 9
IR order parameter of the CN stretching band, S_{IR}(CN), **(a)**, and the corresponding tilt angle of the local director with respect to the pore axes, Θ, **(B)**, in dependence on the reduced temperature, $T_{red} = T/T_c$ (T_c ... nematic-isotropic transition temperature) in 5CB/CB15 filled ANOPORE membranes for the weight fractions of CB15 x_{CB15}=0, 0.05, 0.02, 0.05, 0.1, 0.25.

nematic liquid crystals in ANOPORE-membranes the local director field is tilted with respect to the channel axes. The mean tilt angle increases with decreasing pitch. These results confirm the results obtained by ^{13}C-NMR measurements [19, 8].

The ellipsometric parameters of the adsorbate system in the range from 400nm to 1300nm reveal the significant changes in the optical properties of the liquid crystal material upon confinement to the cylindrical pores: sign reversal of optical activity, absence of selective reflectivity, and no Mauguin limit even for very low concentration of CB15.

Using the values of AP-birefringence and of the tilt angle of the director inside the pores, the measured optical rotary power spectra cannot be explained by a simple de Vries like formula. An unambiguous model for the structure of the chiral confined director field is hardly to be established.

ACKNOWLEDGMENTS

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