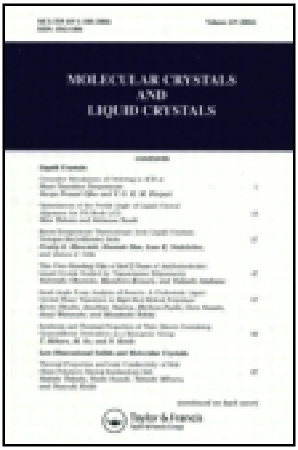

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# NMR DIFFUSION MEASUREMENTS IN CHOLESTERIC LIQUID CRYSTALS - PITCH LENGTH, TEMPERATURE AND TIME DEPENDENCE

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## ABSTRACT

This paper presents NMR measurements of diffusion in helix direction in twisted nematics. We found an exact Arrhenius type temperature dependence of the diffusion coefficient. The pitch length dependence is less than of square order, although diffusion decreases at shorter pitch lengths. The diffusion coefficient decays with increasing observation time over an interval of several miliseconds.

## INTRODUCTION

Diffusion in the cholesteric liquid crystalline phase shows interesting features quite different from the closely related nematic mesophase. We were particularly interested in the diffusion coefficient $D_P$ in helix direction. Experimentally, this coefficient was found by $^2$D NMR measurements (1) to depend upon the pitch length $p_0$ by a relation $D_P \approx p_0^2$. Moreover, a decay of $D_P$ with increasing observation time was measured by Blinc with field gradient NMR (2). In this paper we applied different NMR methods to confirm these results.

## THEORY

The cholesteric phase was induced by addition of a small amount of chiral dopant to nematic n-alkyloxyphenyl-m-alkyloxybenzoates (nO.Om). In such samples with positive magnetic susceptibility anisotropy $\Delta\chi$, the helical axes arrange perpendicular to the spectrometer field $\vec{B}_0$. At this orientation of the helices, the average molecular orientation $\vec{n}$ with respect to the magnetic field will change if the molecules move in helix direction z. Such a translational diffusion, coupled to the rotational reorientation, during the recording of the NMR signal influences the line shape of $^{2}$D NMR(1,3), $^{13}$C NMR(4), or $^{1}$H NMR (5) spectra. We have studied the temperature and pitch length dependence of $D_P$, by fitting proton decoupled $^{13}$C NMR spectra after a simple $\Pi/2$ or CP pulse sequence with the model described in (4)

The dependence of $D_P$, having the meaning of the proportionality factor between the average square displacement in pitch axis direction $\langle (z(t)-z(0))^2 \rangle$ and observation time t , upon time range is difficult to determine by $^{13}$C NMR due to the not very precisely defined time scale. We applied proton NMR line shape fitting using a special preparation pulse sequence described in (5)

## EXPERIMENTAL

The samples were prepared by mixture of chiral cholesteryl-undecylcarbonate (ChUC) with nO.Om homologues of different chain lengths n,m ( 10-06, 10-08, 50-06, 60-07 ). The molar concentrations $m_c$ of ChUC were in the range of 1..4% with corresponding pitch lengths of 2..8 μm ( $p_0 \cdot m_c = 8.2 \mu m \cdot \%$ ). $^{13}$C experiments were performed at $B_0$=1.46 T corresponding to 15.68 MHz resonance frequency. The proton NMR investigations were made with a Bruker 32 MHz pulse spectrometer at $B_0$=0.7 T with 16..64 accumulations for each spectrum.

The liquid crystalline compounds were kindly provided by the MLU Halle LC Group and by VEB Spezialchemie Lützschena.

## RESULTS AND DISCUSSION

A characteristic temperature dependence of $D_P$ is shown in Fig.1. Straight lines corresponding to an Arrhenius behaviour show that no additional temperature dependence is present, particularly no order parameter dependence as is found for related viscous properties. Diffusion coefficients in the isotropic phase were measured by field gradient NMR. Their values coincide for all mixtures.

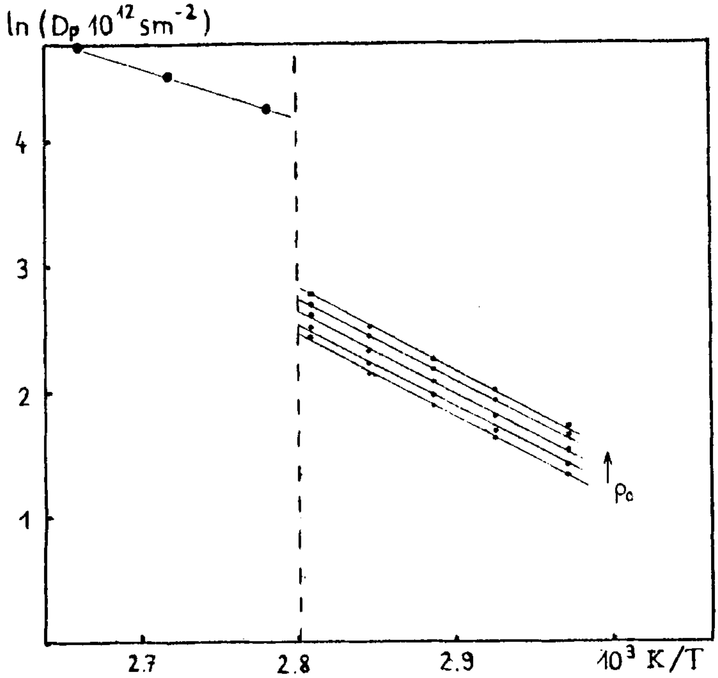

**FIGURE 1:** Arrhenius plot of the diffusion coefficients $D_P$, $D_{iso}$ of 50.06 at $p_O$= 2.3, 3.3, 4.4, 5.7 and 7.2 μm.

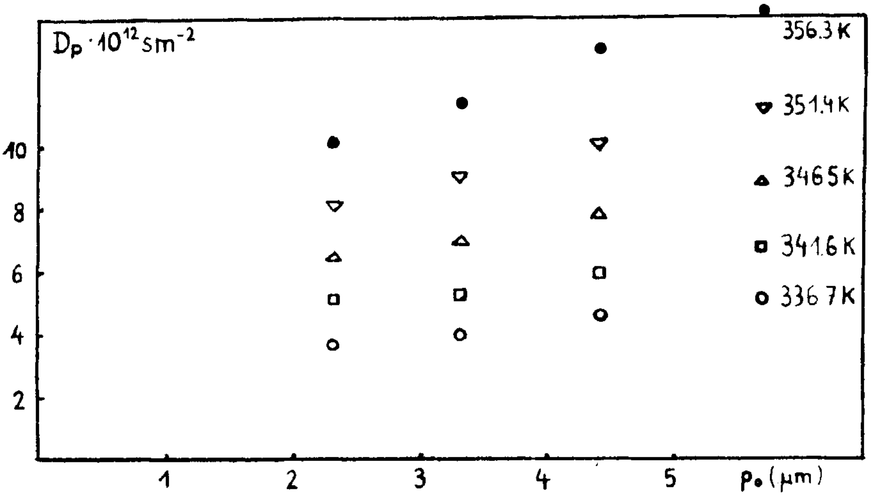

**FIGURE 2:** $D_p$ for different pitch lengths, sample 50.06. The pitch range corresponds to the righthand part of Fig.3.

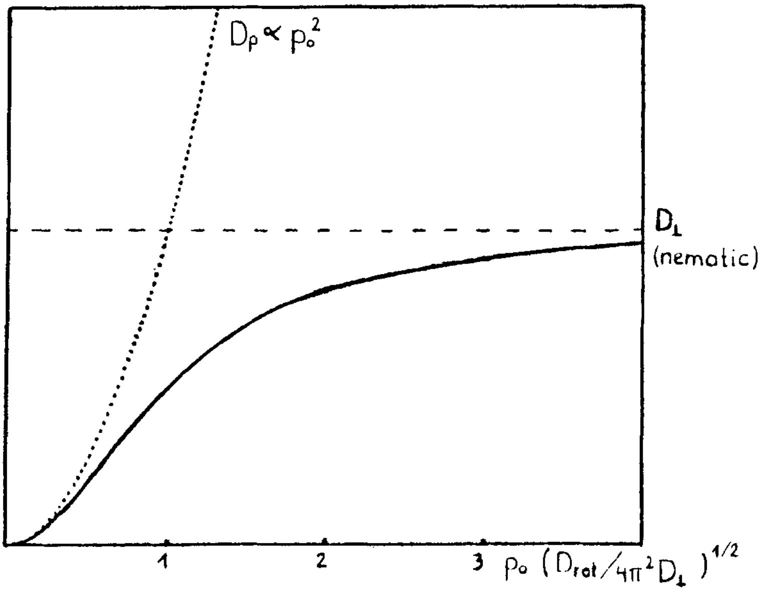

**FIGURE 3:** Theoretical pitch length dependence of $D_P$. $D_\perp$ is the coefficient of the nematic, perpendicular to $\vec{n}$.

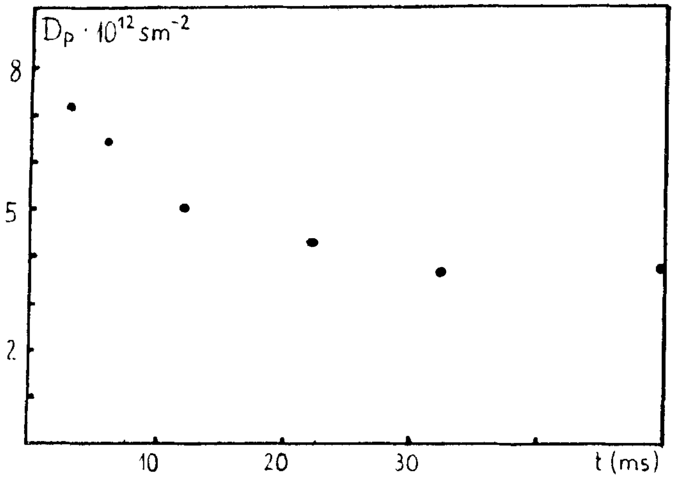

**FIGURE 4:** Time dependence of $D_P$ for 50.08, T=337 K, $p_0$= 6.1 μm.

Figure 2 gives a characteristic pitch length dependence of $D_P$. It is present, but weak. Surely it is less than of square order. This is not in contradiction with results of Yaniv(1) for shorter pitch lengths. Fig. 3 shows the theoretical $D_P(p_0)$ curve resulting from a model presented elsewhere, that accounts for a coupling of translational and rotational mobility(6). The quantity $D_{ROT}$ (Fig. 3) can be related to $\gamma_1$. A rough approximation of an equation derived from the Einstein relation,

$$D_P = N k_B T p_0^2 / ( 4 \pi^2 \gamma_1 )$$

( N being the number of diffusing particles per volume, $\gamma_1$ the rotational viscosity, the equation holds in the short pitch range ), shows that N cannot be connected with single molecules. The rotational motions must involve collective processes of at least some $10^6$ molecules in order to account for the low values of the diffusion coefficient $D_P$ measured in cholesterics.

The time dependence of diffusion parallel to the helix(2) is confirmed by our experiments. The coefficient $D_P$ decays with diffusion time, as is depicted in Fig. 4. For samples with $p_0$ in the μm range, as investigated here, a constant long-time limit value is established only after more than about 50 ms. The observation time scale in the reported $^{13}C$ NMR experiments is approximately 3..5 ms.

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