Helical twist in cholesteric mesophases

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We review the theoretical and experimental studies on the helically twisted supermolecular structure of cholesteric liquid crystals (CLCs). We discuss the problem of the nature of the forces responsible for the helical twist, generalize the results of studying the orientational order in CLCs, and treat the features of the supermolecular structure of CLCs in the region of pretransition phenomena. We pay special attention to the temperature- and concentration-dependences of the pitch of the helix in different cholesteric systems. We analyze critically the theoretical models that have been proposed to describe these dependences. We examine in detail the approach based on averaging the angle of twist in the mean-molecular-field approximation for various types of angular dependence of the intermolecular interaction energy (modified Keating-Böttcher theory). We undertake an attempt to treat from a unitary standpoint the types of cholesteric systems known up to now (cholesterics proper, chiral nematics, nematic-cholesteric mixtures, and systems of a nematic with an optically active additive) and other types of mesophases that possess helical twist (chiral smectics-C, cholesteric polymers, and lyotropic CLCs). We discuss the features of the supermolecular structure and of the intermolecular interaction in the stated systems. We treat in detail the nematic-cholesteric mixtures and cholesteric systems having nonmesogenic components, which are important in application.

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1. INTRODUCTION

One of the most vigorously growing fields of physics of the condensed state is the study of liquid crystals.[1-6] The cholesteric liquid crystals (CLCs) are especially interesting and promising (and yet least studied). Their most important property is their ability to reflect light selectively, which arises from their helically twisted supermolecular structure.[7-11] The wavelength of maximum reflection λ_{max} (i. e., the visible color of a layer of the CLC) is associated with the helix p by the relationship $\lambda_{max} = np$, where n is the refractive index. The pitch of the helix of particular concrete systems depends in a definite fashion on external factors. This makes it possible to employ CLCs for indicating temperatures, visualizing thermal fields, electromagnetic radiations, and ultrasonic vibrations, in electrooptics, and for purposes of chemical analysis, etc.[4,8,12]

Up to now the relatively well developed fields have comprised the optics of CLCs (i. e., solving the problem of relating the experimentally observed selective optical properties to the parameters of the supermolecular structure), and also the electrooptics of CLCs— studying (mainly by optical methods) the changes in the supermolecular structure in electric and magnetic fields. The advances in these two fields are summarized respectively in the review of Belyakov, Dmitrienko, and Orlov[11] and in the pertinent sections of the review and monograph of Blinov.[6]

At the same time, the attention paid to studying the supermolecular structure itself has been evidently insufficient. The lack of both a generally accepted molecular-statistical theory of helical twist and of generalizing publications on the problems involving the pitch of the helix have extremely hampered the directed synthesis of cholesteric systems having required characteristics, and have seriously retarded the development of studies of CLCs.

This review aims to fill in this gap to some extent. We have undertaken here an attempt to systematize and present on unitary bases the results of theoretical and experimental studies of the helically twisted supermolecular structure in cholesteric systems of various types. As it seems to us, this review can be useful both for inventors and practitioners and for researchers working on general problems of the physics of liquid crystals (since a necessary condition for the adequacy of any theoretical description of the mesomorphic state is that one should be able to extend it to helically twisted mesophases).

2. SUPERMOLECULAR STRUCTURE OF CLCs

a) Classification of cholesteric mesophases

The source of helical twist is the chirality (i.e., the mirror asymmetry) of the molecules of one or several components existing in the cholesteric system.[1] Depending on the nature of the mesogenic molecules, one can single out the following types of cholesteric mesophases:

1. Cholesterics proper—derivatives of cholesterol (esters, halides) and of several other steroids (individual substances or mixtures).

2. The so-called "chiral nematics," i.e., substances whose molecules are analogous in structure to the molecules of typical nematics, but have asymmetric carbon atoms in the alkyl chain.

3. Cholesteric systems formed a dissimilar mesogenic components, in particular, mixtures of ordinary or chiral nematics with derivatives of cholesterol, which we shall be designated below as nematic-cholesteric mixtures (NCMs).

4. Cholesteric systems with induced chirality, i.e., systems of a nematic + an optically active additive (OAA).

Moreover, nonmesogenic additives (NMA) can enter into all the stated systems in small amounts.

CLCs can also be classified according to the sense of twist (right- or left-hand helix). Here one can single out especially the so-called compensated mixtures, which consist of components of opposite signs.

Cholesteric systems are also distinguished according to whether they exist in a region of pretransition phenomena under the given thermodynamic conditions (i. e., near the point of a transition to a translationally ordered smectic-A).

As we shall show below, besides the properties common to all CLCs, there are features characteristic of certain specific types of cholesteric systems.

b) The model of quasinematic layers

At present it is generally accepted to treat a CLC as a variety of nematic liquid crystal (NLC) that possesses helical twist. The model representation of a CLC in the form of a set of quasinematic layers is widely applied. Here the axes of the preferential molecular orientation of adjacent layers are related by the twist angle $\bar{\theta}_p$, which is defined by the expression

$$\bar{\theta}_p = \frac{2\pi a}{p}. \tag{2.1}$$

Here a is the distance between the quasinematic layers, which corresponds to the mean distance between neighboring molecules in the direction of the axis of the helix.[8,14-16] The smallness of the ratio a/p (real CLCs have $\bar{\theta}_p \sim 10^{-2}$) allows us to assume that the local structure of CLCs and NLCs is analogous at distances $r \ll p$ to an accuracy of $(a/p)^2$.

Naturally, a quasinematic layer cannot be treated as a real macroscopic object.[2] However, since a certain degree of close-range order in the arrangement of the centers of gravity of the molecules is unavoidable, this model must be a rather good approximation for constructing a molecular-statistical theory that takes explicit account of the interaction of only a small number of neighboring molecules.

An alternate model has been proposed[17] that pictures a CLC as a set of linear helical chains whose phases in planes perpendicular to the axes of the helix are random. However, as was pointed out in Ref. 18, without a correlation of the stated phases within a macroscopic region of the plane perpendicular to the axis of the helix, it would be impossible to speak of long-range orientational order giving rise to the existence of the mesophase. The acknowledgment of such a correlation actually returns us to the model of quasinematic layers.[3]

c) Orientational order in CLCs

Within a given quasinematic layer the orientational order of a CLC is characterized, analogously to an

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[1]The hypothesis has been advanced[13] of the possible formation of a cholesteric helix unassociated with chirality of the molecules owing to manifestation of long-range van der Waals forces; however, such mesophases have not yet been found experimentally.

[2]Chiral smectics-C having an angle of inclination θ_t close to 90° might be treated as cholesterics with quasinematic layers having a real existence (see Sec. 6).

[3]A situation has been described[158] that can occur for certain CLCs in the close vicinity of the phase transition point to the isotropic liquid when the contrast between a CLC and an NLC is essential even at small distances, and the model of quasinematic layers is not applicable. However, there are no experimental data on the features of the supermolecular structure of such systems.

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NLC, by order parameters that are defined by the self-consistency equations:

$$\langle P_L (\cos\theta)\rangle = \frac{\int_0^1 P_L (\cos\theta)\exp\left[-\beta V (\cos\theta)\right] d(\cos\theta)}{\int_0^1 \exp\left[-\beta V (\cos\theta)\right] d(\cos\theta)}$$

(2.2)

Here θ is the angle between the long molecular axis and the axis of preferential molecular orientation of the given quasinematic layer, we define $\beta = 1/kT$, and P is the Legendre polynomial:

$$V(\cos\theta) = \sum_i \sum_j v_{ij} \langle P_{2i} (\cos\theta)\rangle P_{2j} (\cos\theta).$$

(2.3)

Here the v_{ij} are constants that characterize the anisotropic component of the intermolecular interaction energy.[4]

If we take into account only the terms containing P_2, we get an approximation that is usually called the Maier-Saupe theory.[22,23] Henceforth we shall use the notation $\langle P_2 (\cos\theta)\rangle \equiv \eta$. As has been shown in Refs. 2, 24, and 25, the experimental data for NLCs agree fully with the theoretical $\eta(T)$ relationship in this approximation. The existing discrepancies are eliminated to a considerable extent by taking into account another term, namely $v_{22} \langle P_4 (\cos\theta)\rangle P_4 (\cos\theta)$, in the expansion of (2.3).[26,27] This term can be positive or negative, with the negative values corresponding to a deviation of $\eta(T)$ toward lower values of the order parameter. As was shown in Ref. 28, this means that a supplementary intermolecular interaction seems to operate that tends to arrange the molecules at a certain angle to the axis of preferential orientation.

Having examined these theoretical concepts, let us proceed to discuss the experimental results from determining $\eta(T)$ in CLCs. These studies are rather few in number, since most of the methods that have been successfully applied for nematics are inapplicable to CLCs owing to the helical twist. The existing data have been obtained by the NMR method,[29-31] by analyzing the temperature-dependence of the birefringence with account taken of the anisotropy of the local internal field,[32,33] and also by starting with the experimental temperature-dependence of the circular dichroism[34] [Fig. 1(a)]. Here the nature of the variations and the numerical values of $\eta(T)$ are analogous to an NLC. Hence we can conclude that the mechanism of orientational ordering and the nature of the intermolecular interaction caused by it are the same in major features in NLCs and CLCs. The same conclusion was drawn also in Ref. 21 on the basis of a quantitative estimate of the anisotropic component of the dispersion interaction energy of the various mesogenic molecules.

A regular lowering has been noted[34] in the values of η at constant relative temperature T/T_i (T_i is the transition temperature to the isotropic phase) with increasing length of the radical in the cholesteryl alkanoates. This

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[4]The onset of orientational order in the mesophase is due to the anisotropic dispersion attractive forces and also to the mutual steric repulsion of the anisometric mesogenic molecules. For a discussion of the relative role of the stated forces, see Refs. 19–21.
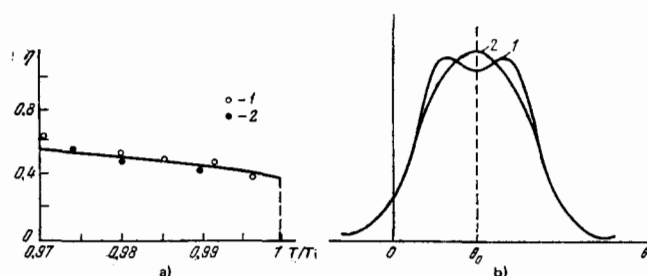

FIG. 1. a) Temperature-dependence of the orientational order parameter η for cholesteryl pelargonate. 1—data of Ref. 34, 2—data of Ref. 32, solid curve—Maier–Saupe theoretical curve; b) form of the distribution function of the molecules with respect to mutual-orientation angles with the conformational energy of the end groups (1) taken into account, or (2) not taken into account.

phenomenon can be explained by taking into account the conformational mobility of the hydrocarbon radical. As has been shown in Ref. 35, when one takes into account the conformational energy of the end groups as an extra term in the intermolecular interaction energy, the angle between the long axes of the molecules that corresponds to the minimum overall interaction becomes $\theta_0 \pm \Delta\theta$, instead of θ_0. This spreads out the distribution function of the molecules with respect to their relative orientation angles [Fig. 1(b)] and correspondingly diminishes the orientational order (the case $v_{22} < 0$).

d) Supermolecular structure of CLCs near phase transition points

The supermolecular structure of CLCs has a number of essential features near phase transition points. Thus, in the region of pretransition phenomena near T_i, the transition point to the smectic-A, nuclei are formed of a translationally ordered mesophase, the so-called smectic clusters. In spite of the general acceptance of this view, direct experimental studies of smectic nuclei in a cholesteric mesophase are very few. In Ref. 36 an estimate of the dimensions of the clusters (at a single temperature) was made by x-ray diffraction. In Ref. 18 the processes of nucleation in the pretransition region were studied by optical methods. It was noted in particular that the process passes through the following stages with decreasing temperature:

1) a general increase in the close-range translational order without the onset of marked heterogeneity; here a certain elevation of the orientational order parameter beyond the Maier-Saupe theory takes place[5];

2) formation and growth of nuclei of the low-temperature phase;

3) a stage in which the merger of small nuclei into large ones takes on decisive significance.

In stages 2 and 3, the orientational order parameter determined by the optical anisotropy of the quasinematic layer, which is calculated from the experimental

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[5]An analogous phenomenon has been noted[37] on the basis of very precise measurements of the birefringence in the pretransition region.

curves for the selective circular dichroism,[34] sharply falls to zero. This is accompanied by untwisting of the cholesteric helix, a decrease in the intensity, and an increase in the half-width of the selective-reflection peaks. At the same temperatures, η as determined by NMR continues to rise slowly. This involves the sensitivity of the selective optical characteristics to the existence of macroscopic defects of the helix having dimensions of the order of the wavelength of the incident light.

The formation of a so-called "blue phase" has been noted near the transition point to an isotropic liquid.[38-41] According to the data of Ref. 42, it amounts to a set of small (~0.5-1 μm) domains, each of which maintains its original supermolecular structure. As was noted in Ref. 43, the jump in volume in transforming from the cholesteric to the "blue" phase is extremely small. This also favors the absence of any distinction between the two phases at the microscopic level.

3. TEMPERATURE-DEPENDENCE OF THE PITCH OF THE CHOLESTERIC HELIX

a) Theoretical models of helical twist

The theoretical models of helical twist are based on a treatment of the angular dependence of the interaction energy of chiral molecules lying in adjacent quasinematic layers.

According to Goossens,[14] the dispersion interaction energy (DIE) is determined by using the quantum-mechanical perturbation theory:

$$V_{12} = V_{\text{disp}} = - \sum_{\substack{r \neq 0, \\ s \neq 0}} \frac{\langle \Psi_0^{(1)} \Psi_0^{(2)} \mid H' \mid \Psi_r^{(1)} \Psi_s^{(2)} \rangle^2}{W_r^{(1)} - W_0^{(1)} + W_s^{(2)} - W_0^{(2)}}. \tag{3.1}$$

Here H' is an operator that corresponds to the electrostatic interaction energy. In expanding it in terms of multipoles, we take into account the dipole–dipole and dipole–quadrupole terms:

$$H' = - T_{\alpha\beta}^{(2)} \mu_\alpha^{(1)} \mu_\beta^{(2)} - \frac{1}{3} T_{\alpha\beta\gamma}^{(3)} (\mu_\alpha^{(2)} \Theta_{\beta\gamma}^{(1)} - \mu_\alpha^{(1)} \Theta_{\beta\gamma}^{(2)}). \tag{3.2}$$

Here we have $T_{\alpha\beta}^{(21)} = \nabla_\alpha \nabla_\beta (R_{21}^{-1})$ and $T_{\alpha\beta\gamma}^{(21)} = \nabla_\alpha \nabla_\beta \nabla_\gamma (R_{21}^{-1})$, where R_{21} is the radius vector from the center of molecule 2 to the center of molecule 1. After transformations and averaging the DIE over all the positions of the centers of gravity of the molecules in adjacent quasinematic layers, Goossens obtains

$$V_{12}(\theta) = K \left(A \cos 2\theta - \frac{2B}{a} \sin 2\theta \right). \tag{3.3}$$

Here we have $K = (3/16)a^{-4}$, and A and B are quantities related in a complicated way to the polarizability of the molecules. By using the London-Buckingham approximation,[44] we can express A and B in terms of the components of the tensors $\alpha_{\alpha\beta}$ of the dipole and $A_{\alpha\beta\gamma}$ of the quadrupole polarizabilities. In particular, if the centers of the molecules being studied lie on a single normal to the planes of the quasinematic layers, we have[45]:

$$A = (\alpha_\parallel - \alpha_\perp)^2, \quad B = (\alpha_\parallel - \alpha_\perp)(A_{123} + A_{213}). \tag{3.4}$$

Upon minimizing (3.3), we get

$$\theta_0 = \frac{B}{aA}. \tag{3.5}$$

We can easily see that, when $\theta_0 \ll 1$, we can treat (3.3)

in the form

$$V_{12}(\theta) = -\nu P_2 (\cos(\theta - \theta_0)). \tag{3.6}$$

By analogy with the Maier-Saupe approximation for an NLC [see Eq. (2.3)] and assuming that we can neglect the effect of the helical twist with $\theta_0 \ll 1$ on the orientational order, we can naturally write the model potential of a chiral molecule in the mean field in the form

$$V(\theta) = -\nu\eta P_2 (\cos(\theta - \theta_0)). \tag{3.7}$$

This expression has been treated by Wulf[15] without specifying the nature of the intermolecular interaction more precisely. Below we shall call this approach the Goossens-Wulf model. Here the $V(\theta)$ curve is symmetrical with respect to θ_0 [Fig. 2(a)]; the pitch of the helix does not depend on the temperature to a first approximation. A more exact treatment shows that the decrease in η with increasing temperature near T_i increases the number of molecules for which θ becomes opposite in sign to θ_0. These molecules partially compensate the overall twist, and lead to a slight increase in the pitch with increasing temperature.[10] This problem has been analyzed in detail in Ref. 46, where the values were obtained of $(1/p)dp/dT \approx 0.004$ for $T = T_i - 10$ K.

An important supplement to the Goossens-Wulf model is to take into account the rotation of the molecules about the long axis.[47,48] For CLCs this rotation is not entirely free—one of the two mutually perpendicular directions of the short axis of the molecule is energetically more favorable. This gives rise to some degree of rotational order in the system. To describe it quantitatively, Stegemeyer and Finkelmann[47] have introduced the rotational order parameter

$$S_R = \frac{\int_0^\pi (1 - 2 \sin^2 \psi) \exp [- U(\psi)/kT] \, d\psi}{\int_0^\pi \exp [- U(\psi)/kT] \, d\psi} \tag{3.8}$$

Here $U(\psi)$ is taken in the form $U(\psi) = U_0(1 - \cos 2\psi)/2$. Here the angle of twist varies from the maximum value $\bar{\theta}_p = \theta_0$ for $S_R = 1$ to zero in the complete absence of or-
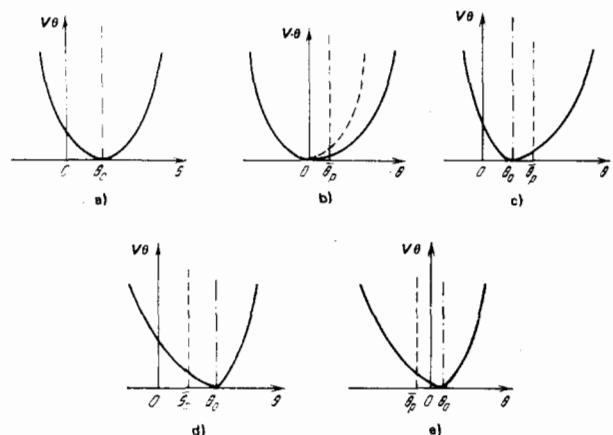

FIG. 2. Angular dependence of the interaction energy of chiral molecules. (a) According to Goossens, (b) according to Keating, (c–e) according to the hypothesis of Ref. 58. For the cases (b–e), we have $\bar{\theta}_p \to \theta_0$ with decreasing temperature.

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dered orientation of the short molecular axes. Quantitatively this relationship is expressed[47,48] in the form

$$\bar{\theta}_p = \theta_0 S_R(T). \qquad (3.9)$$

Hence, when $U_0 \ll kT$ (which is assumed valid for cholesteric systems with induced chirality), we have $S_R = U_0/4kT$ and $(1/p)dp/dT = 1/T$. When $U_0 \gtrsim kT$ (which can be realized among mesogenic molecules with a clearly marked basal plane, in particular, cholesteryl esters[49]), we have $S_R \lesssim 1$.

Another approach to describing helical twist is the hypothesis of Keating[50] (subsequently developed by Böttcher[16]). Here the minimum of the intermolecular interaction energy lies at $\theta_0 = 0$, but the branches of the $V(\theta)$ curve are asymmetric owing to the chirality of the molecules [Fig. 2(b)]; therefore the rotational vibrations performed by the molecules with respect to a parallel mutual orientation ($\theta = 0$) are anharmonic. Upon averaging θ over the time, Keating[50] obtains a nonzero value of the angle of twist that increases linearly with the absolute temperature. Hence $(1/p)dp/dT = -1/T$.

We must bear in mind that the two mechanisms described above cannot lead to helical twist in bulk, since generally the cholesteric helix is not stable with respect to fluctuations upon increasing the thickness of the layer.[51] Experimentally one begins to observe a distortion of the helix upon increasing the thickness of the layer of CLC even at $d \gtrsim 50 \ \mu$m.[52] According to Böttcher,[16] a quasinematic layer possessing an internal molecular field is formed by the ordered adsorption of molecules at the bounding surface (substrate, cover glass, phase boundary, etc.). The chirality causes the molecules of the second quasinematic layer to be oriented at a certain angle to the axis of preferential molecular orientation of the first layer, etc. According to Wulf,[15] the presence of the bounding surfaces is also a necessary condition for helical twist—this is precisely how the interacting molecules "know" whether they lie in the same or in adjacent quasinematic layers.

Analysis of the existing experimental data shows that some cholesteric systems are better described by the Goossens-Wulf model (e.g., the system of a nematic + optically active additive[48]) and others by the Keating-Böttcher model (derivatives of cholesterol[53,54]). A certain inner contradiction of Goossens' approach is the fact that, strictly speaking, the validity of the expansion of the intermolecular interaction energy in terms of multipoles is highly problematical for real CLCs. In these the distance between neighboring molecules in the direction of the axis of the helix (~5 Å) is substantially smaller than the dimensions of the molecule itself in the direction of its long axis (~25 Å). In order to overcome the difficulties that arise, an approximate method of calculating the dispersion interaction energy of the chiral molecules has been proposed.[55,45] It is based on representing the molecules of complicated geometrical form as a set of harmonic oscillators that are rigidly bound to one another. Let us start with the expression[56] for the dispersion interaction energy:

$$V_{\text{disp}} = - \int d^3 r^{(1)} \int d^3 r^{(2)} \frac{\rho(r^{(1)}) \rho(r^{(2)})}{|d - r^{(1)} + r^{(2)}|^6}. \qquad (3.10)$$

Here we have $\rho(r^{(n)}) = \sum_{i=1}^{N} k_i \delta(r - r_i^{(n)})$, where $r_i^{(n)}$ is the coordinate of the ith oscillator of the nth molecule, the k_i are the dispersion interaction constants for the individual isotropic oscillators, and d is the radius vector from the center of molecule 1 to the center of molecule 2. Also let us take into account the fact that $\int d^3 r f(r) \delta(r - r_0) \equiv f(r_0)$. Then, by adopting the data on the structure of the molecules,[57,21] we can numerically calculate the qualitative character of the $V(\theta)$ relationship. The results of the calculations show that the $V(\vartheta)$ curve has a minimum at a certain $\theta = \theta_0$, and moreover has a small asymmetry with respect to θ_0. Distortions in the shape of the $V(\theta)$ curve can also be introduced by the short-range steric repulsion forces.

Upon taking into account what we have presented above, we must evidently deem the generalized model[58-60] proposed by a set of authors to be a fundamentally correct approach. It takes into account both the shift of the $V(\theta)$ curve by the amount θ_0 with respect to $\theta = 0$ and its asymmetry with respect to θ_0. Here the Goossens-Wulf and Keating-Böttcher models arise as special cases. As we see from Figs. 2(c)-(e), here we can describe all the known cases of variation of pitch with temperature (we have $\bar{\theta}_p \to \theta_0$ with decreasing T). However, the derived expressions for $p(T)$ are very unwieldly and contain a large number of different parameters whose connection with the structure of the molecule remains unelucidated; one can calculate the model curves only on high-power computers. It does not seem possible to interpret the concrete experimental data on the basis of this model (as has been emphasized, in particular, in Ref. 48).

In closing the treatment of the models of helical twist, let us recall the study by Khachaturyan,[61] which stands somewhat apart. He showed the following model to be theoretically noncontradictory: the quasinematic layers of a CLC amount to "liquid ferroelectrics" with an ordered parallel arrangement of the dipoles owing to a preferred "head-to-tail" orientation. In trying to decrease the dipole–dipole interaction energy, the molecules form a cholesteric helix. Although, to all appearances, such a mechanism is not realized in real crystals, the possibility is not ruled out of future synthesis of materials that are liquid ferroelectrics fitting the scheme of Khachaturyan.[6]

b) Anharmonic vibrations of chiral molecules (modified Keating-Böttcher theory)

In order to find the theoretical $p(T)$ relationship while preserving the main idea of Refs. 58–60, let us write the angular dependence of the potential energy of a chiral molecule in the mean molecular field in the form

$$V(\theta) = -\eta [v P_2(\cos(\theta - \theta_0)) + u R(\theta)]. \qquad (3.11)$$

Here u and $R(\theta)$ are respectively the force constant and the angular dependence of the intermolecular interaction forces that are not taken into account by the first term.

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[6]According to Meyer[62] the known liquid ferroelectrics are of a different nature, being chiral smectics rather than cholesterics (see Sec. 6, a).

We can find the temperature-dependence of $\bar{\theta}_p$ in general form as:

$$\bar{\theta}_p = \frac{\int_{-\pi/2}^{\pi/2} \theta \exp[-V(\theta)/kT]\,d\theta}{\int_{-\pi/2}^{\pi/2} \exp[-V(\theta)/kT]\,d\theta}. \tag{3.12}$$

Thus the problem of finding the temperature-dependence of the pitch of the helix in the mean-molecular-field approximation is reduced to integrating (3.12) for various $R(\theta)$ functions that are assigned in accordance with the views on the intermolecular interaction existing in the concrete system.

Let $R(\theta)$ be determined by the factors that give rise to the anharmonicity of the rotational vibrations. Upon restricting the expression to the cubic term in the expansion of $R(\theta)$ in powers of the angle of deviation from the equilibrium position $\phi \equiv \theta - \theta_0$ and assuming the vibrations to be small ($\sin\phi \approx \phi$), we can write

$$\bar{\theta}_p = \frac{\int_{-\pi/2}^{\pi/2} \theta \exp\{\alpha[\cos^2(\theta-\theta_0)+\beta\sin^3(\theta-\theta_0)]\}\,d\theta}{\int_{-\pi/2}^{\pi/2} \exp\{\alpha[\cos^2(\theta-\theta_0)+\beta\sin^3(\theta-\theta_0)]\}\,d\theta}. \tag{3.13}$$

Here we have

$$\alpha \equiv \frac{3}{2}\frac{v\eta}{kT} \equiv \frac{3\eta(t)}{2t}, \quad \beta \equiv \frac{2}{3}\frac{u}{v} \equiv 2u_c.$$

When $\beta \ll 1$, we obtain

$$\bar{\theta}_p = \frac{\int_{-\pi/2}^{\pi/2} \theta e^{\alpha\cos^2(\theta-\theta_0)}[1+\alpha\beta\sin^3(\theta-\theta_0)]\,d\theta}{\int_{-\pi/2}^{\pi/2} e^{\alpha\cos^2(\theta-\theta_0)}[1+\alpha\beta\sin^3(\theta-\theta_0)]\,d\theta} \tag{3.14}$$

or, upon introducing the notation $J(\alpha)$ for the functions that enter into (3.14),

$$\bar{\theta}_p = \frac{J_1(\alpha)+\alpha\beta J_2(\alpha)}{J_3(\alpha)+\alpha\beta J_4(\alpha)}. \tag{3.15}$$

Here $J_3(\alpha) \equiv \pi\exp(\alpha/2)I_0(\alpha/2)$, where I_0 is the modified Bessel function. For conditions corresponding to real CLCs, it was shown in Ref. 46 that $J_1(\alpha) = \pi\theta_0[\exp(\alpha/2)I_0(\alpha/2)-1]$. Analogously we have $J_4 = -2\theta_0$. That is, we find that $\alpha\beta J_4 \ll J_3$. However, the integral $J_2(\alpha)$ cannot be expressed in terms of elementary functions nor the known special functions. In order to obtain an approximate solution, analogously to Ref. 50, we replace the limits of integration:

$$\frac{J_2}{J_3} \approx \frac{\int_{-\infty}^{\infty} \theta^4 e^{-\alpha\theta^2}\,d\theta}{\int_{-\infty}^{\infty} e^{-\alpha\theta^2}\,d\theta} = \frac{3}{4\alpha}. \tag{3.16}$$

In the same approximation we have

$$\frac{J_1}{J_3} = \theta_0\left[1-\frac{\exp(-\alpha/2)}{I_0(\alpha/2)}\right] \approx \theta_0. \tag{3.17}$$

Hence we find that

$$\bar{\theta}_p = \theta_0 + u_v\frac{t}{\eta(t)}. \tag{3.18}$$

We note that $t = 0.22T/T_i$, in line with the Maier-Saupe theory. Evidently, it is valid to use this approximation only under the condition

$$\frac{\theta_0}{\exp(\alpha/2)I_0(\alpha/2)} \ll u_v\frac{t}{\eta(t)}. \tag{3.19}$$

In real CLCs we find that $\exp(\alpha/2)I_0(\alpha/2) \sim 10^1-10^2$,

and $t/\eta(t) \sim 0.3$. That is, Eq. (3.18) is applicable for all systems having $u_v \gtrsim \theta_0$.

As has been shown in Ref. 63, Eq. (3.18) allows us to describe quantitatively the $p(T)$ relationships for the aromatic derivatives of cholesterol, which have a broad temperature interval ΔT of existence of the cholesteric mesophase. Here the values of u_v prove to increase regularly as one introduces substituents into the molecule that can act as potential sources of anharmonicity of the rotational vibrations, owing to their position in the molecule.

As regards the nonsmectogenic cholesteryl alkanoates, the narrowness of the interval ΔT causes them to exhibit only a region of almost linear decrease in the pitch with the temperature.[53]

In order to treat systems having $u_v < \theta_0$, one must employ either the general expression (3.14) with numerical integration of $J_2(\alpha)$ (Fig. 3 shows the model curves for various values of θ_0 and u_v) or the essentially identical expression[64]

$$\bar{\theta}_p(t) = \left[\theta_0 + u_v\frac{t}{\eta(t)}\right]\left[1-\frac{\exp(-\alpha/2)}{I_0(\alpha/2)}\right]. \tag{3.20}$$

One can take into account the rotation of the molecules about the long axis, analogously to (3.8), by multiplying the right-hand side of (3.20) by $S_R(T)$. The factor $S_R(T)$, which varies slowly with the temperature, introduces no substantial changes into the course of the model curves. Taking account of it leads only to a certain change in the numerical values of θ_0 and u_v.

When $u_v \ll \theta_0$, we get the Goossens-Wulf model, which allows one to describe the data[47,48] for NLC + OAA systems. The Keating model corresponds to the case $u_v \gg \theta_0$ for $\eta(t) \approx$ const (i.e., for $|d\eta(t)/dt| \ll 1$). Finally, if the signs of u_v and θ_0 differ, then we have $p^{-1} \to 0$ at the temperature corresponding to $u_v t/\eta(t) = -\theta_0$. This can explain the anomalous increase of $p(T)$ for cholesteryl-2(2-ethoxyethoxy)ethylcarbonate.[66]

c) The $p(T)$ relationship in the region of pretransition phenomena

Near T_S, the transition temperature to a smectic-A, the cholesteric helix untwists as $p \to \infty$. This is usually interpreted on the basis of the analogy noted by de Gennes[67] between a smectic-A and a superconductor (see also the review of Ref. 68). Here we find $p \sim (T$
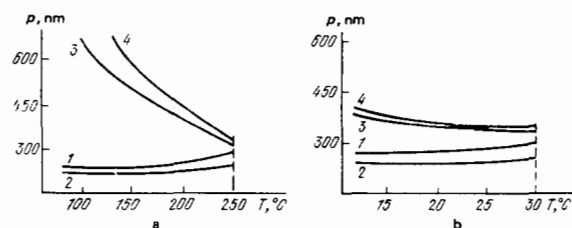

FIG. 3. Model $p(T)$ curves calculated by Eq. (3.20). 1— $\theta_0 = 0.01$, $u_v = 0.005$; 2—$\theta_0 = 0.01$, $u_v = 0.01$; 3—$\theta_0 = 0.02$, $u_v = 0.02$, 4—$\theta_0 = 0$, $u_v = 0.025$. For all the curves we have $a = 5$ Å, $T_i = 250$ °C (a), and 30 °C (b).

$-T_S)^{-\nu}$, where ν is the critical exponent. It was noted in Ref. 69 that the quantity ν depends on the composition of the cholesteric system.. A set of empirical and phenomenological $p(T)$ relationships that enable one to describe the experimental curves has been presented also in Refs. 50, 70–72. In particular, Ref. 72 showed that, although de Gennes' analogy is valid, yet the fluctuations are small in the temperature region in which one usually observes untwisting of the cholesteric helix, and the pretransition phenomena cannot be described by universal power functions. However, the non-power-function $p(T)$ relationships proposed by the authors of Ref. 72 have not been subjected to quantitative comparison with the experimental data. This same paper theoretically predicted some consequences of de Gennes' analogy, in particular, the so-called surface smecticity (i. e., the appearance of translational order at the surface of a CLC near the phase transition point). Various features of the structure of the surface in the CLC-smectic-A phase transition that confirm de Gennes' theory have been studied experimentally in Ref. 73.

The untwisting of the helix in the pretransition region occurs simultaneously with the formation of smectic clusters (see Sec. 2, d). A theoretical $p(T)$ relationship near T_S has been derived[18] under the assumption that the untwisting of the helix under the action of the "smectic field" created by the clusters is formally analogous to the untwisting of the helix in an electric field in line with the Meier-de Gennes theory.[2,6] Attempts to describe quantitatively the variation of p depending on the concrete mechanism of cluster growth have also been undertaken in Refs. 71 and 74.

However, up to now there has been no theoretical relationship that would relate the course of the $p(T)$ curve near T_S to the parameters of the structure of the molecules. However, we should expect that the magnitude of the intrinsic pitch of the helix in the given system (i. e., the value of p corresponding to the angle of twist in the absence of pretransition phenomena) will exert a substantial influence on the steepness of $p(T)$—with low enough intrinsic pitches, the untwisting will begin even in the ultraviolet region. Evidently, the course of formation of systematic clusters and the width of the pretransition region will be affected by whether the phase transition in question in a given concrete system is a second-order or a weak first-order transition.[75,76]

The set of problems being discussed is allied to the problem of the influence exerted by introducing different additives into a cholesteric system on the value of T_S (and hence on the position of the region of untwisting of the helix). A set of experimental data of this type has been presented in Ref. 77. It has been shown theoretically[78] that the existence in mesogenic molecules of considerable axial components of the dipole moment (up to 3–4D) makes an additional contribution to the energy of translational ordering that is comparable in order of magnitude with the contribution of the dispersion forces. The physical reason for this is that the tendency of the polar molecules toward antiparallel orientation of the permanent dipoles implies a simultaneous tendency to a mutual arrangement of the centers of

gravity that allows the greatest dipole–dipole interaction energy. This conclusion has been confirmed experimentally in Ref. 79, where it was established that the introduction into a cholesteric system near T_S of nonsmectogenic substituted cholesteryl benzoates shifts the region of color variation to higher temperatures. Here this shift becomes greater as the axial component of the dipole moment increases.

We note also Ref. 80, where a systematic study of $p(T)$ for smectogenic aromatic derivatives of cholesterol was first performed.

4. MULTICOMPONENT CHOLESTERIC SYSTEMS

a) Concentration-dependence of the pitch

The quantitative description of multicomponent cholesteric systems is based on the hypothesis of Adams and Haas[81] that the reciprocal of the pitch is additive with respect to the concentrations of the components in the absence of a specific intermolecular interaction:

$$p^{-1} = \sum_i w_i p_i^{-1}. \tag{4.1}$$

Here W_i is the weight fraction of the ith component (more exactly, the fraction of the area of the quasinematic layer occupied by the molecule of the ith component).

The validity of (4.1) for a set of systems based on cholesterol derivatives in the absence of pretransition phenomena has been demonstrated in Refs. 54, 82, 83. The quantity p_i has been termed[83] the "effective pitch" of the given component i. The values of p_i for a number of substances were determined experimentally in Refs. 54, 84.

Generally the magnitude of p_i depends on the temperature, as had been noted in Ref. 83: the $p_i(t)$ relationship of cholesteryl pelargonate proved very similar to the actually measured $p(t)$ for cholesteryl propionate.[53] Also the $p_i(t)$ relationship for cholesteryl chloride found in Ref. 85 for a broad temperature range is characterized by the same qualitative features (reversal of the sign of d^2p/dT^2, increase of $|dp/dT|$ near T_i) as the $p(t)$ curves for substituted cholesteryl benzoates[63] in Sec. 3.b.

On the basis of these facts, the hypothesis has been advanced[64] that, if we take the temperature-dependence of the effective pitch in the form (3.18), we can write Eq. (4.1) in the form

$$\bar{\theta}_p = \sum_i \left[\theta_{0i} + u_{vi} \frac{t}{\eta(t)} \right] w_i. \tag{4.2}$$

Here the values of t are determined by the value of T_i of the given mixture.

Equation (4.2) implies that $\bar{\theta}_p$ vanishes (the so-called compensation sets in) at a certain temperature and ratio of the components of opposite-sense of twist that corresponds to the condition

$$\frac{t}{\eta(t)} = -\frac{\sum_i \theta_{0i} w_i}{\sum_i u_{vi} w_i}. \tag{4.3}$$

The untwisting of the cholesteric helix upon approaching the compensation point at constant temperature or concentration has been studied in a number of papers.[54,82,86,87] It is noted that the optical properties and the supermolecular structure of a cholesteric system at the compensation point are analogous to an NLC.[88]

A necessary condition for compensation is that the component having the greater θ_0 should simultaneously have the smaller value of u_v. This agrees with the existing views on the structure of the molecules of the components of the known compensated systems.

As was shown in Ref. 64, one can quantitatively describe the $p(T, w)$ relationships by using Eq. (4.2) for a cholesteryl chloride-cholesteryl pelargonate mixture in the ranges of concentrations corresponding to both left-hand and right-hand twist.

b) Specific interaction of dissimilar components. Nematic-cholesteric mixtures

A natural generalization of (4.1) to the case of cholesteric systems having a specific intermolecular interaction of dissimilar components is the expression

$$\bar{\theta}_p = \sum_i \sum_j \bar{\theta}_{ij}(t) \, w_i w_j. \qquad (4.4)$$

Here $\bar{\theta}_{ii}$ is the twisting power of the ith component, as defined in line with (3.18) or (3.20), while $\bar{\theta}_{ij}$ with $i \neq j$ has the physical meaning of the angle of twist between adjacent quasinematic layers that would be established if the first layer were made only of molecules of type i and the second only of molecules of type j.

An expression analogous to (4.3) but without allowing for the temperature-dependence of $\bar{\theta}_{ij}$, has been treated by Adams and Haas[89] for a number of binary systems, while in Ref. 90 it was experimentally confirmed for ternary mixtures. Here the values of $\bar{\theta}_{ij}$ did not vary in comparison with those found for binary mixtures, and no need arose for introducing terms of the type $\bar{\theta}_{ijk} w_i w_j w_k$.

The most widely studied type of cholesteric system having a sharply expressed nonlinearity of the reciprocal pitch as a function of the concentration is the nematic-cholesteric mixture (NCM) (Fig. 4). In spite of a number of attempts,[91-103] the nature of the specific intermolecular interaction that gives rise to the anomalously high values of $\bar{\theta}_{ij}$ for $i \neq j$ for NCMs had remained unelucidated until recently.

Various phenomenological models have been proposed to describe the $p^{-1}(w)$ relationship in NCMs. In particular, these models have dealt with the distortions of the long-range order introduced by the chiral molecule into the nematic matrix,[93] and have introduced the induced twisting power of the nematic component as a parameter.[92] A considerable decrease (by a factor of 1.5–2) in the distance between the quasinematic layers with increasing concentration of the cholesteric component has been assumed[94] to obtain a fit with the experimental curves. However, this hypothesis is not confirmed by the x-ray diffraction data.[95]
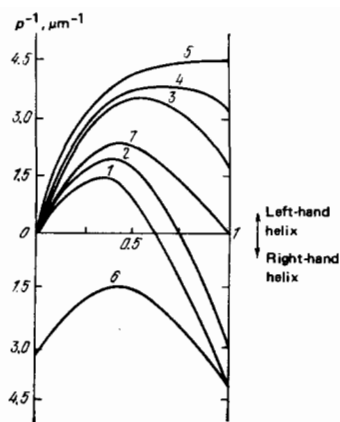
We note Ref. 96, where it was shown theoretically

FIG. 4. Typical relationships of the reciprocal pitch to the concentration of the cholesteric component in nematic-cholesteric mixtures.[91,99] 1—BBBA + cholesteryl chloride, 2—BBBA + cholesteryl pelargonate, 5—BBBA + cholesteryl oleate, 6—CBAC + cholesteryl chloride, 7—BBBA + a mixture of cholesteryl chloride and cholesteryl pelargonate (38 mole % pelargonate); BBBA = p-butoxybenzylidene-p'-n-butylaniline, CBAC = isoamyl-p-(p'-cyano-benzylidene)-aminocinnamate.

within the framework of a phenomenological approach that the free energy of an NCM is minimized by formation of a unitary common helix by the molecules of the nematic and the cholesteric with a definite value of the pitch.

Stegemeyer and Finkelmann[97,98] have tried to explain the anomalous concentration-dependences of p in NCMs on the basis of the features of the dispersion interaction. Their approach was subsequently developed in Ref. 99. An extension of (3.3) to binary cholesteric systems yields

$$V = -K \left(A_{11} v_1^2 + 2A_{12} v_1 v_2 + A_{22} v_2^2 \right) \cos 2\theta$$
$$+ \frac{2}{a} \left[B_{11} v_1^2 + (B_{12} + B_{21}) v_1 v_2 + B_{22} v_2^2 \right] \sin 2\theta. \qquad (4.5)$$

One finds the value of θ_0 from this analogously to (3.5). The coefficients A_{ij} and B_{ij} are determined by analogy with Goossens' theory for the interaction of the i and j molecules. In Refs. 97–99, the v_i are taken to denote the mole fractions. However, even in this case (as was pointed out, in particular, in Ref. 104), it would be more correct to employ the weight (or volume) fractions.

For an NCM (the twisting power of the nematic component is zero) we have $B_{22} = 0$ and $B_{12} = 0$. We obtain the following expression[105] for $p^{-1}(v)$:

$$p^{-1}(v) = p_x^{-1} \frac{[1 - (B_{21}/B_{11})] v^2 + (B_{21}/B_{11}) v}{[1 - 2(A_{12}/A_{11}) + (A_{22}/A_{11})] v^2 + 2[(A_{12}/A_{11}) - (A_{22}/A_{11})] v + (A_{22}/A_{11})}. \qquad (4.6)$$

Here p_c^{-1} is the reciprocal effective pitch of the cholesteric component (extrapolated to $v = 1$). The approach treated here allows a quantitative description of the experimental data for a number of NCMs. However (as is acknowledged by the authors of Ref. 99), the features of the dispersion interaction of dissimilar molecules could not lead to such large deviations from linearity; actually we have only a highly convenient and pictorial phenomenological description.

Reference 100 gives an alternative variant of the extension of the Goossens theory to NMCs—account is taken of the quadrupole–quadrupole terms. In Ref. 101 the sense of the excess twist (in the terminology of the authors, the induced circular dichroism) is associated with the direction of polarization of the electronic transitions of the molecule of the nematic. However, as later studies[102] have shown, the excess twist is always left-handed, independently of the structure of the nematic component. It was proposed in Ref. 91 that the molecules of the NLC are oriented parallel not to the long axis of the cholesterol molecule as a whole, but to the steroid nucleus, and partially compensate its inherent right-hand twist.

Kats[103] treats an arbitrary three-particle complex consisting of two molecules of a nematic and one molecule of a cholesteric. The total van der Waals interaction energy of the molecules A, B, and C (A is the cholesteric, and B and C are nematics) is

$$U = U_{AB} + U_{BC} + U_{CA} + U_{ABC}. \qquad (4.7)$$

Here it turns out that the sign and magnitude of U_{ABC} depend on the mutual arrangement of the centers of mass of the molecules. With a linear arrangement, the three-particle forces detract from the effect of the pair forces, while with a triangular arrangement they increase it. According to Kats, the experimental $p^{-1}(w)$ relationships in a NCM can be explained by assuming that the molecules of dextrorotatory cholesterics (e.g., cholesteryl chloride) lie in a line with the molecules of the nematic of the given three-particle complex. Yet, if the cholesteric is levorotatory, then the centers of mass of the molecules A, B, and C lie at the vertices of a triangle. As the author himself points out, the reason for this arrangement of the molecules remains unelucidated within the framework of the given approach.

A model has been proposed[106] in which the forces of specific steric repulsion (SSR) between the steroid nucleus of the molecule of the cholesteric and the molecule of the nematic are viewed as the source of the nonlinearity of the $p^{-1}(w)$ relationship. Being short-range, in contrast to the dispersion forces, these forces are manifested only in a narrow range of angles of mutual orientation of the long molecular axes, while making an extra contribution to the anharmonicity of the rotational vibrations of the molecules.

The physical reason for the appearance of the SSR forces in nematic-cholesteric mixtures is the existence in the structure of the molecule of the so-called "angular" methyl groups, which sharply protrude above the plane of the steroid nucleus and destroy the geometric regularity of the shape of the molecule [Fig. 5(a)]. Thus the steroid nucleus proves to be a source of steric hindrance that obstructs the molecules of the nematic (and also, as will be shown below in Sec. 4.c, the molecules of a number of nonmesogenic additives) from occupying certain orientations with respect to the molecule of the cholesteric.

For a quantitative description of the helical twist in such systems, one can approximate the function $R(\theta)$
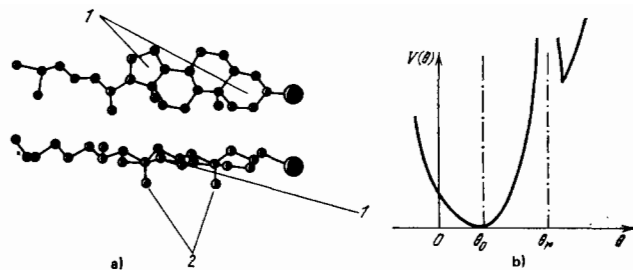

FIG. 5. a) Relative arrangement of the elements of the molecule of a cholesterol derivative from x-ray structural analysis data[157] (1—base plane, 2—angular methyl groups); b) angular dependence of the intermolecular interaction energy with the SSR forces taken into account.

from (3.11) in determining $\bar{\theta}_{ij}$ ($i \neq j$) by using (3.12), e.g., in the form of the step function:

$$R(\theta) = \begin{cases} 1 & \text{when } \theta_r - \vartheta < \theta < \theta_r + \vartheta, \\ 0 & \text{For other values of } \theta. \end{cases} \qquad (4.8)$$

Here θ_r is the angle corresponding to maximal SSR, and $\vartheta \equiv \Delta\theta_r/2$ is the half-width of the CCO region. Just as for individual cholesterics, the values of $\bar{\vartheta}_{ij}$ are determined according to (3.20). The minimum interaction energy of the dissimilar molecules is reached at $\theta = \theta_{0ij}$ [by analogy to Ref. 98, we take $\vartheta_{0ij} = (\theta_{0ii} + \theta_{0jj})/2$] [Fig. 5(b)]. Let us assume the condition $|\theta_r - \theta_{0ij} + \vartheta| \ll 1$ (i.e., the maximum of SSR lies not too far from θ_{0ij} and is not too broad). Then, after transformations, we obtain

$$\bar{\theta}_{ij}(t) = \frac{A(t)\theta_{0ij} - KC(t)\Delta\theta_r\theta_r}{B(t) - KC(t)\Delta\theta_r}. \qquad (4.9)$$

Here we have

$$\left. \begin{array}{l} A(t) = \pi\left[\exp\left(\frac{\alpha}{2}\right)I_0\left(\frac{\alpha}{2}\right) - 1\right], \\ B(t) = \pi\exp\left(\frac{\alpha}{2}\right)I_0\left(\frac{\alpha}{2}\right), \\ C(t) = e^\alpha(1 - e^{-\alpha\beta}). \end{array} \right\} \qquad (4.10)$$

Also, α and β are defined analogously to (3.13), and K is a quantity that characterizes the fraction of the area that is occupied in the quasinematic layer by the molecules of the nematic, and which lies directly over the steroid nuclei. As the results of calculations[106] show, the quantity $\bar{\theta}_{ij}$ is of the same order of magnitude as ϑ_0 but opposite in sign (which corresponds to the experimental data for the MBBA-cholesteryl chloride mixture) when θ_r is approximately equal to the angle between the straight line drawn through the angular groups and the long axis of the molecule of the cholesteric.[54]

When one cholesteric in a NCM is replaced by another, the values of K increase in proportion to the ratio of the length of the steroid nucleus to the total length of the molecule (Fig. 6). This has been noted in qualitative from in Ref. 91 [we note that the $p^{-1}(w)$ relationship in nematic-chiral nematic mixtures is linear[107]: $K = 0$]. Conversely, when one nematic is replaced by another, the degree of deviation from linearity increases with increasing length of the alkyl chain of the nematic molecule (while if the chain length remains the same, it increases with increasing tendency toward smectic order among nematics of different homologous series).
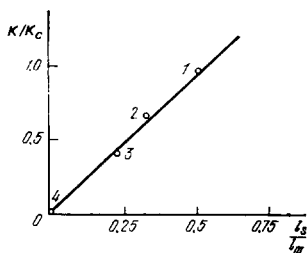
FIG. 6. Correlation between the quantity K and the ratio of the length of the steriod nucleus to the length of the molecule.[106,107] 1—cholesteryl chloride $(K=K_c)$, 2—cholesteryl pelargonate, 3—cholesteryl oleate, 4—chiral nematic.

All three noted regularities follow naturally from the theoretical model under discussion: a) the tendency toward correlation of the centers of gravity, which increases with increasing smectogenicity, facilitates the manifestation of short-range repulsive forces; b) increasing length of the nematic molecule increases the probability that it will "bump" its alkyl "tail" into the angular methyl groups of the steroid nucleus; c) increasing length of the alkyl radical of the cholesteric molecule, in contrast, will decrease the relative density of steroid nuclei, which are the source of the SSR forces.

Substitution of the $\bar{\vartheta}_{ij}(t)$ relationships obtained from (4.5) into (4.4) allows one to calculate model $p(T)$ relationships for NCMs having differing contents w_n of the nematic component. Here the theory predicts a possible reversal of sign of dp/dT at a certain w_n. This phenomenon has been experimentally observed.[108] Moreover, one can describe the features of the $p(T)$ relationships in a nematic-cholesteryl chloride system near the point of reversal of the sense of the helix noted in Ref. 109.

Along with the molecular-statistical approach that we have discussed above, one can also treat an NCM from the physicochemical standpoint—as a binary system with interacting components.[110] Pochan and Hinman[111] have pointed out the possible formation of intermolecular associations in an NCM, and proposed considering them to be one of the components of the mixture, with its own inherent value of the effective twisting power. In Refs. 112, 113 a theoretical $p^{-1}(w)$ relationship that agrees with the experimental data was obtained by using the mass-action law under the assumption that the association has a constant stoichiometry. A number of experimental indications supporting the formation in an NCM of intermolecular associations has been presented in Refs. 113 and 114.

The two approaches (physicochemical and molecular-statistical) are not mutually exclusive. The existence of any form of association increases the short-range order in the distribution of the centers of gravity of the molecules. In turn, this facilitates the manifestation of the specific repulsive forces. The twisting power p_{ass}^{-1} of the association can be treated as a phenomenological parameter whose meaning is revealed in the microscopic model.

In closing, we note Refs. 79, 115–117, which noted

c) Cholesteric systems with nonmesogenic additives (NMAs)

Introduction of an NMA into a cholesteric system can lead to an appreciable change in p, even for small w_g (chemichromic effect).[118] This property of CLCs opens up possibilities of employing them in chemical analysis. The substance being studied can be either introduced into the cholesteric mixture, or exist in the vapor state over a layer of CLC.[119]

The elucidation of the nature of the chemichromic effect is highly important for the general theory of helical twist. The hypothesis has been advanced[71] that the action of an NMA on a cholesteric system is analogous to a rise in temperature. A quantitative theory of the interaction of an NMA with a cholesteric matrix has been developed in Refs. 64, 120, 122. It is based on the assumption that the introduction of an NMA in the absence of specific interactions weakens the orienting molecular field acting on the mesogenic molecule. Consequently, it lowers the reduced temperature t, which is the generalized thermodynamic parameter in the modified Keating-Böttcher theory (Sec. 3.b). The loss of orientational order that occurs here has been noted experimentally.[123] Upon substituting the new values of t into (3.20) and (4.4), we obtain the following relationship of Δp to w_g:

$$p' - p \equiv \Delta p = T \frac{\partial p}{\partial T} w_g \qquad (4.11)$$

(for systems having $T|\partial\bar{\vartheta}_p/\partial T| \gg |\bar{\vartheta}_p|$ and in the absence of a specific interaction). In the general case we have

$$\bar{\vartheta}'_p - \bar{\vartheta}_p \equiv \Delta\bar{\vartheta}_p = \left(\gamma T \frac{\partial\bar{\vartheta}_p}{\partial T} - \bar{\vartheta}_p + k_\theta\right) w_g - \left(\gamma T \frac{\partial\bar{\vartheta}_p}{\partial T} + 2k_\theta\right) \frac{w_g^2}{2} \cdot \qquad (4.12)$$

Here $\bar{\vartheta}_p$ is the twist in the original system, γ is a coefficient of the order of unity that allows for the effective anisometry of the NMA molecule,[71] and k_θ is a constant that allows for the effect of the specific interaction forces. Equations (4.11) and (4.12) have been tested experimentally in Refs. 120, 121, 125. Here it turned out that the values of k_θ are of the same order of magnitude ($\sim 2.5 \times 10^{-2}$) for typical nematics, and, e.g., for nonmesogenic saturated hydrocarbons having the same molecular length. This result is another piece of evidence favoring the view of the decisive role of steric factors in the origin of the extra helical twist in NCMs.

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[7] The case in which the introduction of an NMA into the mesophase elevates T_i (e.g., in forming a charge-transfer complex[124]), formally corresponds to $\gamma < 0$; for mesogenic molecules we have $\gamma = 0$.

5. CHOLESTERIC SYSTEMS WITH INDUCED CHIRALITY

a) The helical inductive power

The cholesteryl esters usually employed as components of cholesteric systems have a number of defects: high viscosity, which prevents one from obtaining short response times; complexity of preparation of compositions having broad intervals of existence of the mesophase; low chemical stability, etc. At the same time, the choice of nematic systems having the required viscoelastic and mesomorphic characteristics is very broad. In this regard the question arises of inducing helical twist in an NLC. This can be attained either by attaching an active radical to the molecule of a nematic (synthesis of chiral nematics) or by adding optically active materials to an NLC.

At low enough concentrations of the OAA, the relationship of the reciprocal pitch to the content of the additive is linear:

$$p^{-1} = \beta_w w = \beta_\alpha \alpha. \tag{5.1}$$

Here w is the weight fraction and α is the mole fraction of the OAA. We can call the coefficient β the helical inductive power of the given OAA. An important problem is to search for additives having maximal values of β (since it is desirable to introduce OAAs in minimal quantities so as not to impair the orientational order in the mesophase).

The values of β for various OAAs in different nematic matrices have been given in Refs. 47, 48, 126–130. We should stress that the experimental data of this type are very few; a systematic analysis of the interrelation between the values of β and the structural features of the molecules of the OAAs is hindered by the fact that mainly natural optically active compounds and their derivatives have been used for the studies. The structure of these molecules is often very complicated and is amenable to modeling only to a very limited extent. On the basis of the existing results, we can single out the following fundamental factors that affect the helical inductive power [the symbols are analogous to (3.9)]:

1) the degree of asymmetry of the OAA molecule that determines θ_0. Here there is no correlation between the optical activity and the twisting power, neither in magnitude nor in sign [a set of characteristic examples has been given by Eq. (3.5) with account taken of (3.4)];

2) the values of the function $S_R(T)$, which are determined both by the magnitude of U_0 (a property of the OAA) and by the value of T for a given T/T_c (a property of the nematic matrix). The larger values of U_0 (and hence also of S_R) are associated with a flat shape of the OAA molecule, which hinders its rotation about the long axis;

3) finally, in some cases[131,129] a specific interaction of the OAA with the molecules of the nematic exerts an effect.

b) Temperature-dependence of the pitch

When nonsmectogenic nematics are employed as the matrix, the pitch depends weakly on the temperature.

Here we can distinguish two cases:

1. The case of $dp/dT > 0$. This is typical for a mesophase with induced chirality; it corresponds to (3.20) for $\theta_0 \gg u_\nu$ with allowance for $S_R(T)$.[48,132]

2. The case of $dp/dT < 0$. In the absence of pretransition phenomena, it has been noted upon employing tigogenin and its derivatives as the OAA.[132] Probably this involves the shape of the molecule of this substance, which favors anharmonicity of the rotational vibrations.

The hypothesis that steric factors can play a role in determining the sign of dp/dT of an NLC + OAA system has also been advanced in a recent paper by van der Meer and Vertogen.[133]

A course of the curve having $p \to \infty$ as $T \to T_c$ is realized when one employs a smectogenic nematic.[134] Interestingly, the untwisting of the helix occurs independently of whether the NLC forms a smectic-A or smectic-C mesophase.

c) Chiral nematics

For a long time, isoamyl p-cyanobenzylidene-p'-aminocinnamate was essentially the only example of a chiral nematic (CN). In recent years a large number of CNs of various homologous series have been synthesized from among the Schiff bases,[135–138] azo compounds,[107] esters,[139] biphenyls,[140–143] etc. However, as a rule the authors of these studies have limited themselves to merely announcing the fact of having prepared new CNs. Data on studies of their supermolecular structure are very few. It has been shown[107] that $dp/dT > 0$ for mixtures of NLCs + CNs. It was noted in Ref. 138 that the sign of dp/dT becomes negative with elongation of the alkyl radical. This evidently involves an enhancement of the tendency toward translational order. Refs. 143, 140, 155 have noted an untwisting of the cholesteric helix with $p \to \infty$ with decreasing temperature for smectogenic chiral cyanobiphenyls and certain other compounds. The relationship between the sense of the helical twist and the molecular structure of CNs has been discussed in Ref. 142. Just as for OAAs, here there is no correlation between the optical activity (in the isotropic phase or in solution) and the twisting power.

The birefringence and anisotropy of the dielectric permittivity of the racemic and optically active forms of NLCs have been studied in Refs. 144, 145. Here it was shown that the orientational order is the same in the NLC and in the quasinematic layer of a CN.

6. HELICAL TWIST IN VARIOUS TYPES OF MESOPHASES

a) Chiral smectics-C

Helical twisting of the supermolecular structure can exist not only in cholesterics proper and in the thermodynamically analogous NLCs having chirality induced in some way, but also in mesophases of a number of other types. The most clearcut example is the chiral smectics-C (smectics-C*).

The contrast between the supermolecular structure of a CLC and a SLC-C* consists of the fact that the latter have the axes of preferential molecular orientation lying at a certain angle ϑ ($\vartheta = (\pi/2) - \theta_t$, where θ_t is the tilt angle, or characteristic parameter for smectics-C) to the plane of the quasinematic layers. In contrast to a CLC, the quasinematic layers themselves are a physical reality, for these are precisely the smectic layers that are characteristic of any type of smectic mesophases.

As has been shown in Ref. 11, the optical properties of smectics-C are very similar to those of CLCs. In this regard the problem of measuring the pitch p of the helix and its temperature-dependence in these systems is of great interest. Although data of this type are very few, yet we can already conclude that the mechanism of helical twist in CLCs and SLC-C*s is analogous in many ways. Thus the pitch of the helix in DOBAMBC (p-decyloxybenzylidene-p'-aminomethylbutylcinnamate) has been measured[146] by diffraction of monochromatic polarized light from the helicoidal structure, and values of p were obtained in the range of 4–9 μm. Here an untwisting of the helix with rising temperature was noted, with a sharp increase in the pitch near T_S, the transition temperature from the smectic-C to the higher-temperature smectic-A. The optical rotation of the plane of polarization of a layer of DOBAMBC has been studied in Ref. 147. With increasing temperature, the optical rotation ρ sharply falls to zero near T_S. Evidently this corresponds to untwisting of the helix. With falling temperature, ρ increases slightly, and after transition to the low-temperature chiral smectic-H*,[8] it subsequently becomes practically constant. Thus in chiral smectics, just as in CLCs, the sharp variation in pitch with the temperature is characteristic of the region of pretransition phenomena rather than of the mesophase itself.[156]

Compounds were described in Ref. 140 that form a smectic-C* mesophase and show selective reflection in the visible. Here a weak increase in the pitch of the helix with rising temperature was noted.

In closing we note that the most clearcut feature of chiral smectics is that they manifest properties of liquid ferroelectrics. In order not to interrupt the overall tenor of the presentation, however, we refer the readers interested in this problem to the appropriate reviews.[62,148,149]

b) Cholesteric polymers

The so-called liquid-crystalline polymers[150] amount to mesophases in which the mesogenic monomers are attached as side groups to a hydrocarbon polymer chain. The polymer chain is rather flexible, and hence, if the mesogenic monomers (or part of them) are chiral, then helical twist can set in analogously to ordinary cholesterics.

Figure 7 shows the results of an experimental study of selective reflection in one of these systems.[151] Here, as in an ordinary nematic-chiral nematic system, the reciprocal pitch is directly proportional to the concentration of the optically active monomer. However, in contrast to the latter system, a cholesteric polymer has $dp/dT < 0$, which corresponds to $u_v \geq \theta_0$ in (3.18). Evidently this involves the binding of the mesogenic monomer to the polymer chain, which gives rise to an asymmetry of the angular dependence of the interaction energy of the monomers with one another and a corresponding asymmetry of the rotational vibrations.

c) Lyotropic CLCs

Another type of mesophase in which helical twist can arise is the lyotropic liquid crystal. This denotes substances that exist in a mesomorphic state when dissolved in appropriate solvents in a certain concentration range. The best known lyotropic cholesteric is poly-γ-benzyl-L-glutamate (PBLG).[152-153] As was shown in Ref. 154, the helical twist in lyotropic CLCs can be described on the basis of the Goossens theory (here $dp/dT > 0$[153]). The features of the interaction of the molecules of the lyotropic CLC with the molecules of the solvent play a substantial role. Thus, the above-mentioned PBLG shows opposite senses of twist when dissolved in dioxane and in dichloromethane, while compensation sets in with $p \to \infty$ in a mixture of these solvents at a certain ratio. We note that the value of p of lyotropic CLCs is very large ($\sim$50–100 μm) even in the absence of compensation.

7. CONCLUSION

Thus the helical twist of the supermolecular structure, which was treated by many investigators even 5–10 years ago as some curious anomaly inherent in a very narrow group of materials, has proved to be a very general property inherent in a broad set of liquid-crystalline systems that have found varied practical applications. Moreover one can describe the helical twist in different concrete systems on the basis of a unitary general approach.

In speaking of the fundamental directions of further studies in this field, we should first cite the preparation and study of the properties of induced cholesteric mesophases—nematic + optically active additive systems and chiral nematics. Study of different systems of this type is necessary, both for a final solution of the
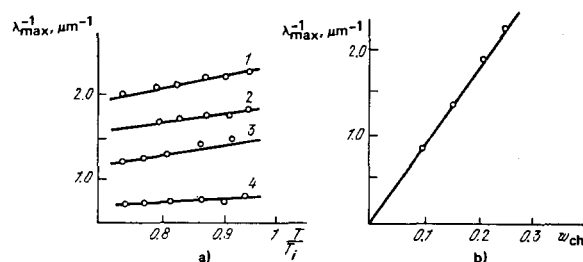

FIG. 7. Dependence of the reciprocal pitch on the temperature (a) and on the fraction of the chiral monomer (b).[150] 1—$w_{ch} = 0.247$, 2—$w_{ch} = 0.202$, 3—$w_{ch} = 0.164$, 4—$w_{ch} = 0.094$.

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[8]A smectic-H mesophase differs from a smectic-C in the same way as a smectic-B differs from a smectic-A, i.e., in the presence of translational order also *inside* the smectic layer.

problem of the relation between the structure of the molecules and the parameters of the supermolecular structure, and in connection with the broad prospects of using the electro- and thermochromic properties of CLCs with induced chirality. Much interest is also aroused by chiral smectics-C and cholesteric polymers, for which only isolated experimental data currently exist.

It seems highly desirable to obtain direct experimental data and to carry out further theoretical studies on the rotation of chiral molecules about their long axes in connection with the substantial role played by the degree of hindrance of this rotation in determining the pitch of the helix of a CLC with induced chirality. Experimental data on the comparative study of orientational order in cholesteric systems having various chemical structures of the molecules would be of great interest.

Evidently, we should expect in the field of theory to see studies on a more rigorous substantiation of the employment of the mean-molecular-field approximation and the model of quasinematic layers, which on the whole have acquitted themselves well in the theory of CLCs, and studies in which the model potential would be more directly related to the parameters of the molecular structure, and also should expect the development of a quantitative description of the untwisting of the helix in the pretransition region on a microscopic, rather than a phenomenological level.

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