Determination of components of the order parameter tensor of cholesteryl myristate by ^{1}H NMR data

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The order parameter and orientation of the "long axis" of a cholesteryl myristate molecule have been determined by the second, fourth, and sixth moments of the ^{1}H NMR line of a "polycrystalline" sample in the smectic phase. The effects of molecular diffusion in the cholesteric phase are discussed.

Key words: moments of ^{1}H NMR line, order parameter.

^{1}H NMR spectroscopy is one of the most exact methods for studying the degree of orientation ordering of molecules in liquid crystals (LC) and is widely used for studying nematic LC (NLC), in which isolated pairs of protons are formed due to dipole-dipole interaction. These pairs give a doublet splitting in the spectrum, which is proportional to the value of order parameter S.[1,2] The structure of molecules of cholesteric liquid crystals (CLC) is more complex, and no individual pairs of nuclei can be isolated; therefore, the doublet structure is not manifested in ^{1}H NMR spectra. The method of moments suggested by Van Vleck (Ref. 3) should be used for studying molecular ordering of cholesteric and smectic phases of such substances. The method of moments has been used in Ref. 4, it has been shown that the second moment M_2 of the ^{1}H NMR line of CLC is proportional to S^2, and the proportion factor depends on the molecular structure,[5] the structure of CLC, and the parameters of spatial molecular motion. The dependences of the second moment on the direction and on the value of the external magnetic field have also been studied for solutions of cholesteric and nematic components. In Refs. 6 and 7, M_2 was used for studying the temperature dependence of the relative S value in "polycrystalline" samples (samples with a chaotic distribution of the axes of a twisting spiral).

In this work, the procedure of using the method of moments for determining the absolute S value and orientation of axes of the order parameter tensor (OPT) in the molecular system of coordinates in mesomorphic phases of substances that form typical CLC is suggested.

Procedure of calculation

To explain the approach suggested, let us take into account interactions that affect the shape of ^{1}H NMR lines, namely: the Zeeman interaction between magnetic moments of nuclei and an external magnetic field and the intramolecular dipole-dipole interaction of nuclei. Assuming that rotations of molecules around one another are rather fast and do not correlate with one another, let us consider that intermolecular dipole-dipole interactions are averaged to zero. Since the Zeeman splitting is considerably greater than the maximum value of the dipole-dipole splitting ($\delta\omega$), only the secular part of the hamiltonian of the dipole-dipole interaction can be used for description of the shape of the ^{1}H NMR spectrum.[1–3] This truncated hamiltonian takes the form:

$$H = \frac{1}{2}\sum_{ij} B_{ij}\left(3I_{iz}I_{jz} - \left(I_iI_j\right)\right), \qquad (1)$$

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

$$B_{ij} = \gamma^2\hbar^2 r_{ij}^{-3} < P_2\left(\cos\theta_{ij}\right) > \left(1 - \delta_{ij}\right), \qquad (2)$$

where γ is the gyromagnetic ratio of a proton, θ_{ij} is the angle between $\vec{B}$ and the vector $\vec{r}_{ij}$, which connects the ith and the jth protons, and P_2 is the Legendre polynomial.[8] Brackets mean time averaging of molecular orientations around local directions of the $\vec{N}$ director and averaging caused by translation diffusion of molecules between LC regions with different local directions of the $\vec{N}$ director. The latter averaging is typical of the case of "fast diffusion" in the cholesteric phase of a substance with a small step P of the spiral and a sufficiently high coefficient of translation diffusion D, when $P^2D^{-1}\delta\omega \ll 1$. Only the first averaging remains in the opposite case of "slow diffusion."[2] Considering that the

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local distribution of molecular orientations has $D_{\infty h}$ symmetry, we can obtain

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

where $\alpha = 0.1$ corresponds to "slow" and "fast" diffusion in CLC phases; ϑ_0 and ϑ_1 are the angle between the local direction of $\vec{N}$ and $\vec{B}$ and the angle between the local direction of the cholesteric $\vec{h}$ axis and $\vec{B}$, respectively; D^2_{mn} are the Wigner D-functions;[9] ϑ_{ij} and ψ_{ij} are the polar and azimuth angles in the fixed molecular system of coordinates (MSC); φ, ϑ, and ψ are Euler angles describing rotation of the MSC relative to the basic system of coordinates (BSC) of the order parameter tensor. S and D are parameters that characterize ordering of the "long" axis and the difference in ordering in two axes perpendicular to the "long" axis and are related to the main values of the OPT by the correlations:[2]

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

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

where z' indicates the direction of the main axis of the OPT corresponding to the largest intrinsic value ("long" axis) and x' and y' are the directions of other main axes of this tensor ("short" axes).

Since $Sp\hat{S} = 0$, parameters S and D completely determine the order parameter tensor in the BSC.

Thus, it follows from Eqs. (1)—(5) that a ^{1}H NMR spectrum contains the complete information about the main values of the OPT and orientation of the BSC relative to the MSC specified by the Euler angles (φ, ϑ, and ψ). Therefore, to obtain this information, one should know five independent parameters that characterize this spectrum.

The dipole splitting can be one of these parameters in the case of NLC. Information about the structure of typical CLC can be obtained from moments of the ^{1}H NMR line. Odd moments are equal to zero in the approximation of high temperatures, and the M_{2n} moments can be calculated from the general Van Vleck expressions:

$$M_{2n} = N^{-1}2^{2-n} Sp\left\{\left[H,\left[H,\left[\ldots\left[H, I_x\right]\ldots\right]\right]\right]^2\right\}, \quad (6)$$

where [...,...] denotes the commutator and is repeated n times in Eq. (6).

Using formulas (1), (2), and (3) and taking into account the distribution of the $\vec{N}$ and $\vec{h}$ directions, Eq. (6) can be written as

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

where

$$\eta_n = < P_2(\cos\vartheta_{\alpha}) >_s, \quad (8)$$

and <...> designates averaging over all molecules and $a_{mn}(\varphi, \vartheta, \psi)$ is the function of angles describing rotation of the MSC relative to the BSC, which also depends on the intramolecular configuration of protons.

The η_n factor in Eq. (8) describes the dependence of M_{2n} on the magnetic field orientation and can usually be obtained for a particular structure of CLC. To determine the orientation of the BSC relative to the MSC and S and D parameters from experimental values of moments of the ^{1}H NMR line, one should know the arrangement of protons in a molecule and exact analytical expressions for first five even moments. Calculations of higher moments are related to large calculational difficulties, and reliable expressions for first three moments have been obtained to date: M_2, M_4 (Ref. 3), and M_6 (Ref. 10). However, a disadvantage of this information can be partially compensated by some additional assumptions concerning values of unknown parameters.

For this purpose, we have analyzed the arrangement of protons in a cholesteryl myristate molecule (Fig. 1). It can be seen that the molecule is stretched, and the position of the "long" axis is close to that of the axis of the inertia tensor corresponding to the lowest value of the inertia moment. Therefore, the second term in Eq. (3) makes a small contribution. In addition, according to the data in Ref. 2, the D parameter is 0.1 S to 0.2 S, which allows one to neglect the second term in Eq. (3). To confirm these considerations, we have studied the dependences of moments on the values of the D parameter and ψ angle as the D value is changed from 0.1 S to 0.3 S and the ψ angle ranges from 0° to 180°.

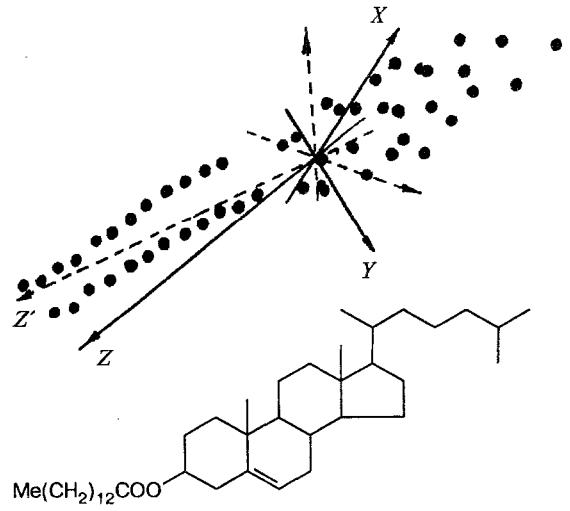

Fig. 1. Configuration of protons and the structural formula of a cholesteryl myristate molecule (according to data in Ref. 9). Axes of the inertia tensor are presented by solid lines. Basic axes of the order parameter tensor calculated from ^{1}H NMR data are presented by dashed lines.

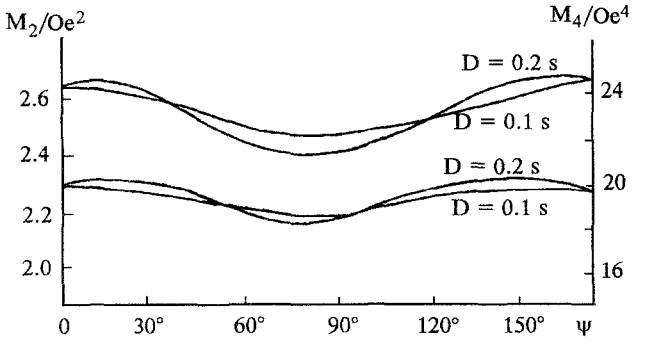

Fig. 2. Dependence of moments of the Euler angle ψ at various values of the D parameter.

The results of numerical calculations are presented in Fig. 2.

Neglecting the second term in Eq. (3), we find that M_{2n} is independent of the ψ angle. In this case,

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

where

$$\eta_2 = \frac{1}{5}, \quad \eta_4 = \frac{3}{35}, \quad \eta_6 = \frac{35}{1001}, \qquad (10)$$

for the "polycrystalline" sample with the chaotic distribution of $\bar{N}$ and $\bar{h}$. Equation (9) was used for studying the temperature dependence of the relative S value.[5,6]

Thus, the moments M_2, M_4, and M_6 can be used for determining the value of the order parameter S, the angle ϑ (the angle between the direction of the "long" axis and the axis corresponding to the minimum value of the inertia moment of a molecule), and the azimuth angle φ. The results of numerical calculations of the dependences of moments are presented in Fig. 3.

Experimental

Measurements were carried out on an RYa-2301 ^{1}H NMR spectrometer using broad lines and on a Bruker instrument at ≈20 °C. The magnetic field of H ≅ 3000 and 9000 Oe used in the experiments exerted no effect on the sample structure. The temperature dependence of M_2 calculated for the ^{1}H NMR spectra of the "polycrystalline" sample of cholesteryl myristate in cholesteric and smectic LC phases is shown in Fig. 4. Since there is no modulation of the dipole-dipole interaction caused by translation diffusion in the smectic phase, the M_2, M_4, and M_6 moments are independent of the diffusion rate, which corresponds to "slow" diffusion (α = 0).

Using M_2 (Fig. 4), M_4, and M_6 values and solving the system of equations (9), we find that at 72 °C ϑ = 23°, φ = 50°, and S = 0.8 in the smectic LC phase (CLC phase). This value of S agrees well with the results of optical measurements of S for these samples (Fig. 5).

Comparison of the temperature dependences of the second moment M_2 and the order parameter S measured by optical methods for the same crystals allows one to draw the conclusion that the jump of M_2 observed for the SLC—CLC transition is only partially related to the change in structure and

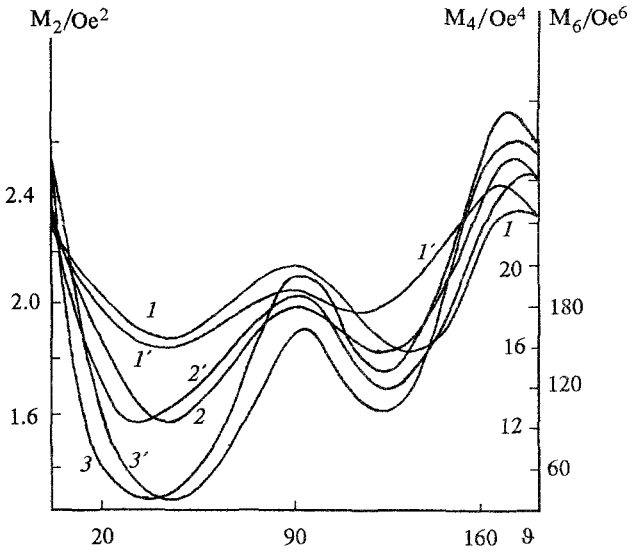

Fig. 3. Dependence of the M_2 (*1, 1'*), M_4 (*2, 2'*), and M_6 (*3,3'*) moments on the φ angle. *1, 2, 3* for φ = 0°; *1', 2', 3'* for φ = 45°. Curves for other angles lie between the curves presented.

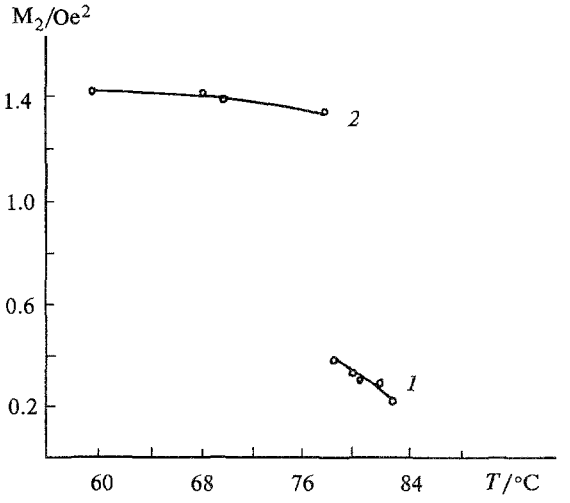

Fig. 4. Temperature dependence of M_2 for the "polycrystalline" sample of cholesteryl myristate in the CLC (*1*) and SLC (*2*) phases obtained from ^{1}H NMR data.

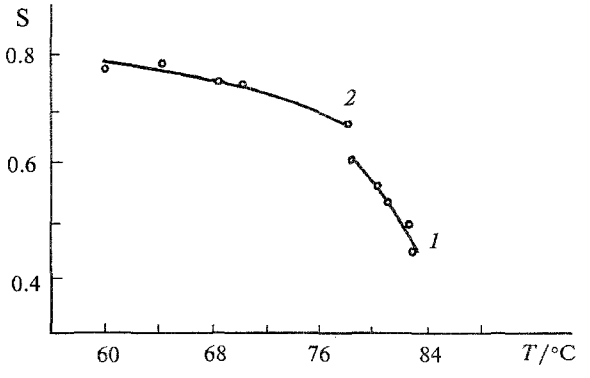

Fig. 5. Temperature dependence of the order parameter S in the CLC (*1*) and SLC (*2*) phases obtained by measuring double refraction.

local ordering and can be explained by a switching-on of the mechanism of translation diffusion of molecules along the CLC axis.

To estimate the effect of translation diffusion, let us compare the experimental value $B^e_2 = M_2/S^2$ and theoretically predicted values for limiting cases of "slow" and "fast" diffusion (B^0_2 and B^1_2 from Eq. (9)). Considering that the direction of the long axis is unchanged in the cholesteric phase, $B^0_2 = 0.6$, $B^1_2 = 2.4$, and $B^e_2 = 1.02$ to 1.04 are obtained. According to the data in Ref. 11, for the diffusion coefficient D and the spiral step P this corresponds to the estimation $P^2D^{-1}\delta\omega \cong 1$ (Refs. 5 and 6) and shows that no limiting cases are realized in this substance. Therefore, additional theoretical investigation of all factors of translation diffusion is necessary for studying the effect of translation diffusion on ^{1}H NMR spectra.

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