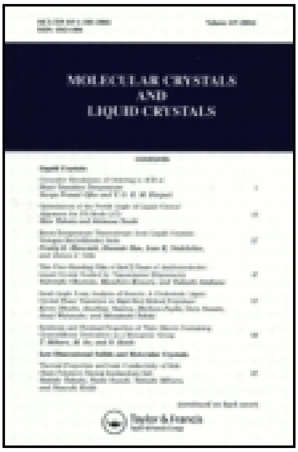

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Investigation of the Alignment of Cholesterylmiristat Liquid Crystal Phases by Proton NMR

V. A. Andreev [a] , Yu. A. Marazuev [a] , L. V. Nedbaeva [a] & I. V. Oleynikova [a]

[a] Department of Physics, Kiev Taras Shevchenko University, Kiev, Ukraine

Version of record first published: 04 Oct 2006.

To cite this article: V. A. Andreev , Yu. A. Marazuev , L. V. Nedbaeva & I. V. Oleynikova (1995): Investigation of the Alignment of Cholesterylmiristat Liquid Crystal Phases by Proton NMR, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 265:1, 477-485

To link to this article: http://dx.doi.org/10.1080/10587259508041715

Mol. Cryst. Liq. Cryst. 1995, Vol. 265, pp. 477–485
Reprints available directly from the publisher
Photocopying permitted by license only

INVESTIGATION OF THE ALIGNMENT OF CHOLESTERYLMIRISTAT LIQUID CRYSTAL PHASES BY PROTON NMR

V.A.ANDREEV, YU.A.MARAZUEV, L.V.NEDBAEVA, I.V.OLEYNIKOVA
Department of Physics, Kiev Taras Shevchenko University,
Kiev, Ukraine

Abstract Order parameter and the orientation of the molecular "long axis" were determined from second and fourth NMR line moments of the "polycrystalline" samples of cholesterylmiristat in smectic phase. The effects of the molecular diffusion in cholesteric phase are discussed.

INTRODUCTION

NMR is one of the most exact methods to investigate the degree of molecular oreintational ordering in liquid crystals (LC) and is widely used to study nematic LC, molecules often possess a isolated pairs of the protons coupled by the dipole-dipole interactions, providing the doublet splitting of the NMR spectra, proportional to the LC order parameter S [1,2]. The molecules of typical cholesteric liquid crystals (ChLC) have no isolated proton pairs and proton NMR lines show no structure, so to study the molecular alignment in their cholesteric and smectic phases one needs to use Van Vleck's method of NMR line moments [3]. Some works were done in this direction. Second moment (M_2) dependence on the magnitude direction of external magnetic field ($\mathbf{B}$) was studied for admixture of cholesteric and nematic components [4] and M_2 angular dependence was studied for a stack of cells containing the ChLC [5]. The temperature dependence of relative value of S was investigated in "polycrystalline" samples in ChLC and smectic (SLC) phases [6,7].

In this paper we present a method to determine the absolute value of S and the orientation of the order parameter tensor axis in the molecular base from second and fourth NMR line moments of the "polycrystalline" samples of cholesterylmiristat LC in smectic and cholesteric phases, using the data on the intramolecular configuration of protons obtained by the X-Ray structure analysis of solid phase [8].

METHOD OF NMR LINE MOMENTS FOR INVESTIGATION OF ORDER PARAMETER TENSOR AND STRUCTURE OF LC

To explain the proposed approach we shall take into account interactions, exerting influence on the NMR lineshape: Zeeman interaction of proton magnetic moments with external magnetic field **B** and intramolecular dipole-dipole interaction. Intermolecular interactions are assumed to average to zero, therefore rotational motion of molecules one by one occurs sufficiently fast and uncorrelated with each others. Then the Zeeman splitting considerably exceeds the maximum value of dipole-dipole splitting ($\delta\omega_m$) and only the secular part of intramolecular dipole-dipole interaction Hamiltonian should be used for description of the NMR lineshape. This truncated Hamiltonian has the form [1,2,3]:

$$H = \frac{1}{2}\sum_{ij} B_{ij}(3I_{iz}I_{jz} - (I_i I_j)) \qquad (1)$$

where I_{iz} denotes the component of spin $\mathbf{I}_i$ for proton number i along the external magnetic field **B** , i=1...N, N is the number of protons in the molecule,

$$B_{ij} = \gamma^2 h^2 r_{ij}^{-3} < P_2(\cos\kappa_{ij}) > (1-\delta_{ij}) \qquad (2)$$

where γ is proton gyromagnetic ratio, κ_{ij} is the angle between **B** and the vector $\mathbf{r}_{ij}$ connecting the ith and jth protons, P_2 is the Legendre polynomial [9] and the angular brackets indicate the time average over molecular reorientations around the local axis of the "director" (**n**), which the direction of the molecular "long" axis preferred orientation, and also due to the translational diffusion of molecule between regions of LC with different local directions of **n**. The last averaging should be done in the case of "fast diffusion" in cholesteric phase with small helix pitch P and sufficiently large translational diffusion constant D, when $P^2D^{-1}\delta\omega_m << 1$. In the opposite case of "slow diffusion" only the first averaging should be performed [2]. Assuming the $D_{\infty h}$ local symmetry of the LC structure, we have

$$< P_2(\cos \kappa_{ij}) > = \frac{1}{2^\alpha} P_2(\cos \theta_\alpha) \sum_{m\ n}^{2} D^2_{0m}(0, \theta_{ij}, \psi_{ij}) \cdot \\ \cdot D^2_{mn}(\varphi, \theta, \psi)(\delta_{n,0}S - \frac{1}{\sqrt{6}}(\delta_{n,2} + \delta_{n,-2})D) \quad (3)$$

where $\alpha = 0,1$ stend for "slow" and "fast" diffusion in the ChLC phase, respectively and θ_0, θ_1 are respectively the angle between the local **n** and **B** and the angle between the local direction of cholesteric helix axis **h** and **B**; D^2_{mn} is the Wigner D-function [9]; θ_{ij}, ψ_{ij} are polar and azimuth angles of in the fixed molecular coordinate system (MCS) and φ, θ, ψ are the Euler angles, describing the rotation from MSC to the order parameter tensor principal coordinate system (OSC). The principal values of order parameter tensor are connected with usual order parameter [1,2]:

$$S = < P_2(\cos\lambda) > = \frac{3}{2} S_{z'z} \quad (4)$$

where λ is the angle between **n** and the "long molecular axis" z', determined as the principal axis of the order parameter tensor, which corresponds to the largest principle value, and

$$D = \frac{3}{2}(S_{y'y'} - S_{x'x'}) \quad (5)$$

which is a measure of the difference of the alignment of the two transverse axes along the director [2].

As it was mentioned above in typical cholelesteric systems NMR line is broadened by dipolar interactions, but isn't splitted. So the information on the LC structure should be extracted from the NMR line moments. At high temperatures approximation the odd moments have zero values and even moments M_{2n} could be calculated from general Van Vleck's expression [3]

$$M_{2n} = N^{-1} 2^{2-n} Sp\{H,[H[\ldots[H,I_x]\ldots]]]^2 \tag{6}$$

were [...,...] denotes the commutator and appears in the Eq. (6) n times.

Using the Eqs. (1), (2), (3) and taking into account the spatial distribution of the directions of **n** and **h** we can therefore express the Eq. (6) as

$$M_{2n} = 2^{-2\alpha n} \eta_n \sum_{m=0}^{2n} a_{nm}(\varphi,\theta,\psi) S^{2n-m} D^{m} \tag{7}$$

where

$$\eta_n = \langle P_2(\cos\theta_\alpha)\rangle_s \tag{8}$$

and $\langle\ldots\rangle_s$ indicates an average over all the molecules. $a_{nm}(\varphi,\theta,\psi)$ is the function of the angles describing the rotation from MSC to OSC and depends also on the intramolecular configuration of protons.

The factor η_n, Eq. (8), describes the dependence of M_{2n} on the magnetic field orientation and could be easily evaluated for given LC structure. So it was possible to explain the experimental results on the M_2 angular dependence in ChLC without detailed consideration of the molecular structure and order parameter tensor [3].

Then to evaluate the five independent components of symmetrical traceless order parameter tensor, or to determine the orientation of the OSC in fixed molecular base and values of S and D from the experimental data on the NMR line moments it is necessary to know the intramolecular configuration of protons and explicit analytical expressions for five first even moments. Unfortunately at present we have the reliable expressions only for M_2 and M_4 [3] and the evaluation of the analytical expressions for higher moments is still pretty difficult [10]. Therefore we use the van Vleck's formula to evaluate the dependence of M_2 and M_4 on the angles φ, θ, ψ and make some additional assumptions concerning the values of unknown parameters.

Considering the molecule of ChLC which have strongly stretched form (Fig. 1) we assume that S >> D. It means that the difference of the alignment of the two transverse axes along local **n** is much smaller than the alignment of "long axis".

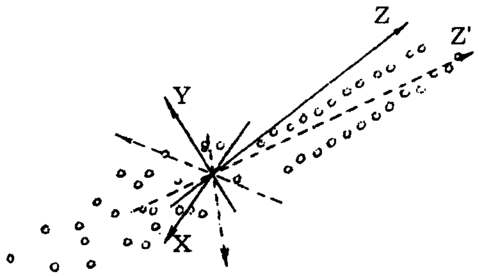

FIGURE 1 Configuration of protons in the molecule of cholesterylmiristat (from data of ref.[8]). The axes of inertia are presented by solid lines Dashed line shows the principal axis of the order parameter tensor, determined from the NMR data (this work).

In this case

$$M_{2n} = 2^{-2\alpha n}\eta_n a_{n0}(\varphi,\theta)S^{2n} = B^{\alpha}_{2n}S^{2n} \qquad (9)$$

with

$$\eta_2 = \frac{1}{5}, \ \eta_4 = \frac{3}{15} \tag{10}$$

for the "polycrystalline" sample with chaotic distribution of **n** and **h** . Eq. (9) was used to evaluate the temperature dependence the relative value of S [5,6].

Neglecting the D value in comparison with S we have from the Eq. (3) that M_{2n} are independent on the angle ψ. Moreover, again because of ChLC molecule strongly stretched form, when the MSC is connected with axes of inertia of the molecule we could suppose that the axis which correspond to the smallest moment of inertia is close to the "long axis" [2] and expect weak dependence of M_{2n} on the angle φ. This was confirmed by numeral calculations (Fig. 2). So moments $M_2$and M_4 could be used to estimate values of the order parameter S and the angle θ between the "long axes" and the axis which correspond to the smallest moment of inertia of the molecule.

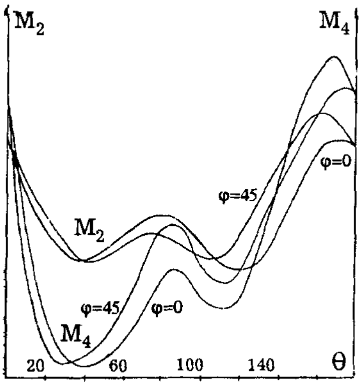

FIGURE 2 Dependence of moments M_2 and M_4 from angle θ for two fixed value of φ. Curves for other values of and φ this situated between this two curves.

THE ANALYSIS OF THE EXPERIMENTAL RESULTS

Measurements were carried out on NMR spectrometer of wide lines RY-2301 and "Bruker" spectrometer from room temperature. Magnetic fields, used in these experiments (3000 and 9000 Oe) have no influence on the structure of the sample. The temperature dependencies of M_2 and M_4 calculated from the NMR spectra of "polycrystalline" sample of cholesterylmiristat, in ChLC and SLC phases are shown in Fig. 3.

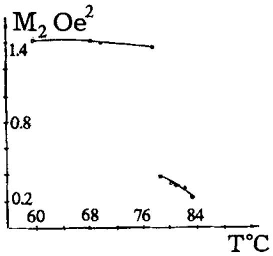

FIGURE 3 M2 temperature dependence for "polycrystalline" sample of cholesterylmiristat in ChLC and SLC phases calculated from the experimental data.

As in the SLC phase the modulation of dipole-dipole interaction caused by translational diffusion is absent, this case corresponds to the "slow diffusion" limit ($\alpha = 0$).

Using values of M_2 and M_4 (Fig. 2) and solving Eq. (9), we have found, that at the temperature of 72°C in the SLC $\theta = 15°-20°$ and S = 0.8. This S value is in good agreement with the results of optical measurements carried out for the same samples (Fig. 4).

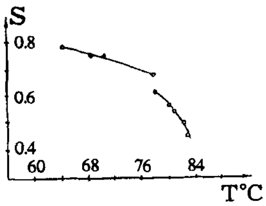

FIGURE 4 Temperature dependence of order parameter S in ChLC and SLC phases by investigations of birefringence.

The comparison of the temperature dependence of M_2 and optical order parameter measurement for ChLC allows to conclude that the bound of M_2 under transition SLC-ChLC is only partially connected with the change of the structure and local ordering and can be explained by inclusion of mechanism of translational diffusion of molecules along axis of ChLC.

To estimate of influence of translational diffusion, experimental value of $B_2^{e} = M_2 / S^2$ was compared with theoretically predicted values for limits of "slow" and "fast" diffusion (B_2^0 and B_2^1 Eq.(9)). Assuming that the "long axis" direction is the same both for SLC and ChLC phases, we obtained B_2^{e} = 1.02 - 1.04, B_2^0 = 0.6, B_2^1 = 2.4 , and. It correlates with the estimation $P^2D^{-1}\delta\omega_m \sim 1$ [5,6] and points that neither "fast" nor "slow" diffusion limits are realized. Therefore the additional theoretical research of factors of translational diffusion for arbitrary values of as well as the evaluation of the analytical expressions for higher moments should be carried out to achieve the necessary generalization of theory for interpretation of the ChLC NMR spectra.

REFERENCES

1. P.G. de Gennes, The Physics of liquid crystal (Clarendon Press,Oxford, 1974), Chap. 1-2.
2. V.J. Stephen and J.P.Straley, Rev. Mod. Phys., 46, 617 (1974).
3. V.A. Andreev et al., Zhurn. exp. teor. phys. (rus), 72, 6 (1977).
4. P.J. Collings et al., Phys. Rev., 11A, 2 (1975).
5. V.A. Andreev et al., Fizika Zhidkogo Sostoyanya, 8, 29 (1980).
6. V.A. Andreev et al., Fizika Zhidkogo Sostoyanya, 10, 14 (1982).
7. B.M. Kreven and G.T. DeTitta, J.C.S.Perkin II, 14 (1975).
8. J.H. Van Vleck, Phys. Rev., 74, 1168 (1948).

9. D.A. Varshalovitch et al. Quantum Theory of the Angular Momentum (Nauka, Leningrad, 1978).
10. S.J.K. Jensen and E.K. Hansen, Phys. Rev. B, 7, 2910 (1973).