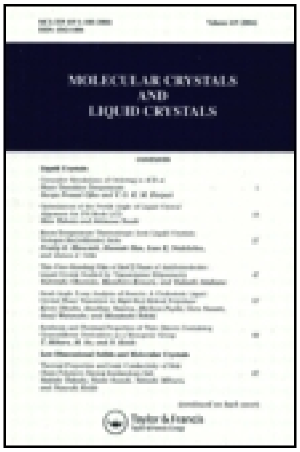

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Cholesteric liquid Crystals: Physical Properties and Molecular-Statistical Theories

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Cholesteric Liquid Crystals: Physical Properties and Molecular-Statistical Theories

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I. INTRODUCTION

It seems certain now that cholesteric liquid crystals (cholesterics, or CLC, for short) have been the first examples of mesomorphic state of matter known to humankind. Apart from the well-known discovery of the two-stage melting of cholesteryl benzoate made by Reinitzer in 1888[1] and cited in almost all the textbooks, one may recall some other papers where the authors, quite unaware of the real significance of their observations, presented undeniable evidence of the liquid crystalline state of matter. E.g., Professor Planer from the Lvov University as early as in 1861 did observe, putting it in the present-day terms, selective reflection from the planar texture of cholesteryl chloride forming a monotropic cholesteric mesophase on cooling.[2] One should also note that the works of Fergason,[3,4] outlining the prospects of practical applications for CLC, did, in fact, precede similar endeavors by Heilmeier in the field of nematics. From the viewpoint of organic chemistry, a number of mesogenic cholesterol derivatives had been already synthesized and thoroughly studied[5] by the time the name of MBBA (p-methoxybenzylidene-*p*′-*n*-butylaniline), to say nothing about cyanobiphenyls, was not yet known to anybody. The mere listing of CLC prospective applications[6,7] seems so impressive that, keeping in mind the above-described historical background, one should expect to find cholesterics in a key position in the field of liquid crystal science.

Looking over a subject or citation index, one is, however, a little discouraged. In fact, during the last five or ten years new kinds of exotic smectics (nearly outnumbering the letters of the Latin alphabet), discotics, different columnar, carbonaceous, lyotropic or "blue" phases formed the main field of interest for the "pure" liquid crystal science. From the other side, most of the practically-minded researchers directed their work toward nematic displays. Cholesterics became sort of Cinderellas in the liquid crystal family, but there are many indications that this situation is but a temporary one.

We shall mention here a few arguments in favor of CLC. To begin with, cholesterics are an excellent testing field and a touchstone for different theories of nematic ordering. No theory pretending to be an adequate description of orientationally ordered mesophase may be considered viable enough if it does not offer possibilities of its extension to describe helical twisting in cholesterics. Cholesteric mesophases are an excellent medium for observing quasi-chemical intermolecular interactions. No other macroscopic parameter seems to be so sensitive to the smallest changes in molecular structure and composition as the helical pitch. Thus, cholesterics are indispensable for statistical thermodynamics and physical chemistry, providing a useful means of development for these branches of science. It seems to be a general feeling that medical thermography and electrooptical effect of the field-induced cholesteric-nematic transition are not the only possibilities of the practical use of cholesterics—the main achievements are definitely still ahead.

It seemed quite appropriate to make an attempt of generalizing experimental and theoretical results obtained in the field of cholesterics. The present review is partly based upon the ideas of our previous ones,[8,9] with an emphasis upon the most recent results. We tried to present a unified treatment of scattered and sometimes contradictory data from the standpoint of our understanding of the problem. The concepts and ideas are largely based upon our own experience of practical work with real cholesterics, both cholesterol derivatives and nematics with induced chirality.

II. PHYSICAL PROPERTIES: A REVIEW OF EXPERIMENTAL DATA

A. A classification scheme for cholesterics

To avoid possible misunderstanding, it is necessary to begin with an outline of a classification scheme for CLC. The reason is the great variety of systems designated by the same term 'cholesterics.' In fact, if we compare a mixture of cholesteryl nonanoate and cholesteryl oleyl carbonate with, say, MBBA doped with 2% of 4-(2-methylbutyl)-4′-cyanobiphenyl, we shall have some difficulty in finding a physical property which would be quite similar in both systems. Apart from the presence of helical twisting and long-range orientational order, most of their features are quite different. Regardless of this, in many papers, especially those written by specialists in theoretical physics or electronics it is implicitly assumed that one and the same phenomenological theory or microscopic model should be equally suitable for all the systems labeled in their minds as 'cholesterics.' Judging from our own experience, it is often a major factor of confusion, especially for newcomers to the field of cholesterics. Therefore, we begin with an outline of classification and terminology to be used throughout this paper.

Firstly, cholesterics may be subdivided into thermotropic and lyotropic ones; next, thermotropic cholesterics can be monomeric or polymeric; monomeric cholesterics are subdivided into helically twisted discotics and helically twisted 'calamitics' (using the terminology of Billard[10]); the latter are helically twisted nematics or helically twisted smectics —C, H (or G), etc.

Our field of interest is restricted in the present review to the helically twisted nematics, which can be, in turn, subdivided in the following ways:

—According to the chemical nature of the constituent molecules;

a) steroids (e.g., cholesterol esters) and their mixtures with each other;

b) non-steroidal cholesterics, or "chiral nematics';

c) induced cholesteric systems (cholesteric systems with induced chirality, nemato-chiral systems), comprising a nematic matrix and an optically active dopant (OAD), usually in small (<10–15%) quantities;

d) mixed cholesteric systems, i.e., mixtures formed by the components of different chemical structure, where specific intermolecular interactions are not negligible. The examples are the so-called nematic-cholesteric mixtures (i.e., mixtures of nematics with mesogenic steroids in the broad concentration range), mixtures of chiral nematics of different chemical classes, etc.

One should note that border lines between subclasses b), c) and d) are not sharp and, in many respects, conventional. On the contrary, there is a wide gap between a) and b)—a cholesteric mesogen can either be a steroid or have nematic-like molecular structure with an optically active group (e.g., 2-methylbutyl) attached to it. No intermediate forms are known. Synthesis of a mesogenic optically active substance with molecular structure essentially different from steroids or typical nematics would be of fundamental importance for molecular theory of cholesteric mesophase.

—Depending upon relative temperature ranges of the cholesteric phase and of the low-temperature smectic phase (actual or virtual) one may distinguish between 'genuine' ('pure') cholesteric phase and cholesteric phase in the region of pre-transitional phenomena (sometimes called 'cybotactic' or 'heterogeneous' cholesteric phase, referring to the presence of smectic clusters). E.g., cholesteric phase of cholesteryl nonanoate + cholesteryl oleyl carbonate mixtures lies entirely within the temperature range of pre-transitional phenomena.

—Cholesterics may have a right-handed (cholesteryl chloride) or a left-handed helix (cholesteryl nonanoate). A special case are so-called 'compensated' mixtures, comprising components with different helix sense. Under certain conditions one can observe in such systems temperature-induced unwinding of helix with formation of nematic mesophase and inversion of helix sense.

We must also mention here 'reentrant' cholesteric phases—a phenomenon which is quite similar to its nematic counterpart. Such phases were reported both for induced cholesterics (reentrant nematic + OAD)[11,12] and for individual substances (non-steroidal cholesterics).[13] Recently[14] a pressure-induced reentrant phenomena was reported for certain cholesterol ester mixtures. Pitch-temperature dependences in both cholesteric phases were reported[15] for a number of induced cholesterics; there is, however, not enough information upon the subject to make definite conclusions.

In a narrow temperature range close to the cholesteric to isotropic phase transition so-called 'blue phase' is observed, which is considered by some authors as a separate phase, and by others as a specific form of cholesterics. The question was treated recently in detail in a number of reviews (e.g., Refs. 16,17) and will not be considered here.

B. Orientational order and anisotropy of physical properties

1. Orientational long-range order parameter S. A generally accepted view is that cholesterics are helically twisted nematics. Therefore, they can be characterized by the orientational order parameter, $S = \langle P_2(\cos\theta)\rangle$, where P_2 is the Lengendre polynomial, and θ is the angle between the long molecular axis and the local director $\vec{n}$ ($n_x = \cos q_0 z$, $n_y = \sin q_0 z$, $n_z = 0$, $q_0 = 2\pi p^{-1}$). The presence of twisting with the helical pitch p complicates greatly the problem of determining S, for many of the methods applied successfully to nematics are of no use in the cholesteric phase.

One of the most reliable ways is to use the NMR technique. Collings, McKee and McColl,[18] presenting $S(T)$ dependences for cholesteryl *o*- and *m*-fluorobenzoates, were the first to make a conclusion that orientational ordering mechanism is essentially the same in nematic and cholesteric phases, with differences in the molecular structure between steroids and typical nematogens being of a surprisingly little importance. Deuterium NMR in the smectic, cholesteric and 'blue' phases of cholesteryl nonanoate and myristate was used in Ref. 19, where deuterium quadrupole splittings and the corresponding orientational order parameter values were determined. The wide line NMR data are reported in Ref. 20 for cholesteryl benzoate, methyl carbonate, ethyl carbonate, and laurate; it is argued that for these substances S values are somewhat lower, comparing with the typical data for nematics.

In Ref. 21 electron resonance spectroscopy was used to determine the order parameter of a spin probe dissolved in cholesterics. The structure of the spin probe had to resemble that of the cholesteric solvent—a definite drawback of the method; as it was clearly shown for nematics,[22] the use of 'guest' molecules is an essentially unreliable way of getting an insight into the molecular ordering. One may mention also, for example, the use of the surface plasmon technique,[23] etc. It seems unlikely, however, that such methods could be of practical use to determine $S(T)$ for a considerable number of different cholesterics with the aim of studying the influence of molecular structure upon orientational order. In this respect optical methods, being relatively simple, look much more promising.

A crude estimate of $S(T)$ in cholesterics was made by Korte,[24] who used the measured values of the selective reflection and optical rotation amplitudes in comparison with the theoretical ones. More rigorous approaches within the same ideology were presented in Refs. 25,26, where not only the amplitudes, but the complete intensity v. wave-length curves were used. In Ref. 26 the circular dichroism spectra were measured for the planar texture of cholesteryl alkanoates, and a set of optical anisotropy parameters was determined by computer fitting to the theoretical circular dichroism v. wavelength curves. In the vicinity of isotropic transition temperature T_i values obtained were clearly underestimated because the planar texture deterioration-monodomain regions became comparable in size with the optical beam cross-section. At lower temperatures ($T \leqslant T_i - 5°$) however,

S values were in fair agreement with the NMR data, supporting credibility of the method.

Birefringence data were used to determine orientational order in Ref. 27. Refractive indices were measured using an Abbe refractometer, and, using estimates of polarizability anisotropies, S values were determined for cholesteryl propyonate, nonanoate and decanoate. The values obtained were ~0.7–0.8 in the smectic A phase and ~0.2–0.4 in the cholesteric phase, which is certainly an underestimate. The discrepancy may be due to the non-uniformity of the planar texture—multiple crossings of disinclination lines by the light beam could cause a decrease in the apparent birefringence values.

An interesting method of determining $S(T)$ in cholesterics using birefringence data was proposed by Averyanov.[28] The method is a natural development of the Vuks-Neugebauer technique, allowing to account for internal field anisotropy. The S values are obtained as

$$S = \frac{3M\,(n_\parallel + n_\perp)\,\Delta n}{2\pi N_A\,\rho\,(n^2 + 2)\,\Delta\gamma} \tag{1}$$

where M is the molecular mass, N_A is the Avogadro's number, ρ is the mesophase density. The effective anisotropy of molecular polarizability $\Delta\gamma$ may be estimated in at least three different ways:

(i) from the expression

$$\Delta\gamma = \frac{3M\,(n_\parallel + n_\perp)\,\Delta n}{4\pi N_A\,\rho\,(n^2 + 2)} \tag{2}$$

where refractive indices are to be measured in the single crystal formed from the corresponding mesogen on cooling (which, however, is not a routine operation).

(ii) using the Haller-type approximation

$$S = S_0(1 - T/T^*)^\eta \tag{3}$$

and plotting $\log(S\Delta\gamma)$ vs. $\log(1 - T/T^*)$, where T^* is a temperature just above the isotropic transition point T_i. Putting $S_0 = 1$, on the condition of the plot linearity we may have some credibility in the $\Delta\gamma$ values thus obtained. The main drawback is an approximate character of Eq. (3)—it is shown in[29] that $S_0 \neq 1$(in fact, $S_0 \sim 1.1 - 1.4$), and T^*, which may differ from T_i by up to several degrees, cannot be determined with a sufficient accuracy. The problem of applicability of Haller-type approximations to the orientational order in mesophases is discussed in detail in.[30]

(iii) $\Delta\gamma$ may be calculated using the additivity rule for bond polarizabilities, or more exactly, using the modified method of Lippincott—δ—function potential model.[31]

In the case of convergence of all three $\Delta\gamma$ values one may, in fact, have some confidence in the order parameter values obtained in such a way.

$S(T)$ curves for cholesteryl nonanoate obtained using the Averyanov method[28] are in good agreement with those determined from the circular dichroism spectra;[26] $S(T)$ values for cholesteryl laurate[31] are confirmed by NMR.[20] A number of $S(T)$ curves for different cholesterol derivatives, obtained by the Averyanov method, are presented in Ref. 32. The character of these dependences is shown in Figure 1.

Unfortunately, there is no information about $S(T)$ in induced or non-steroidal cholesterics; due to the absence of any directly obtained data, it is usually argued that order parameter values do not differ much from the corresponding values in nematics.

2. *Birefringence and dielectric anisotropy.* While reliable absolute S values still remain a largely unsolved problem, one can still obtain some information, comparing $\Delta n(T)$ and $\Delta\epsilon(T)$ curves in dif-

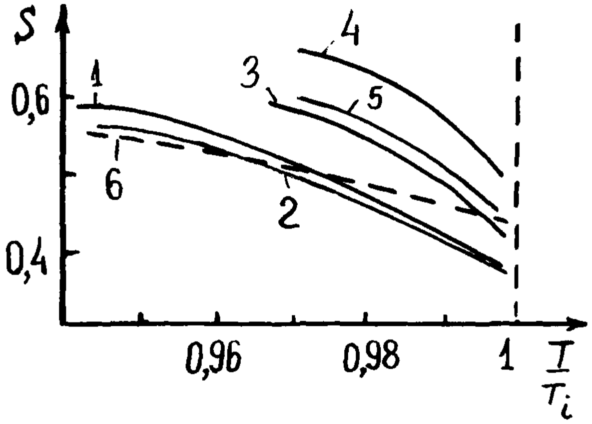

FIGURE 1 Orientational order parameter as function of temperature in the cholesteric mesophase of cholesterol derivatives:[28,33] 1—cholesteryl-β-bromopropyonate, 2—β-chloropropionate, 3—γ-chlorobutyrate, 4—β-brombuthyrate, 5—nonanoate, 6 (dashed line)—theoretical Maier-Saupe curve.

ferent systems (due to low magnetic succeptibility $\Delta\chi$ data for cholesterics are extremely scarce).

Thus, measurements of $\Delta\epsilon$ and precision measurements of Δn by means of determining full internal reflection angle for *p*-methoxybenzylidene-*p*'-isohexacylaniline (MBHA)[33,34] showed that Δn and $\Delta\epsilon$ values were identical within experimental error (e.g., up to ±0.0005 for Δn) for both optically active form (cholesteric phase) and racemic form (nematic phase) in all the mesomorphic region. A similar result was later obtained by Pelzl[35] for other chiral nematics. The implications are obvious—local orientational order in the twisted nematic phase is identical to the bulk orientational order in the corresponding ordinary nematic phase, provided the chemical structure of the constituent molecules is the same. Therefore, there is no need to develop a special molecular statistical theory of orientational ordering in cholesterics—its nature and mechanism should be identical to those in nematics (and vice versa). We shall use this fundamental fact extensively later, considering theories of helical twisting.

In a more strict reasoning, however, one should expect that phase biaxiality of CLC may influence orientational order characteristics.[36] This influence is but a minor one, which can hardly manifest itself in any of macroscopic properties. The data of Ref. 37, where by means of deuterium NMR such an influence was presumably observed, are, in fact, not conclusive, because the system studied was a mixture of MBBA, deuterated in the α-position, and chiral 4-methoxybenzylidene-4'-[(+)-2-methylbutyl] aniline, and not the racemate and the optically active form to enable the complete elimination of the chemical structure effects. As we have stressed already, there are no data available on the $S(T)$ in the induced cholesterics.

Considering Δn in cholesterics, one should mention that for cholesterol derivatives and their mixtures Δn values ($\Delta n \sim 0.02$) are much lower in comparison with typical-nematics used as matrices in induced cholesterics. The value of Δn determines the halfwidth of the selective reflection peak ($\Delta\lambda = \Delta n \cdot p$), which is an additional problem for those developing non-steroidal liquid crystalline thermoindicators—too diffuse peaks may be suitable for many consumers.

C. Helical pitch

1. Textures of cholesterics. Standard conditions for the measurements in cholesteric mesophase are the "sandwich"-type cells, consisting of two glass or quartz plates and a Mylar spacer there between to provide a necessary thickness of cholesteric layer. CLC is introduced into the cell (as a rule—in the isotropic phase with subsequent cooling). Limitations are imposed upon the cholesteric layer thickness values—in the most case, it is kept within the range of 5 to 50 μm. In too thin cells surface effects begin to be sensible, and there is a sharp fall in the reflected light intensity. If the CLC layer is too thick, the structur' loses its uniformity along the helical axis. This effect, experimentally studied and discussed in detail in Ref. 38, is in agreement with theoretical considerations[39] making helical twisting possible only in layers of limited thickness. It is to be kept in mind when large-pitch cholesterics ($p \geqslant 50$–100 μm) are investigated. Unsuccessful attempts to obtain a good planar or focal conic texture in such a system sometimes lead to an erroneous conclusion that "this OAD does not induce twisting," and the reason is ascribed, e.g., to the presumably low optical purity of the OAD. Due to such an effect the authors of Ref. 40 could not observe helical twisting in their systems, and the discovery of helically twisted discotics (in a similar system of discotic + OAD) was reported only three years later.[41]

Other cases of border conditions are realized in cholesterics with one or two free surfaces, or suspended in the form of droplets, with many interesting effects reported for such systems.[42,43]

Returning to the standard case, let us consider four main types of cholesteric textures which are usually obtained in the experiments and observed under a polarizing microscope.

a) planar (Grandjean) texture is observed when the helical axis is normal to the bordering surfaces (Figure 2, a). If the cell thickness is much greater than the helical pitch ($50\ \mu m > d >> p$), the planar texture is readily obtained by a gentle tangential movement of the untreated cover glass. Obtaining a monodomain planar texture is a more complicated problem. Though in most cases it is not necessary—monodomain qualities have practically no effect upon helical pitch or λ_{max} values.

b) focal conic texture may be quite adequately presented as a slightly distorted homeotropic texture with helical axes begin approximately parallel (with many local deviations) to the bordering surfaces (Figure 2, b). This texture is naturally formed when an isotropic liquid cools down to the cholesteric phase; its milky appearance is due to the diffuse light scattering.

c) "fingerprint" texture is a cholesteric variety of the homeotropic texture well known for nematics. Due to a certain pre-treatment of the cover glasses (e.g., with lecythine) molecules tend to align normally, which causes helical axes to align parallel to the bordering

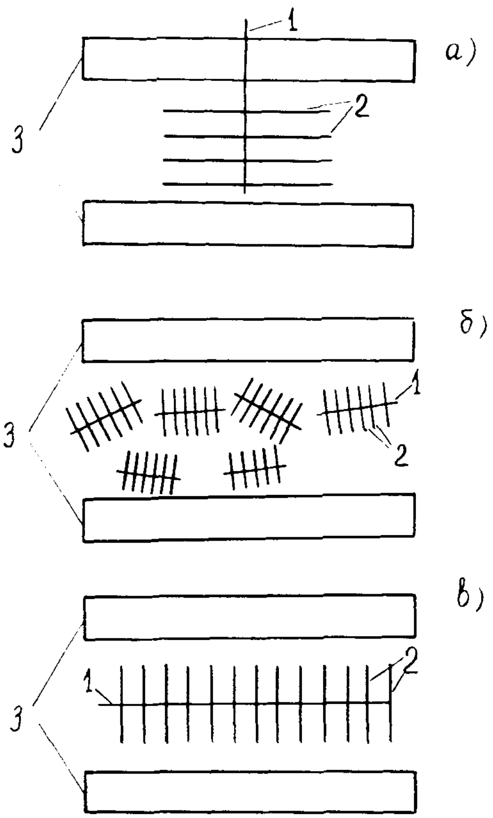

FIGURE 2 Types of textures in cholesterics: a) planar (Grandjean), b) focal conic, and c) homeotropic ("fingerprint"). For all the cases: 1—helical axis, 2—quasi-nematic layers, 3—boundary surfaces.

surfaces (Figure 2, c). The resulting picture, somewhat resembling fingerprints, can be observed in crossed polarizers. Periodic changes in molecular alignment along the helical axis cause periodic changes of the refractivity index, leading to the characteristic stripes pattern, with its period being equal to $p/2$.[44]

d) when surface anchoring energy is greater than the energy of helical twisting, a kind of superstructure is often obtained.[45,46] This superstructure (sometimes called a "strains"-texture) is also periodic, but its period is several times greater than the helical pitch. Bragg scattering from such a texture causes the appearance of two rings, the larger of which corresponds to the equilibrium pitch value, and the smaller—to the period of the superstructure. Very often this texture is a subject of further deformations, with the outer ring gradually disappearing. Characteristics of the superstructure are largely determined by the cell thickness.

2. *Helical pitch measurement technique.* In different cholesteric systems helical pitch values may vary from ~0.1 to ~200 μm, and it is not possible to carry out the measurements in all the range using one and the same experimental technique. Very often one even has to change from one technique to another while studying one and the same cholesteric system, with helical pitch increasing or decreasing by one or two orders of magnitude upon some minor external stimulus. Every technique has its own experimental set-up, its own drawbacks, its own sources of systematic errors. That's why helical pitch measurements in cholesterics, which seem so straightforward and relatively simple from the point of view of classical experimental physics, often meet with a number of methodological problems. To say nothing about the absolute helical pitch values, even the relative figures (e.g. $1/p\ dp/dT$)) are often much less reliable than it could be expected.

Basing upon literature data and our own experience, we will consider the following methods of helical measurements:

(i) Selective reflection from the planar texture. The observed wavelength of maximum reflection $\lambda_{\max}$ is related to the helical pitch p by the formula

$$\lambda_{\max} = np \cos \frac{1}{2}\left[\arcsin\left(\frac{\sin \varphi_i}{n}\right) + \arcsin\left(\frac{\sin \varphi_s}{n}\right)\right] \tag{4}$$

where φ_i and φ_s are the angles of incidence and observation respectively. A major advantage of the method is that $\lambda_{\max}$ is practically insensitive to the planar texture non-ideality (which is, in fact, unavoidable). Planar texture deterioration causes changes in the selective reflection amplitudes and makes the peaks more diffuse, while the values of $\lambda_{\max}$ remain constant. In a series of successive measurements $\lambda_{\max}$ values seem to be reproducible to within ±1–2 nm, except, perhaps, for the narrow temperature region close to the "blue phase" or the isotropic transition. Thus, the selective reflection technique must be considered quite reliable in the visible range of $\lambda_{\max}$ (i.e., $0.2\ \mu m < p < 0.6$).

(ii) Pitches up to 1.5–2 μm can be easily measured from the selective transmission spectra obtained, e.g., using a standard Hitachi 330 spectrophotometer, with $\lambda_{\max}$ related to p by the same Eq. (4). If some components of the cholesteric system studied (an OAD or a nematic matrix) have absorption bands close to λ_{max}, several practical methods can be applied to make an appropriate compensation and to avoid the difficulties.[47]

A drawback of the above-described methods is, of course, a need to know the refractive index values n. In some cases it may lead to some difficulties. In fact, all the literature data concerning substituted cholesteryl benzoates (which form the cholesteric mesophase in the temperature region of 150°–300°C)[48,49] provide only the λ_{max} values—the listed p values were obtained multiplying λ_{max} by 1.5, which was assumed to be an acceptable average n value for all the cholesterol esters. Actual n or p values have never been measured for these substances, which is quite justified, for an eventual increase in accuracy is definitely not worth the amount of experimental work needed for high-temperature refractive index measurements.

(iii) Bragg diffraction from the focal conic texture. The first diffraction maximum is determined by the formula

$$\lambda_{max} = np \sin \frac{1}{2}\left[\arcsin\left(\frac{\sin \varphi_i}{n}\right) + \arcsin\left(\frac{\sin \varphi_s}{n}\right)\right] \tag{5}$$

For $\varphi_i = \varphi_s$, n is canceled out, and

$$\lambda_{max} = p \sin \varphi \tag{6}$$

This technique was described in detail in Ref. 50 and used later rather extensively. The range of measurable p values are limited, from one side, by the angle φ which must not be too close to 90° to provide a well-defined diffraction maximum, and from the other side, for $p \gtrsim d$ (d is the cell thickness) and $d \gtrsim 50$ μm it is extremely difficult to obtain a good focal conic texture, because a deformed superstructure ("strains"-texture) becomes more favorable energetically.[45,46] With a conventional He-Ne laser, reliable data can be obtained for $0.8 < p < 10$ μm.

(iv) The Cano wedge technique[51] may be used in one of its possible modifications.[52,53] Its idea consists in introducing a cholesteric into a wedge-shaped cell, obtaining the planar texture and observing the distance l between disinclination lines, using a polarizing microscope. For small wedge angles α

$$p = 2\alpha l \tag{7}$$

Pitches up to 200–300 μm may be estimated using this method, thought it is definitely less accurate than those described previously.

(v) For the large pitches ($p \gg$ μm) it is possible to use a "fingerprint" texture—the distance between the adjacent lines is approximately equal to $p/2$.[44] The advantage of the method is its extreme simplicity; the values obtained are, unfortunately, not very accurate. This technique may be recommended, e.g., for preliminary determination of the helical twisting power order of magnitude when a new OAD or a new chiral nematic is synthesized, and only a small quantity is available.

Many other methods of helical pitch measurement were proposed; their use is, however, rather limited and is not considered in the present review.

A separate problem is the determination of helical sense (pitch sign). There are still no simple and reliable methods for absolute measurements, one has to compare in one way or another optical rotation or polarization properties of a tested system with these of a known system (e.g. left-handed cholesteryl nonanoate or right-handed cholesteryl chloride). Useful examples may be found, e.g., in Refs. 54,56.

3. Helical pitch: experimental data. a) Pre-transitional region. A well-known fact is the divergence of helical pitch near the cholesteric-smectic A transition point. Pindak *et al.*[57,58] have shown that the dependence in this region can be expressed by the relationship

$$p = p_0 + A(T - T_c)^{-\nu} \tag{8}$$

where ν is the critical exponent. For cholesteryl nonanoate and decanoate ν was found to be close to 0.66—the theoretical value predicted by the scaling law hypothesis and the de Gennes' analogy between superconductors and smectics—A.[59] The values of ν were measured many times in different cholesteric systems; in some cases ν values were quite close to $\nu = 0.66$,[60] while in other cases critical exponents appeared to be composition-dependent in the range of $0.5 < \nu < 1$.[61] Several theoretical approaches not based on the scaling law hypothesis were proposed, such as the model of Wigman and Filyov[62] and the model of Alben,[63] which was later extended[64] to consider an 'effective smectic field' orienting CLC molecules and causing the helix unwinding in an analogy to the helix unwinding by the electric field. The question about the relationship between molecular structure and character of $p(T)$ dependence remained, however, unsolved. Using the most general arguments, one may present a $p(T)$ dependence in the pre-transitional region as shown in Figure 3. Keeping in mind the use of such systems as liquid-crystalline thermoindicators, we consider the temperature range of color play ΔT as an important practical characteristic. Two main factors affect the ΔT value; (i) curvature and steepness of the $p(T)$ plot and (ii) intrinsic pitch value p_0, being the lower limit of p on increasing temperature. The first of these factors seems to depend upon the nature of the phase transition (second-order or weakly first-order), and the second one will be discussed in Section III. The narrowest ΔT value was reported in Ref. 65 for S-cholesteryl 14-phenyltetradecanethioate. There has been, however, no theoretical treatment of the problem on the molecular level.

Helical pitch does diverge not only close to the transition to smectic—A, but on approaching smectic—C phase as well.[66,67] In this case $p(T)$ curves were reported to be much less steep,[67] though no detailed investigation has been carried out. Untwisting of the helix may be caused by pressure, when the pressure-induced cholesteric-to-smectic

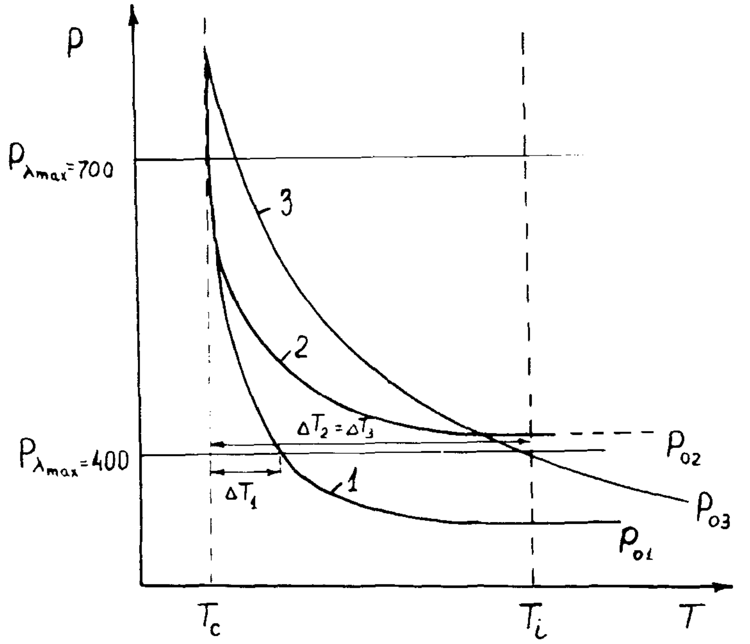

FIGURE 3 Characteristic features of pitch vs. temperature dependences in the vicinity of cholesteric-smectic transition.

phase transition does occur.[68] In the reentrant cholesteric phase helical pitch diverges with an increase in temperature on approaching the high-temperature smectic phase.[11,15]

b) 'Genuine' cholesterics. Practically all the cholesterol derivatives not exhibiting low-temperature smectics are characterized by a slow decrease in p on increasing temperature, with $|1/p\ dp/dT|$ values becoming somewhat larger on approaching T_i (Figure 4). Only two exceptions were reported: cholesteryl 2-(2-ethoxyethoxy)ethyl carbonate[69] and a recently synthesized methyl 3β-nonanoyloxy-cholest-5-ene-24-oate.[70] Reasons for such a behavior still remain unknown.

Chiral nematics usually have $dp/dT \approx 0$; in most of the induced systems $1/p\ dp/dT > 0$, though there are many exceptions. This question will be considered in detail in Section IV.

D. Viscosity

As most of the physical properties, viscosity is anisotropic in the liquid crystalline phases. Measuring of this anisotropy is complicated by the flow effects upon molecular orientations, which is overcome in nematics by applying magnetic fields at low rates of flow. In the cholesteric phase the problem is, however, much more complex.

It is a well established fact that the viscosity in the mesophase of

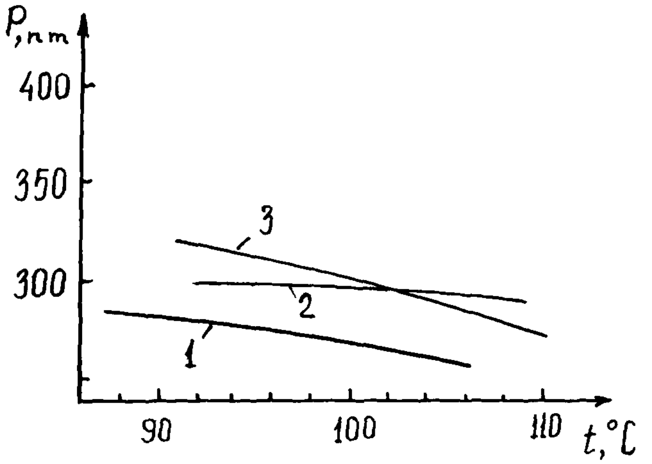

FIGURE 4 Typical pitch vs. temperature dependences in the absence of pre-transitional phenomena:[33,53] 1—cholesteryl valerate, 2—propionate, 3—brombutyrate.

cholesterol derivatives is markedly non-Newtonian for both tube and flat capillaries (for some recent data see, e.g.,[71,72]). A generally accepted interpretation of this fact is based upon the so-called "permeation" model proposed by Helfrich[73] (a generalized theoretical treatment was presented recently by Goossens).[74] The model consists in assuming a kind of anchoring of the molecules to the capillary walls; as a result, helical structure is fixed in space and becomes a source of hindrances to molecular motions—a molecule has to 'penetrate,' to 'permeate' through the fixed helical structure; its translational movements are inseparably coupled with rotations.

The situation is not so clear, however, for induced cholesteric systems. It is often argued that in this case there is but a small dependence of the apparent viscosity η_{app} upon the shear rate, and that η_{app} values have the same order of magnitude as in the conventional nematics, even at low flow velocities.[75] A question then naturally arises—what are the reasons for such differences between these two classes of cholesterics? One may recall also[76] that in a compensated cholesteric mixture (i.e., in a mixture of two cholesterol derivatives with the opposite helical pitch senses) when the pitch $p \rightarrow \infty$ the viscosity properties become quite similar to those of conventional nematics with no peculiar features that could be associated with the steroidal nature of the molecules.

In Ref. 77 viscosity of a number of induced cholesteric systems was measured using an Ostwald viscometer. The OAD used had different helical twisting power values and molecular geometry. It was shown that viscosity changes with increases in OAD concentration were determined primarily by the induced helical twisting, though at higher concentrations an influence of molecular geometry became noticeable.

In order to clarify the situation viscosities at different flow rates for a number of induced systems were measured in[78] using a modified Tsuda viscometer with a flat capillary. In all the systems studied when helical pitch values were sufficiently low a pronounced non-Newtonian behavior was observed, which could be interpreted in terms of the 'permeation' model. The difference between steroids, nematics doped with steroids and nematics with non-steroidal optically active dopants was found to be but quantitative, with no essential difference which could be ascribed to the differences on molecular level between steroidal and non-steroidal cholesterics. Similar results were obtained in Ref. 79 for both plate and tube capillaries.

It is an interesting fact in itself that viscous properties of CLC are very much the same both in plate and tube capillaries (though the absolute viscosity values are larger in the latter case), permeation effect being thus not limited to one peculiar geometry. In flat capillaries, with the helical axis normal to the flow direction, the effect may be presumably due to non-uniformities of the planar texture which in the absence of external fields or special orientation procedures show themselves as disclination lines oriented by flow.

The experimental data concerning CLC seem to imply a definite conclusion that steroidal, non-steroidal and induced cholesterics are physically one and the same system; differences due to molecular structure can show themselves, however, in various physico-chemical aspects.

III. A MICROSCOPIC THEORY OF THE HELICAL PITCH

A. Theoretical models of the cholesteric mesophase

Cholesterics appear to be one of the most complicated systems in the field of liquid crystals. Theory was always lagging behind experimental research and practical uses of cholesterics. One may recall that Maier-Saupe and Oseen-Frank theories of nematics preceded the works of Heilmeier *et al.*, while the sequence for cholesterics was inverse—Keating and Goossens appeared only after the works of Fergason. The years of research and development have not altered the situation. E.g., dealing with electrooptics of nematics, one has to know only quite a limited number of easily measurable macroscopic parameters ($\Delta\epsilon$, viscosity, stiffness constants, Δn), and then many different characteristics of numerous electrooptic effects (threshold voltages, rise and decay times, etc.) can be calculated with quite an acceptable accuracy.[80,81] On the contrary, there is no reliable and generally accepted way of theoretically predicting p or $1/p\ dp/dT$ for a cholesteric system of the known composition until these values are actually measured. A comprehensive theory of the cholesteric mesophase is yet to be developed. Relying largely upon our own experience of practical work in the field of cholesterics, we attempt to present here a brief outline of the existing theoretical situation.

Keating[82] proposed a microscopic model for the description of helical twisting, considering elongated molecules making anharmonic rotational vibrations in the planes normal to the helical axis (i.e., in the quasi-nematic layers). If θ is an angle between the long axes of two molecules situated in the adjacent quasi-nematic layers, the mean field is assumed to be

$$V(\theta) = V_0 + a\theta^2 + B\theta^3 \tag{9}$$

The anharmonic term $B\theta^3$ causes the mean field to be asymmetric about the parallel orientation ($\theta = 0$), and at the temperature T the thermal average of θ gives rise to a non-vanishing twist angle:

$$\langle\theta\rangle = \int_{-\pi}^{\pi} \theta\, e^{-v(\theta)/kT}\, d\theta \Big/ \int_{-\pi}^{\pi} e^{-v(\theta)/kT}\, \mathrm{d}\theta \tag{10}$$

Helical pitch $p = 2\pi a/\langle\theta\rangle$ (here a is the distance between the adjacent planes) is a decreasing function of temperature in this model.

Later on, Boettcher[83] extended physical foundations of the Keating model, providing a realistic picture of the molecular arrangement in the cholesteric phase.

Another approach was proposed by Goossens[84,85] and later extended by Wulf,[86] who assumed the angular dependence of the energy of interaction between two chiral molecules in the adjacent quasi-nematic layers in the form

$$V_{12}(\theta) = -\omega P_2\,[cos(\theta - \theta_0)] \tag{11}$$

where P_2 is the Legendre polynominal (in the paper of Wulf[86] the corresponding expression for the planar case, i.e. $(2\cos^2\theta - 1)$ instead of $P_2(\cos\theta) \equiv 1/2(3\cos^2\theta - 1)$, was used), and θ_0 is the angle between the long axes of the molecules in question in the mutual orientation corresponding to $V_{12}(\theta) = \min$ (Explicit expressions for θ_0 will be discussed later). In the original Goossens theory dispersion forces were considered as the source of chirality, while Wulf did not specify the nature of the relevant intermolecular forces.

The model potential of a chiral molecule in the mean field, in an analogy to Maier-Saupe theory of nematics, may be written down as

$$V(\theta) = -\nu S\, P_2[\cos(\theta - \theta_0)] \tag{12}$$

where S is the orientational order parameter. Substituting Eq. (12) for $V(\theta)$ into Eq. (10) and performing the relevant integrations, in the case of an expression for small θ_0 can be obtained[87]:

$$\langle\theta\rangle = \theta_0\, L(t) \equiv \theta_0 \left[1 - \exp\left(-\frac{\alpha}{2}\right) \Big/ I_0\left(\frac{\alpha}{2}\right)\right], \tag{13}$$

where $\alpha = 3S/2t$, $t = kT/v$, and I_0 is the modified Bessel function. This provides a quantitative description of the partial helix unwinding due to an increase in the number of molecules with orientations tending to compensate the Goossen's twisting (i.e., increasing temperature leads to higher $|\theta - \theta_0|$; for more and more molecules θ values become opposite in sign to θ_0, and the averaged value of $\langle\theta\rangle$ diminishes). Thus, the Goossens–Wulf theory does predict a small increase in p with temperature (for $T = T_i - 10°$ $1/p\ dp/dT \sim 0.004$), as it was noted in Ref. 88.

An account for rotation of chiral molecules about their long axes was made by Stegemeyer and Finkelmann.[89,53] This rotation was assumed to be not quite free (as it would have been in the case of cylindrically symmetric molecules). One of the two mutually perpendicular directions of the short molecular axis is thought to be energetically more favourable, resulting in a certain amount of (at least short-range) rotational order. Generalizing the idea of Wulf,[86] who considered only two discrete orientations of the short axis, Finklemann and Stegemeyer introduced a short-range rotational order parameter

$$S_R = \frac{\int_0^{\pi} (1 - \sin^2\psi) \exp[-U(\psi)/kT]\, d\psi}{\int_0^{\pi} exp[-U(\psi)/kT]\, d\psi} \tag{14}$$

where ψ is the angle which describes the deviation from the coplanar orientation of the corresponding short axes, and $U(\psi)$ is the potential introduced to describe the hindered rotation about the long molecular axis ($U(\psi) = U_0(1 - \cos 2\psi)/2$). The helical twist angle is then

$$\bar{\theta}_r = \theta_0 \cdot S_R(T)$$

$$\text{For } U_0 << kT\ S_R = U_0/4kT, \quad \text{and} \quad \frac{1}{p}\frac{dp}{dT} = \frac{1}{T}, \tag{15}$$

i.e., a slight helical pitch increase with temperature of the same order of magnitude as in the Goossens-Wulf model (Eq. (13)). In many experimentally studied systems $0.005 << 1/p\ dp/dT < 0.007$,[53] which is probably the result of simultaneous action of both these mechanisms. On the other hand, in some systems one may assume $U_0 \sim kT$ and $S_R \lesssim 1$.

The three above-described approaches (i.e., these of Keating-Boettcher, Goossens-Wulf and Finkelmann-Stegemeyer) seem to provide all the necessary physical insight into the problem of helical twisting, outlining the three main groups of affecting factors: (i) chiral terms in dispersion interaction or, in order not to specify the nature of forces, the Goossen's chirality, (ii) steric factors causing rotational vibrations of chiral molecules to be anharmonic, and (iii) the important role of molecular phase biaxialities, closely related to the hindered rotation about long molecular axes. The next step in the development of theory consisted in outlining more comprehensive and self-consistent descriptions, using the same basic principles.

Lin-Liu, Shih, Woo and Tan[90,91] assumed the pair intermolecular interaction energy in a general form

$$V_{12} = V_N(r_{12}, \vec{n}_1 \cdot \vec{r}_{12}, \vec{n}_2 \cdot \vec{r}_{12}, \vec{n}_1 \cdot \vec{n}_2) + (\vec{n}_1 \times \vec{n}_2 \cdot \vec{r}_{12})\, V_x\, (r_{12}, \vec{n}_1 \cdot \vec{r}_{12}, \vec{n}_2 \cdot \vec{r}_{12}, \vec{n}_1 \cdot \vec{n}_2) \quad (16)$$

where $\vec{n}_1$, $\vec{n}_2$ and $\vec{r}_{12}$ are the orientation and position vectors of the molecules 1 and 2. After further assumptions this expression was reduced to the form

$$V_{12} = V_0(r_{12}) + V_2(r_{12})P_2(\vec{n}_1 \cdot \vec{n}_2) + V_4(r_{12})P_4(\vec{n}_1 \cdot \vec{n}_2) + (\vec{n}_1 \times \vec{n}_2 \cdot \vec{r}_{12})\,[V_1'(r_{12})P_1(\vec{n}_1 \cdot \vec{n}_2) + V_3'(r_{12})P_3(\vec{n}_1 \cdot \vec{n}_2)] \quad (17)$$

In the planar case,[90] i.e., when the molecular movements are restricted to the XY planes normal to the helical axis z, $\vec{n}_1 \cdot \vec{n}_2 \rightarrow \cos\theta_{12}$, $\vec{n}_1 \times \vec{n}_2 \cdot \vec{r}_{12} \rightarrow z_{12}/r_{12} \sin\theta_{12}$, and

$$V_{12} = V_0(r_{12}) + \sum_{m=1}^{\infty} [V_{2m}(r_{12}) \cos 2m\theta_{12} + z_{12}\, V_{2m}'(r_{12}) \sin 2m\theta_{12}] \quad (18)$$

It can be easily seen that this approach, is in fact, a synthesis of the Keating and Goossens models (Figure 5). The next step consists in writing down the Helmholtz free energy functional in the mean-field approximation and, after subsequent minimization with respect to the one-particle distribution function, $p(T)$ model dependences are obtained, involving a number of phenomenological parameters. Assuming $V_{12}(\theta_{12})$ in one of the forms presented in Figure 5 (curves

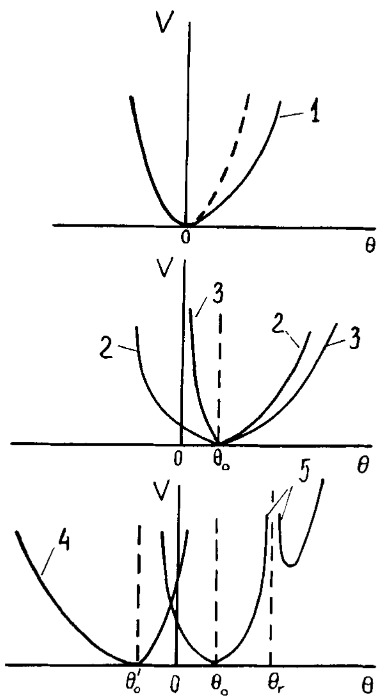

FIGURE 5 Possible types of the angular dependence of the chiral molecules interaction energy.

1 to 4), one can obtain a great variety of $p(T)$ plot types, presumably corresponding to some real cholesteric systems.

Van der Meer,[92,93] within a similar philosophy, modeled the chiral molecule by a cylindrical chiral cogwheel, presumably allowing to combine chirality and cylindrical symmetry. The packing entropy resulting from the hard core repulsions of such bodies was accounted for in the free energy functional.

For Kimura *et al.*[94] the helical twist value appears to be the sum of two contributions: the "polar" effect due to the Maier-Saupe-Goossens dispersion forces, and the "steric" effect, which is proportional to the deflection angle between the principal axes of a pair of molecules closely in contact, depending on the geometrical shape of the molecules. This second term, when prevailing, leads to a Keating-like $p \sim 1/T$ dependence. When there is only the first term, we obtain, as in the Goossen's model (Eq. (13)) a slight increase of the helical pitch with temperature.

The above-described models, though providing a satisfactory description of cholesterics to a specialist in theoretical physics, have many drawbacks from the standpoint of practical research. The model calculations are too complicated, too many phenomenological parameters are involved and there is no idea of how to relate them to the molecular properties. It was argued in Ref. 53 (and this point of view is quite consistent with our own experience) that these models are, unfortunately, of little practical use for a research worker in need of a basis for discussion of experimental data obtained.

Several authors treated the question of the rotational order and biaxiality. Goossens[95] provided an extension of his model[84,85] to account explicitly for the local biaxialities, arriving to an expression relating helical twisting to a set of order parameters describing both long-range orientational and biaxial order, the latter being due to both molecular and phase biaxiality. Model p (T) dependeces were calculated, but no comparison with experimental data was possible. Influence of phase and molecular biaxiality upon the helical pitch was discussed also in Refs. 25,36,37,96–100, though no conclusive data have been obtained.

The problem of helical twisting has been approached in a number of ways. We will but mention here models like,[101] where a temperature-independent pitch is obtained, or,[102] where there is no satisfactory agreement with the experimental data. Some words must be said, however, about a very promising approach, proposed recently in Ref. 103, where the results very much similar to those of Refs. 90–94 were obtained using much simpler calculation procedures.

In the rest of this chapter, we shall outline a physical picture of helical twisting and present its semi- quantitative description to allow a comparison with experimental data.

B. A model of the chiral molecule in the cholesteric mesophase

A natural starting point in constructing a microscopic theory of cholesterics is the question of an adequate model of the cholesterogenic molecule.

In the case of nematics, such a question does not raise any major problems. Hard rods, spherocylinders, bi- or tri-axial ellipsoids—these relatively simple geometrical objects appear to be suitable enough to describe most of the properties of nematics. Unfortunately, the situation is much more complicated in the case of CLC.

An attempt of Van der Meer[93] to reconcile cylindrical symmetry and chirality in a single object (the 'chiral cog-wheel') provides no possibility of introducing features of the real molecular structure into the theory.

A rather realistic model of chiral molecule consisting of two ellipsoids with the long axes $\vec{n}_1$ and $\vec{n}_2$ and the distance between their centers $\vec{r}_{12}$ with the chirality condition $\vec{r}_{12} \cdot [\vec{n}_1 \times \vec{n}_2] \neq 0$, was proposed by Osipov,[104] who, unfortunately, used it only for the chiral smectic-C mesophase. (Paradoxically enough, the presence of the long-range translational order makes chiral smectics an easier object for the rigorous molecular statistical treatment).

We felt intuitively that, to avoid complications which seemed to be unsurmountable if one attempted to account for short-range effects at the stage of statistical averaging procedures, one has to introduce these effects into the model of a chiral molecule. Thus, what we need is a model of the chiral molecule in the real orientationally ordered mesophase, not a model of the chiral molecule by itself.

The relevant properties of a 'matrix' nematic mesophase into which chiral molecules are inserted (or chiral elements are introduced into the structure of nematogenic molecules) cannot be just assumed or derived from some statistical-mechanical formalism like the BBGKY (Bogoliubov-Born-Green-Kirkwood-Yvon) theory. The only realistic way seems to introduce them based upon the experimental data analysis. The resulting theory will thus not be a simultaneous description of the helical twist and molecular ordering in cholesterics; it was meant from the very beginning to be a model of helical twisting only, with all the relevant molecular ordering features being input into the model.

These input features are:

(i) The existence of a short-range translational order ('smectic-like correlations').[105,106] It must not be confused with the formation of smectic clusters in the pre-transitional region; smectic-like correlations do not hinder helical twisting, on the contrary, they favor it. Influence of smectic-like correlations and smectic clusters upon stiffness constants is similar to their influence upon helical twisting.[105] The existence of smectic-like correlations is obviously not important for description of the Goossen's chirality, but the influence of different steric factors upon helical twisting[93,94] (which play a decisive role in determining the character of $p(T)$ curves) cannot be adequately described without taking into account these correlations because even minor displacements of molecular centers of mass can significantly affect the short-range intermolecular repulsion forces.

Therefore, we assume a lattice-like model of the chiral molecule surrounded by its nearest neighbors.

We must stress that these ideas are not new—short-range translational order in cholesterics was considered in Ref. 107, short-range translational order effects in nematics were discussed in Refs. 105,108, and the role of short-range orientational order in the isotropic mesophase is a generally accepted fact.[109,110]

(ii) The existence of a short-range rotational order. As it has been clearly stated by Finkelmann and Stegemeyer,[53] it is a *sine qua non* condition of the helical twisting. Phase biaxiality is often considered as a consequence of the helical twisting.[96,99] The latter, however, in all the known systems is accompanied by a molecular biaxiality. The only exception is the mesophase formed by Van der Meer's chiral cylindrical cog-wheels, since there are no real molecules possessing chirality and not possessing molecular biaxiality. To assume a certain degree of correlation between molecular biaxiality and phase biaxiality, and to regard the latter as closely related to the short-range rotational order of Refs. 59,83 did not seem to us too artificial. This ideology is strongly supported by the experimentally established fact that the more 'flat' chiral molecules usually have greater helical twisting powers.[53,9] One may also recall that the 'classic' examples of cholesterogenic molecules, the cholesterol derivatives, are characterized by a well-defined 'basic plane' of the steroidal ring and a pronounced molecular biaxiality.[8,111] An interesting fact is that recently[112] a relationship between molecular structure and biaxial characteristics was found, using the deuterium NMR technique, even for conventional (non-chiral) nematics.

Basing on the above-stated reasoning, we claim that the simplest geometrical structure containing all the elements necessary and sufficient for an adequate description of the helical twisting in real orientationally ordered mesophases may be presented as in Figure 6.

The principal elements of the model chiral molecule are:

(i) An anisometric symmetrical part, defining the molecular coordinate system, which may be represented by a 'basic plane' (e.g., the rectangle ABCD or just three points defining the plane), a triaxial ellipsoid, a hard rod with its movements restricted to the XY plane, or any other similar object.

(ii) A chiral element (i.e., an atom or a group of atoms which under no possible molecular orientation or conformation can have any 'counterparts' situated symmetrically with respect to the coordinate planes or the coordinate origin). Physically, it is represented in most cases by a CH_3 (or some other) atomic group directly linked to an asymmetrical carbon atom. A chiral molecule can have one or several

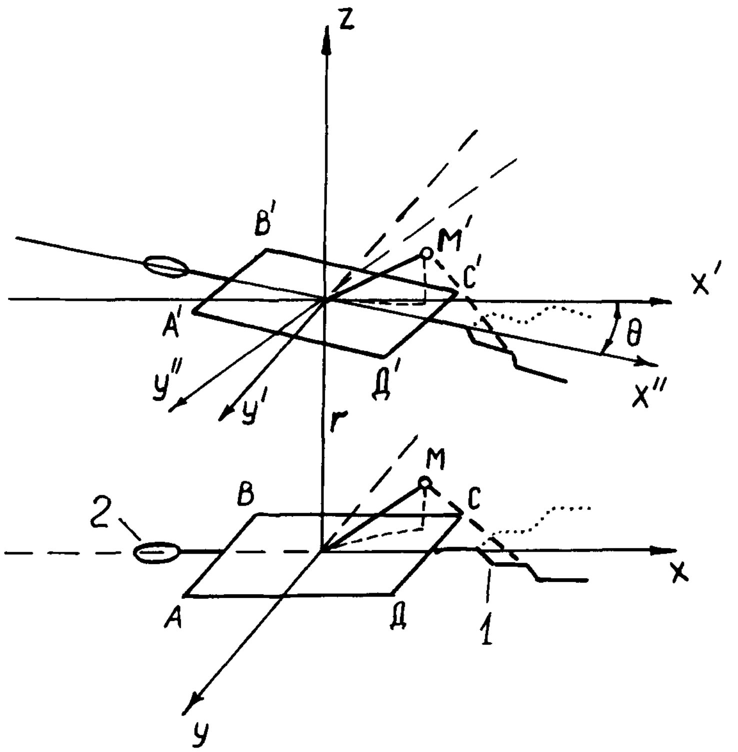

FIGURE 6 A model of interacting chiral molecules in the adjacent quasi-nematic layers *XY* and *X'Y'*. *ABCD* is the basic molecular plane, *M* is the chiral element, 1 and 2 are optional elements (flexible alkyl chains, CN-groups, etc.). Further clarifications are in the text.

chiral elements; a chiral element may belong to the rigid or to the conformationally flexible part of the molecule.

(iii) Optional elements, e.g., alkyl chains or different functional groups (1 and 2 in Figure 6).

The angular dependence of the intermolecular interaction energy may be written down as[113]

$$V(\theta) = V_{n-n}(\theta) + V_{n-ch}(\theta) + V_{ch-n}(\theta) + V_{ch-ch}(\theta) \quad (19)$$

where subscripts n and ch refer to the basic 'nematic' and the chiral element.

It is natural to assume $V_{n-n}(\theta) = v\cos^2\theta$, where v is, like the Maier-Saupe constant, determined by the molecular anisometry. If geometrical deformations caused by the chiral elements are small, $V_{ch-ch}(\theta)$ term may be neglected; for the case of two identical chiral molecules $V_{n-ch}(\theta) = V_{ch-n}(\theta)$, while if only one of the interacting molecules is chiral, $V_{ch-n}(\theta) = 0$. Therefore, we have only to determine $V_{n-ch}(\theta)$, i.e., the interaction energy between the 'basic plane' of the first molecule and the chiral element M of the second one, as function of the angle θ.

Let x, y, and z be the coordinates of M in the coordinate system defined by the first molecule. If $x >> y$, we may express $V_{n-ch}(\theta)$ as $V(d)$, where d is the shortest distance from M' to the long axis of the first molecule, (we recall that the basic plane may be, without loss of generality, regarded as a rigid rod confined to the XY plane). Then, to a first approximation,

$$d = \sqrt{(-x\sin\theta + y\cos\theta)^2 + (z + r)^2} \tag{20}$$

To account for both dispersion attraction and steric repulsion forces, we use Lennard-Jones form for $V(d)$, i.e., $V(d) = ad^{-12} - bd^{-6}$, with the minimum at $d = d_0$. Assuming deviations from the lowest-energy orientation to be small (in the real system $\theta_0 \sim 10^{-2}$), we may imitate the model potential as

$$V(d) = v_1(d - d_0)^2 \tag{21}$$

neglecting the higher-order terms. After some straightforward trigonometry, assuming $d_0 = r$ (which is quite natural for a condensed phase far from phase transition points), we obtain[113]

$$\begin{aligned} V(\theta) &= V_{n-n}(\theta) + V_{n-ch}(\theta) \\ &= -v_0\cos^2\theta - 4v\frac{(x^2 + y^2)}{2r}z \cdot \frac{xy}{(x^2 + y^2)}\sin\theta\cos\theta \end{aligned} \tag{22}$$

and, minimizing $V(\theta)$ with respect to θ,

$$\theta_0 = \frac{v_1}{v_0}\frac{xyz}{r} \tag{23}$$

If several chiral elements are present, $\theta_0 = (\sum_i v_i x_i y_i z_i)/v_0 r$; more rigorous calculations would yield additional terms with higher odd powers of the chiral element coordinates x, y and z.

Rotating the second molecule about its long axis by the angle ψ, we obtain

$$\theta(\psi) = \frac{v_1}{v_0}\frac{x}{r}\left[yz(1 - 2\sin^2\psi) + \frac{z^2 - y^2}{2}\sin 2\psi\right] \tag{24}$$

After the relevant thermal averaging, the sin 2ψ term vanishes, and

$$\langle\theta\rangle = \theta_0\langle 1 - 2\sin^2\psi\rangle = \theta_0 \cdot S_R \tag{25}$$

which is identical to the expression postulated by Finkelmann and Stegemeyer[89,53] (Eq. (15)), with S_R being a measure of short-range rotational order parameter.

In Ref. 114 the 'molecular dynamics' technique was used for numerical calculation of $\langle\theta\rangle$, which was estimated, for a realistic choice of input molecular parameters, to be $\langle\theta\rangle \sim \theta_0 \cdot 1/4$. Thus, Eq. (15) is, in fact, strongly supported on the molecular level.

The expression for θ_0 in the Goossens theory is

$$\theta_0 = B/rA \tag{26}$$

Here B is related to the quadrupole polarizability tensor components equal to zero unless the molecule is chiral, and A, to a first approximation, is determined by the polarizability anisotropy ($A \sim (\Delta\alpha)^2$, where $\Delta\alpha = \alpha_{11} - \alpha_{\perp}$). The equations (26) and (23) are obviously similar in their structure. Advantages of the approach of Ref. 114 are the following: (i) there are strong formal objections to the original Goossens theory, arising from the fact that validity of the multipole expansion in the case of condensed phases and short intermolecular distances is rather doubtful, (ii) both dispersion attraction and steric repulsion forces are accounted for simultaneously, and (iii) there is a possibility of estimating xyz values (and, consequently, θ_0 values) for different chiral molecules.

The above-described approach has much in common with the recently proposed method[116] of describing stiffness constants as function of molecular structure using the notion of 'harmonically distributed forces.' This approach may be regarded as a special case of the methods of atom-atom potentials[117] or effective pair interactions.[118] Earlier, a similar approach to estimate the helical twisting in cholesterics was used in Ref. 118, basing upon the ideas of Ref. 119.

Let us use the Eq. (23) to estimate helical twisting in chiral cyanobiphenyls. Let the x axis to coincide with the long axis of the unsubstituted 4-cyanobiphenyl and the XY plane to maximize the short axes anisometry; the choice of the coordinates origin is rather arbitrary, e.g., let it coincide with the point where the alkyl chain is to be attached to the benzene ring. It is easy to see that the chiral element (i.e., the CH_3 group attached to the asymmetrical carbon atom) would be in the different space octants for 2-methylbutyl and 2-methylbutoxy groups, and in the latter case the θ_0 value is lower. This result is in agreement with experimental data[120,121] and with theoretical treatment of Ref. 122.

C. Temperature dependence of the helical pitch

If in the Eq. (19) the $V_{ch-ch}(\theta)$ term is not neglected and other simplifying assumptions are not made, $V(\theta)$ dependence can be calculated numerically. The $V(\theta)$ curve will have a minimum at $\theta = \theta_0$, but it will not necessarily be symmetric about the $\theta = \theta_0$ axis.

Let us assume $V(\theta)$ in the form

$$V(\theta) = -S[vP_2(\cos(\theta - \theta_0)) + uR(\theta)] \tag{27}$$

where u and $R(\theta)$ are respectively the amplitude and the normalized contribution to the $V(\theta)$ angle dependence not accounted for by the first term, and S in the orientational order parameter. Multiplying by S means that Eq. (27) is an expression for the model potential approximating the interaction energy of the 'trial' chiral molecule with all its surroundings. Due to the assumption of a lattice-like model, our pseudopotential is similar in form to the pair interaction energy ('interaction with all the surroundings' is rather adequately approximated by the 'interaction with the nearest neighbors,' due to the essentially short-range nature of the $V(d)$ in Eq. (21), i.e., of the forces determining the helical twisting).

The $\bar{\theta}_p \equiv 2\pi p^{-1}r$ temperature dependence may be expressed as

$$\bar{\theta}_p = \frac{\int_{-\pi/2}^{\pi/2} \theta \exp[-v(\theta)/kT]\, d\theta}{\int_{-\pi/2}^{\pi/2} \exp[-v(\theta)/kT]\, d\theta} \tag{28}$$

Thus, the problem of determining $\bar{\theta}_p(T)$ in a specific cholesteric system is reduced to (i) assuming a $R(\theta)$, basing upon quantum-chemical calculations or upon chemical intuition and our knowledge about the character of possible intermolecular interactions; (ii) performing the relevant integrations in Eq. (28) using Eq. (27). Such calculations were considered in detail in Ref. 8; here we will only recall the main results. For the Keating-like anharmonic rotational vibrations ($R(\theta) = \sin^3(\theta - \theta_0)$) for $u_v \gtrsim \theta_0$ ($u_v = u/3v$)

$$\bar{\theta}_p = \theta_0 + u_v \frac{t}{S(t)} \tag{29}$$

where t is the Maier-Saupe reduced temperature ($t = kT/v = 0.22019\ T/T_i$).

As it was shown in Refs. 32,123,124, Eq. (29) is in a good agreement with experimental data for a number of cholesterol derivatives in the absence of pre-transitional phenomena. In these papers, $S(T)$ dependence was either approximated by the Maier-Saupe theoretical curve[123,124] or determined from birefringence data using the Averyanov method.[32] In all the cases the values of θ_0 and u_v, found from the linear plots of $\bar{\theta}_p$ vs $t/S(t)$, were correlated with the molecular structure. For example, for p-substituted cholesteryl benzoates[123] u_v increase with an increase in the substituent volume (which is quite natural, for the p-axis of the phenyl ring in these substances is directed at the angle of 25° to the basic plane).[111] The cases of $1/p\ dp/dT > 0$[69,70] may correspond to θ_0 and u_v being of opposite signs; then, at $u_v t/S(t) = -\theta_0$, $p \rightarrow \infty$.

For the case of $u_v << \theta_0$ we obtain $1/p\ dp/dT > 0$, according to Eq. (13). This is, in fact, the typical case for non-steroidal and induced systems, where molecular structure presents no apparent steric reasons for the vibrations anharmonism.

Situations when $u_v \lesssim \theta_0$, cases of specific $R(\theta)$ forms, etc. will be considered in Section IV.

As a final remark, it must be kept in mind that the 'method of model pseudopotentials,' based upon the expressions like Eq. (27), where a quasi-lattice structure is assumed, can be used not only for cholesterics. Such an approach, in which the relevant notion of the short-range order had been input into the model description of pair interaction before any averaging procedures were made, was used for nematics[125] (the case of the molecules with head-tail asymmetry) and smectics—A.[87]

IV. SPECIFIC INTERMOLECULAR INTERACTIONS IN CHOLESTERIC MIXTURES AND THEIR INFLUENCE UPON MACROSCOPIC PROPERTIES

A. Cases of ideal behavior

1. Concentration dependence of the helical pitch and intermolecular interaction parameters. To present a statistical-mechanical description of a system where particles have different size and shape is rather a difficult problem. Existing more or less rigorous theories of nematic mixtures (e.g., Refs. 126–129) are too complicated and contradictory to allow their straightforward extension to the mixtures of cholesterics. One has but to start from some practical assumptions based upon experiment.

Adams and Haas[130,131] were the first to realize that in the mesophase with macroscopic properties depending upon universal interactions between molecules of different size, molar concentrations cannot be natural weighting parameters for the additive properties. (The term 'universal interactions' means here dispersion attractions and steric repulsions, i.e., intermolecular forces which can be described by 'harmonic distributed forces' or 'effective pair interactions' models).[115,117] They postulated the weight concentration additivity of the inverse pitch in the ideal systems (i.e., in the absence of specific interactions):

$$p^{-1} = \sum_i w_i P_i^{-1} \tag{30}$$

This relationship may be explained in the following way. The value of p^{-1} is determined by the twist angle between adjacent quasinematic layers. Each molecule i brings in a contribution p_{0i}^{-1} to the total twisting power of the quasi-nematic layer. The value of p_{0i}^{-1} is determined by the degree of molecular chirality (e.g., v_1xyz/v_0r in Eq. (23)). Molecules of different size may have the same degree of chirality, it is natural to assume that the effective twisting power p^{-1} is determined by the distribution density of chiral elements in the quasinematic layer, i.e., $p_i^{-1} \sim p_{0i}^{-1}/s_i$, where s_i is the area of the projection of the molecule of the i-th component onto the plane of quasinematic layer. It follows that p^{-1} is additive upon the fraction of quasi-nematic layer occupied by the molecules of the i-th component. Assuming then $\rho r \approx$ const (ρ is the density, r is the distance between the adjacent quasi-nematic planes), we obtain the relationship of Eq. (30). Under a somewhat less realistic assumption $r \approx$ const. we obtain the volume additivity of the inverse pitch. (In all the cases we use the notation w_i for the corresponding fraction of the i-th component).

If θ_{ij} is the twist angle between the molecules i and j, then, in the multicomponent mixture, the value of $\overline{\theta}_p \equiv 2\pi r p^{-1}$ is (taking into account only pair intermolecular interactions)

$$\overline{\theta}_p = \sum_i \sum_j \theta_{ij} w_i w_j \tag{31}$$

Introducing the parameter $k_0 = 2\theta_{ij} - (\theta_i + \theta_j)$, we obtain for the binary mixture

$$\overline{\theta}_p = \theta_1 (1 - w) + k_\theta w(1 - w) + \theta_2 w \tag{32}$$

In the absence of specific interactions k_θ may be neglected, and the linear inverse pitch—concentration relationship results.

The same scheme of reasoning may be applied to the Maier-Saupe constant v. In fact, in the system of anisotropic molecules which differ significantly in size, it is not the absolute value of molecular anisotropy, but its 'density' that plays the major role. (E.g., a large ellipsoid with almost equal axes and a long thin rod may have equal values of, say, polarizability anisotropy, but their mesomorphic properties would obviously be different). Thus, if all the components show, at least approximately, the Maier-Saupe behavior, with pair interactions only taken into account,

$$v = \sum_i \sum_j v_{ij} w_i w_j \tag{33}$$

Introducing $k_v = 2v_{ij} - (v_i + v_j)$, one has, for binary systems

$$v = v_1(1 - w) + k_v w(1 - w) + v_2 w \tag{34}$$

Again, neglecting k_v in the case of an ideal system (in fact, most models expressing v via molecular parameters lead to $v_{ij} = (v_i v_j)^{1/2}$; then for realistic v values, $k_v \sim 10^{-2}$).

Hence, for a theoretical treatment of the mixture of nematogens one should consider weight (or volume) concentrations w_i as natural weighing factors. Experimentally observed deviations from the $T_i(w)$ linearity are often caused by the role of higher Lengendre polynomials (i.e., deviations of the components from the Maier-Saupe behavior $T_i \sim v$), and not by any specific interactions of 'packing factors.'

The ideas of using w_i instead of molar fractions is not quite new—it was clearly stated in Ref. 132 and promoted, in fact, in Ref. 133. Still many authors are treating cholesteric or nematic mixtures using the molar fractions (e.g., considering the 'particle number density,' etc.).[134-137] This is the reason for our a bit too extensive explanation of the subject.

On the contrary, if there are reasons to believe that the system is quite far from being an ideal one, it is quasi-chemical specific interaction that play the vital role, and the molar fractions regain their significance.

2. *Mixtures of cholesterol derivatives.* A linear $p^{-1}(w)$ dependence is a characteristic feature of the mixtures of cholesterol derivatives.[138-140] One may refer, e.g., to Ref. 71 to demonstrate that the use of weight concentrations does indeed provide the best fit to experimental data. Deviations from linearity occur, as a rule, in the pre-transitional region due to the helix unwinding. The p_i^{-1} values, extrapolated from linear plots to $w = 0$ and $w = 100\%$, may be considered as inverse 'intrinsic pitches' of the components (Figure 7); a number of p_i values are listed in Refs. 139,141. Speaking about long-chain cholesterol esters (e.g., nonanoate, myristate, oleyl carbonate) one should keep in mind that for all their mixtures with each other and in many cases for their mixtures with other substances temperature range of cholesteric mesophase lies entirely inside the region of pre-transitional phenomena. Physically, these systems differ in many aspects from the 'genuine' cholesterics, steroidal or induced, and the theories outlined in Section III cannot be referred to. The actually measured pitch values, which obey more or less exactly the Eq. (8), are quite different from the extrapolated 'intrinsic pitch' values determined by Eq. (29). For non-smectogenic substances like cholesteryl propionate, however, $p(T)$ and $p_i(T)$ dependence agree fairly well.[142] It is natural to assume that the $\bar{\theta}_p$ dependence on reduced temperature (Eq. (8)) may be generalized as

$$\bar{\theta}_p = \sum_i \left[\theta_{0i} + u_{vi} \frac{t}{S(t)} \right] w_i \qquad (35)$$

with the values of t determined by T/T_i of the mixture studied. In Ref. 143, $p(w, T)$ dependences in the compensated system cholesteryl chloride–cholesteryl nonanoate, were fitted fairly well by Eqs. (35) with $\theta_{0i} = -0.82 \cdot 10^{-2}$ and $u_{v1} = -1.74 \cdot 10^{-2}$, $\theta_{02} = 1.52 \cdot 10^{-2}$

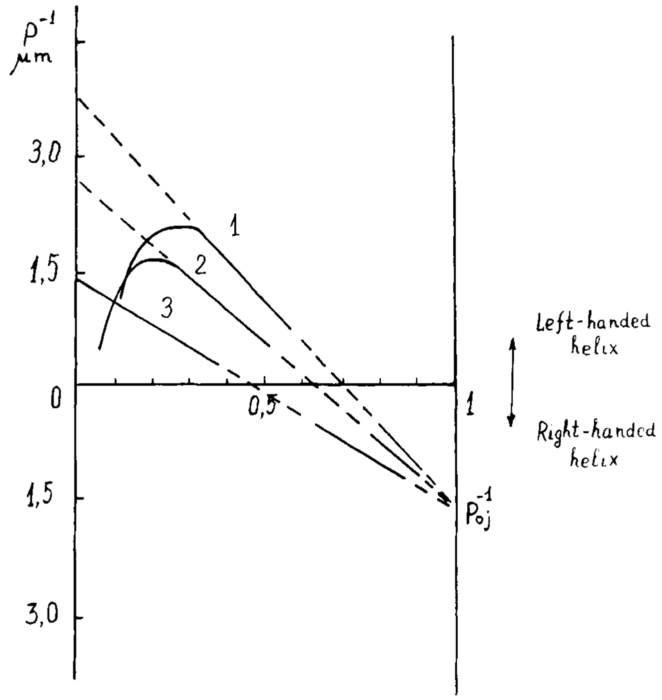

FIGURE 7 Typical inverse pitch vs. concentration dependences in the mixtures of cholesterol derivatives: 1,2—smectogenic esters + chloride, 3—a non-smectogenic ester + chloride. Solid lines: measured values. Dashed lines: extrapolated values.

and $u_{v2} = 0.5 \times 10^{-2}$ for chloride and nonanoate, respectively. The compensation point is found as (for the binary system)

$$\frac{t}{S(t)} = -\frac{\theta_{01} w_1 + \theta_{02}(1 - w_1)}{u_{v1} w_1 + u_{v2}(1 - w_2)} \tag{36}$$

Equation (35) may be further generalized, accounting for $S_R(T)$ as in Eq. (15) ($\overline{\theta}_p \rightarrow \overline{\theta}_p(t)\, S_R(T)$), etc.

There are, however, exceptions to the inverse pitch additivity rule—e.g., systems comprising substituted cholesteryl benzoates show a pronounced non-linearity,[144] reflecting a non-ideal behavior.

3. Induced cholesteric systems (mixtures of nematics with optically active dopants). In the case of ideal behavior, $p^{-1}(w)$ plots are linear. In most cases, however, it is possible to measure only a small part of the total plot, due to the loss of mesomorphic properties at $w \gtrsim 10\%$. By means of extrapolation helical twisting power (HTP) values $\beta = 1/p \cdot w$ or corresponding virtual intrinsic pitches can be determined for an OAD in a given nematic solvent. In the low-concentration region there is no essential difference between the use of $\beta = 1/p \cdot w$ or $\beta_m = 1/p \cdot \alpha$ (α being the molar fraction of the OAD). Many authors prefer the latter, because it allows to present more clearly the role of chemical structure of the OAD molecule and to account for possible specific interactions. A more accurate expression for β or β_m reads $\beta_m = 1/p \cdot \alpha \cdot r$, where r is the enantiomeric purity of the OAD.

If a chiral nematogen is used as an OAD, the whole $p^{-1}(w)$ plot can be obtained.[145]

$p(T)$ data for induced systems are rather scarce. In[53] for a number of dopants $1/p\ dp/dT \gtrsim 1/T$ values are reported.

A systematic study of $p(T)$ dependences in induced systems was carried out.[146-150] The results obtained may be summarized as follows:

(i) If effects of rotational vibrations anharmonicity may be neglected (small u_v); which is presumably the case for l-menthol derivatives and nematic-like substances containing an optically active 2-methylbutyl group, $1/p\ dp/dT > 0$, corresponding to the simultaneous effects of the mechanisms described by Eqs. (13) and (25).

(ii) In the opposite case, i.e., large u_v, onto the above-described pitch increase with temperature an effect of anharmonic rotational vibrations (Eq. (29)) is superimposed. The expression for $\bar{\theta}_p(T, w)$ reads as

$$\bar{\theta}_p = \sum_i \left[\theta_{0i} + u_{vi} \frac{t}{S(t)} \right] L(t)\, S_R(T)\, w_i, \tag{37}$$

with $L(t)$ defined in Eq. (13).

As a consequence, a certain concentration w_x does exist where the sign inversion of $1/p\ dp/dT$ occurs. ($1/p\ dp/dT > 0$ for $w < w_x$, and vice versa). For cholesterol derivatives $w_x \sim 20\%$,[150] while the tygogenyn derivatives $w_x \leqslant 3\%$.[146,147] The corresponding u_v values for the tygogenyn derivatives are much higher ($\sim 5.10^{-2}$) than the values for the cholesterol derivatives ($\sim 1.10^{-2}$), which is quite understandable, keeping in mind the geometrical shape features of the molecules—the potential sources of anharmonism are much more obvious in the former case. Large u_v values lead, according to Eqs. (30, 37), to large helical twisting powers; correspondingly, relatively small ($\sim 10-12\%$) quantities of tygogenyn derivatives introduced into the nematic matrix allow to obtain selective reflection in the visible range.[146,149]

(iii) In the case of a smectogenic nematic matrix, another source of negative $1/p\ dp/dT$ appears; the picture in general is similar to that described in Section II,C,3. One must pay attention to the possibility of T_c being just below the crystallization point, with the smectic phase actually not formed, but an influence of pre-transitional phenomena upon the helical pitch clearly felt.

Induced systems with $1/p\ dp/dT$ in the absence of pre-transitional phenomena were reported in Ref.151. (Negative $p(T)$ dependence is necessary to compensate for a decrease of stiffness constants K_{ii} with temperature, ensuring temperature-independent threshold voltages; pre-transitional phenomena are to be avoided in order to keep viscosity at a sufficiently low level).[152] A more complicated case was studied in Refs. 153,154, where two dopants of opposite signs of HTP were introduced into a nematic matrix; the mixture obtained showed a behavior which was quite similar to the 'compensation' in mixtures of cholesterol derivatives.

Extensive studies are being carried out on the induced cholesteric systems, and the bulk of information is yet to be obtained. The central question is the relationship between the molecular structure and the values of helical twisting power. This problem is still largely unsolved, especially in the case of specific interactions between the dopant and the matrix molecules.

B. Systems with specific interactions

1. Nematic-cholesteric mixtures. The case of nematics mixed with mesogenic steroids forming a twisted nematic mesophase in the wide concentration range is of special interest due to the striking anomaly in $p^{-1}(w)$ dependences. There is still no generally accepted explanation of these properties, making nematic-cholesteric mixtures (NCM) a natural testing field for theories of helical twisting.

The anomaly in question was first reported in Refs. 155,156; a systematization of experimental data is presented in Ref. 157. It is illustrated by Figure 8—$p^{-1}(w)$ plots are strikingly non-linear. The non-linearity is most pronounced for cholesterol derivatives with shorter substituents in the 3β-position, e.g., for shorter alkyl chains. The 'extra' twisting is invariably left-handed, irrespective of whether the cholesterol derivative forms a left-handed or a right-handed mesophase by itself. There are no differences in behavior between nematics and chiral nematics.

The problem of NCM was treated by a number of researchers. A review of such papers was presented in Ref. 8; here we mention only some of the most representative.[158-160,137] No conclusive results were,

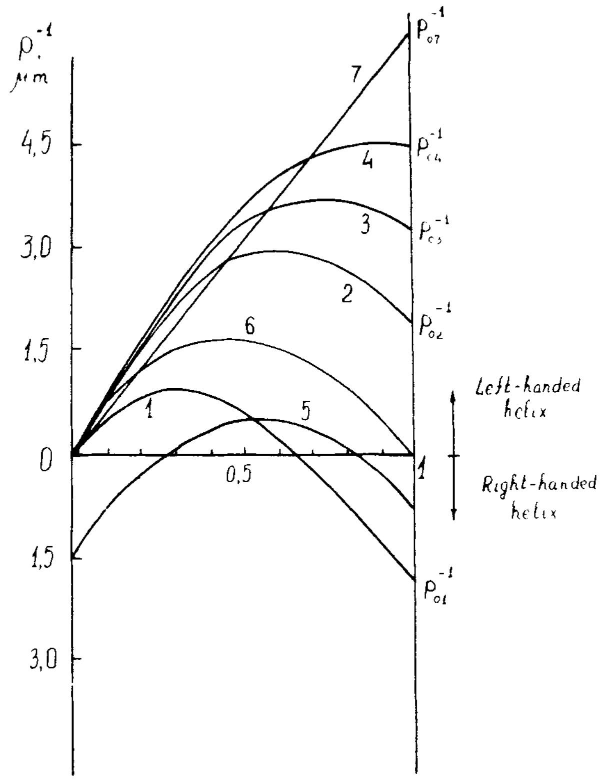

FIGURE 8 Typical inverse pitch vs. concentration dependences in the nematic-cholesteric mixtures: 1—4—nematics + cholesterol derivatives with different intrinsic pitches P_{0i}, 5—chiral nematic + cholesterol derivative, 6—nematic + compensated mixture of cholesterol derivatives, 7—nematic + chiral nematic of the similar structure.

however, obtained, and the nature of intermolecular forces causing such a deviation from the ideal behavior remained obscure.

Within the framework of the model presented in Section III,B,C the strange features of NCM have, however, a natural and rather simple explanation. When there are short-range translation and short-range rotational order in the system, steric factors and packing effects begin to play a decisive role. For example, the so-called 'angular' methyl groups of the steroidal ring may hinder rotational vibrations of the molecules of the nematic component situated in the adjacent quasi-nematic layers. Some mutual orientations may become energetically unfavourable due to the short-range repulsive forces. Thus, rotational vibrations of the nematic molecule with respect to the cholesteric one become anharmonic. The form of corresponding $V(\theta)$ curve is presented in Figure 5 (curve 5).

Approximating $R(\theta)$ by a step function

$$R(\theta) = \begin{cases} 1 \text{ for } \theta_r - \vartheta < \theta < \theta_r + \vartheta \\ 0 \text{ for other } \theta \end{cases} \tag{38}$$

and performing the relevant integrations in,[28] we can obtain the twist angle between the molecules of nematic and cholesteric θ_{ij} as function of temperature and molecular parameters; substituting it into Eq. (31) lead to model curves providing a good fit to the experimental data.[8,150,161] Similar results were obtained in Refs. 162,163, where the assumption of short-range translational order was replaced by a physically similar assumption of the intermolecular association between the molecules of different kind.

Thus, specific steric repulsions appear to be the only realistic reason of the $p^{-1}(w)$ anomaly in NCM. This, in turn increases our confidence in the models of the Figure 6 type where effect of short-range forces and short-range order is deliberately overestimated—for in the real cholesteric systems they, in fact, play a major role.

To be complete, one has to mention that mixtures of substituted cholesteryl benzoates show $p^{-1}(w)$ non-linearities[144] which can be ascribed to the same physical reasons as those in NCM, i.e., specific steric repulsions between aromatic and steroidal rings of neighboring molecules.

2. *Cholesterics with non-mesogenic dopants.* One more interesting type of cholesteric systems is a steroidal, non-steroidal or induced cholesteric to which small quantities of non-mesogenic nonchiral dopants (NMD) are added.

Introducing NMD into a cholesteric or nematic matrix has nearly no influence upon the orientational order parameter dependence on the reduced temperature $S(T/T_i)$, though the T_i values are changed significantly.[164] Thus, NMD effect upon cholesteric matrix is equivalent to the effect of increasing temperature. Due to the fact that helical twisting is determined primarily by T/T_i, and the role of the slowly changing with temperature $S_R(T)$ factor is a minor one in this context, we may apply similar descriptions for $p(w)$ and $p(T)$ dependences. The idea of temperature increase and introducing a NMD being equivalent was first stated in Ref. 165; quantitative description of $p(w, T)$ data in the systems cholesterols esters + NMD was presented in Refs. 143,164,166–168.

For the ideal system, at low NMD concentrations

$$p(w) - p(0) = T\frac{\partial p}{\partial T}w \tag{39}$$

Taking into account the possibility of specific interactions

$$\bar{\theta}_p(w) - \bar{\theta}_p = \left(\gamma T\frac{\partial\bar{\theta}_p}{\partial T} - \bar{\theta}_p + k_\theta\right)w - \left(\gamma T\frac{\partial\bar{\theta}_p}{\partial T} + 2k_\theta\right)\frac{w^2}{2} \tag{40}$$

An interesting result was reported in Refs. 168,169; k_θ are found to be of the same order of magnitude for cholesterol esters and, e.g., non-mesogenic alkanes of the same molecular length. Qualitatively, the effect consists in the prevailing role of helix untwisting due to the 'dilution' of the system and pitch changes due to the decreasing orientational order in the case of 'short' NMD molecules. For molecules with longer alkyl chain additional contribution to the left-handed twisting appear, quite similar to the same phenomenon in nematic-cholesteric mixtures.

Pronounced deviations from ideality occur in the systems where alcohols and other substances containing the OH-group are used as NMD. Presumed formation of the hydrogen bond between the OH-group and the —C=O group of the cholesterol esters[169,170] cause significant deviations of $\bar{\theta}_p(w)$ from its values according to Eq. (40).

Non-steroidal and induced cholesterics are especially interesting systems, as for their possible specific interactions with NMD; research work is going on in this direction.

V. CONCLUSION

To complete our review, we shall try to anticipate readers' criticism and to summarize briefly some aspects of cholesterics which, due to the lack of space, were not considered in detail.

(i) Synthesis of new chiral substances. To mention but some of the papers which appeared after the publication of our earlier review[9] one may refer to Refs. 120,171,172. New classes of effective chiral dopants presented in these papers offer many possibilities of future research and a basis for understanding of the molecular structure effects upon helical twisting. An interesting group of chiral dopants—substituted arylidene-*l*-menthones—was presented in Ref. 173. These substances have a pronounced basic plane (providing high S_R) and chiral elements stretching out of the basic plane and corresponding would-be symmetry planes (large *xyz*). In a complete accord with Eq. (23), (25), helical twisting power values for arylidene-*l*-menthones are significantly higher than for *l*-menthol derivatives of a comparable anisometry.

(ii) In our review we did not mention chiral smectics—C*, for we have decided to confine ourselves to the helically twisted nematics. Taking, however, into consideration a paradoxical fact (mentioned in Section III, B) that for a specialist in statistical physics chiral smectics are simpler objects than cholesterics, we can say that cholesterics may be considered as chiral smectics—C with the tilt angle close to 90° and with the long-range translational order of the smectic layers transformed into the short-range translational order in the adjacent quasi-nematic layers. One may, consequently, make an attempt to formulate a molecular theory of chiral smectics—C, starting from the model of cholesterics (Section III,B) and introducing the tilt angle as an input parameter.[174] This approach may be useful, e.g., for treatment of chiral smectic systems with specific interactions.

(iii) We did not mention the vast field of electrooptics, mainly due to our feeling that at the present moment the highway of further development is not a search for some new electrooptic effects, but obtaining new cholesteric materials with improved characteristics. For this purpose, however, a new stage in our understanding of cholesteric mesophase is needed.

(iv) Speaking about practical uses of CLC, we want to underline that the main idea of this review was the idea of close relationship between cholesterics of different chemical classes. This close relationship is manifested in orientational order, viscous properties, nature of helical twisting and many other aspects. Therefore, numerous ways of practical application, outlined in Refs. 6,7 for steroidal CLC, can and definitely will be extended by the new nonsteroidal and induced cholesteric systems to be synthesized in future. These systems, combining selective reflection in the visible range with a set of improved physical and physico-chemical characteristics, will provide a basis for the imminent expansion of the field of cholesterics.

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References

1. F. Reinitzer, *Monatsh. Chem.*, **9**, 421 (1888).
2. Prof. Planer, *Ann. Chem.*, **118**, 25 (1861).
3. J. Fergason, *Sci. Am.*, **211**, 77 (1964).
4. J. L. Fergason, *Mol. Cryst.*, **1**, 293 (1966).
5. G. W. Gray, *J. Chem. Soc.*, p. 3733 (1956).
6. G. Meier, E. Sackmann and J. G. Grabmaier, "Applications of liquid crystals," Springer, Berlin, e.a., 1975.
7. P. L. Carroll, "Cholesteric liquid crystals: their technology and applications," Ovum Ltd., London, 1973.
8. G. S. Chilaya and L. N. Lisetski, *Usp. Fiz. Nauk*, **134**, 289 (1981).
9. G. Chilaya, *Rev. Phys. Appliq.*, **16**, 193 (1981).
10. J. Billard, *J. Chim. Phys. et Phys.-Chem. Biol.*, **80**, 127 (1983).
11. J. Billard, *Compt. Rend. Acad. Sci.*, **292**, 881 (1981).
12. N. A. P. Vaz, Z. Yaniv and J. W. Doane, *Mol. Cryst. Liquid Cryst. Lett.*, **92**, 75 (1983).
13. N. H. Tinh, C. Destrade, J. Malthete and J. Jacques, *Mol. Cryst. Liquid Cryst.*, **72**, 195 (1982).
14. P. Pollmann and B. Wiege, *Mol. Cryst. Liquid Cryst. Lett.*, **102**, 119 (1984).
15. G. S. Chilaya, C. Destrade, Z. M. Elashvili, S. P. Ivchenko, L. N. Lisetski, N. H. Tinh and K. D. Vinokur, *J. de Phys.* (*Lett.*), **46**, L-75 (1985).
16. P. L. Finn and P. E. Cladis, *Mol. Cryst. Liquid Cryst.*, **84**, 159 (1982).
17. P. P. Crooker, *Mol. Cryst. Liquid Cryst.*, **98**, 31 (1983).
18. P. J. Collings, T. J. McKee and J. R. McColl, *J. Chem. Phys.*, **65**, 3520 (1976).
19. Z. Luz, R. Poupko and E. T. Samulski, *J. Chem. Phys.*, **74**, 5825 (1981).
20. N. C. Shivaprakash and J. Shashidhara Prasad, *J. Chem. Phys.*, **76**, 866 (1982).
21. S. G. Carr, S. K. Khoo, G. R. Luckhurst and H. J. Smith, *Mol. Cryst. Liquid Cryst.*, **45**, 161 (1978).
22. L. G. P. Dalmolen, E. Egberts and W. H. de Jeu, *J. de Phys.*, **45**, 129 (1984).
23. N. M. Chao, K. C. Chu and Y. R. Shen, *Mol. Cryst. Liquid Cryst.*, **67**, 261 (1981).
24. E. H. Korte, *Mol. Cryst. Liquid Cryst.*, **44**, 151 (1978).
25. D. W. Berreman and T. J. Scheffer, *Phys. Rev.* **A5**, 1397 (1972).
26. A. V. Tolmachev, V. G. Tischchenko and L. N. Lisetski, *Fiz. Tverd. Tela*, **19**, 1886 (1977).
27. P. Adamski, L. A. Dylik-Gromiec and M. Wojcechowski, *Mol. Cryst. Liq. Cryst.*, **75**, 33 (1981).
28. E. M. Averyanov and V. F. Shabanov, *Kristallografia*, **24**, 184 (1979).
29. R. K. Sarna, V. G. Bhide and B. Bahadur, *Mol. Cryst. Liquid Cryst.*, **88**, 65 (1982).
30. R. J. A. Tough and M. J. Bradshaw, *J. de Phys.*, **44**, 447 (1983).
31. N. C. Shivaprakash, M. M. M. Abdoh, Srinivasa and J. Shashidhara Prasad, *Mol. Cryst. Liquid Cryst.*, **80**, 179 (1982).
32. N. L. Kramarenko, Yu. K. Yarovoy, N. S. Novikova, A. I. Galatina and L. N. Lisetski, *Ukr. Fiz. Zhurn.*, **27**, 1647 (1982).
33. G. S. Chilaya, S. N. Aronishidze, Z. M. Elashvili, M. N. Kushnirenko and M. I. Brodzeli, Abstracts of the 1st LC Conf. of Sozialist Countr., Halle, DDR, 1976, p. 61.

34. G. S. Chilaya, S. N. Aronishidze, Z. M. Elashvili, M. N. Kushnirenko and M. I. Brodzeli, *Soobshch. Akad. Nauk GSSR*, **84**, 81 (1976).
35. G. Pelzl, *Z. Chem.*, **17**, 264 (1976).
36. Y. R. Lin-Liu and M. A. Lee, *Phys. Re. A.*, **28**, 2580 (1983).
37. J. W. Doane, *Israel J. Chem.*, **23**, 323 (1983).
38. F. P. Price and C. S. Bak, *Mol. Cryst. Liquid Cryst.*, **29**, 225 (1975).
39. T. C. Lubensky, *J. Phys. Chem. Sol.*, **34**, 365 (1973).
40. N. H. Tinh, C. Destrade and H. Gasparoux, *Phys. Lett. A*, **72**, 251 (1977).
41. C. Destrade, N. H. Tinh, J. Malthete and J. Jacques, *Phys. Lett.* A, **79**, 189 (1980).
42. M. V. Kurik and A. A. Rudenko, *Ukr. Fiz. Zhurn.*, **24**, 31 (1979).
43. M. V. Hurik and O. D. Lavrentovich, *Mol. Cryst. Liquid Cryst. Lett.*, **72**, 239 (1982).
44. P. E. Cladis and M. Kleman, *Mol. Cryst.*, **16**, 1 (1972).
45. G. S. Chilaya, S. N. Aronishidze, K. D. Vinokur, S. P. Ivchenko and M. I. Brodzeli, *Acta. Phys. Pol.*, **A54**, 651 (1978).
46. M. T. Press and A. S. Arrot, *J. de Phys.*, **37**, 387 (1976).
47. A. V. Tolmachev and V. G. Tishchenko, *Zhurn. Tekhn. Fiz.*, **52**, 121 (1982).
48. E. P. Sukhenko, V. A. Kizel and V. G. Tishchenko, *Zh. Eksp. and Teor. Fiz.*, **77**, 209 (1979).
49. A. V. Tolmachev, *Kristallografia*, **26**, 782 (1981).
50. F. J. Kahn, *Phys. Rev. Lett.*, **24**, 209 (1970).
51. R. Cano, *Bull. Soc. Miner. Cryst.*, **91**, 20 (1968).
52. P. Kassubek and G. Meier, *Mol. Cryst. Liquid Cryst.*, **8**, 305 (1969).
53. H. Finkelmann and H. Stegemeyer, *Ber. Bunsenges, phys. Chem.*, **82**, 1302 (1978).
54. H. Kozawaguchi and M. Wada, *Mol. Cryst. Liquid Cryst.*, **45**, 55 (1978).
55. P. Seuron and G. Solladie, *Mol. Cryst. Liquid Cryst. Lett.*, **56**, 1 (1979).
56. P. R. Gerber, *Z. Naturforsch.*, **35a**, 619 (1980).
57. R. S. Pindak, C. C. Huang and J. T. Ho, *Phys. Rev. Lett.*, **32**, 43 (1974).
58. R. Pindak and J. T. Ho, *Phys. Lett.*, **59A**, 277 (1976).
59. P. G. de Gennes, *Solid State Comm.*, **10**, 753 (1972).
60. S. H. Chen and J. J. Wu, *Mol. Cryst. Liquid Cryst.*, **87**, 197 (1982).
61. C. C. Huang, R. S. Pindak and J. T. Ho, *Phys. Lett.*, **A47**, 263 (1974).
62. P. B. Wigman and V. M. Fiyov, *Zh. Eksp. and Teor. Fiz.*, **69**, 1466 (1975).
63. R. Alben, *Mol. Cryst. Liquid Cryst.*, **20**, 231 (1973).
64. A. V. Tolmachev, V. G. Tishchenko and L. N. Lisetski, *Zh. Eksp. and Teor. Fiz.*, **75**, 663 (1978).
65. R. D. Ennulat, L. E. Garn and J. D. White, *Mol. Cryst. Liquid Cryst.*, **26**, 245 (1974).
66. K. D. Vinokur, S. P. Ivchenko and G. S. Chilaya, *Zhurn. Tekhn. Fiz.*, **49**, 1565 (1979).
67. K. C. Lim and J. T. Ho, *Mol. Cryst. Liquid Cryst.*, **67**, 199 (1981).
68. F. Pakush and P. Pollmann, *Mol. Cryst. Liquid Cryst.*, **88**, 255 (1982).
69. T. Harada and P. Crooker, *Mol. Cryst. Liquid Cryst.*, **30**, 79 (1975).
70. P. M. Agócs and L. Bata, *Mol. Cryst. Liquid Cryst.*, **107**, 391 (1984).
71. S. Pirkl and J. Myl in "Advances in Liquid Crystal Research and Applications," Ed. L. Bata, Pergamon Press, Oxford-Akadé-miai Kiadó, Budapest, 1980, p. 657.
72. I. Miyata and J. Kishimoto, *Chem. Farm. Bull.*, **28**, 619 (1980).
73. W. Helfrich, *Phys. Rev. Lett.*, **23**, 373 (1969).
74. W. J. A. Goossens, *Phys. Lett.*, **85A**, 231 (1981).
75. S. Candau, P. Martinoty and F. Debeauvais, *Compt. Rend. Acad. Sci.*, **B277**, 769 (1973).
76. P. Pollmann, *Z. Naturforsch.*, **27a**, 719 (1972).

77. Z. M. Elashvili, M. D. Mkhatvrishvili, T. S. Piliashvili, G. S. Chilaya and K. G. Japaridze, *J. de Phys. Coll.*, **40**, C3-22.
78. C. S. Chilaya, Z. M. Elashvili, L. N. Lisetski, K. D. Vinokur, M. D. Mkhatvrishvili, "The Tenth International Liquid Crystal Conference," Abstracts, York, England, 1984, C 61. C. S. Chilaya, Z. M. Elashvili, L. N. Lisetski, M. D. Mkhatvrishvili, K. D. Vinokur, *Mol. Cryst. Liq. Cryst.*, **124**, 333 (1985).
79. B. Zoltowski and A. Lipinski, "Fifth Socialist Countries Liquid Crystal Conference," v. 1, pt. II, Odessa, 1983, p. 219.
80. L. M. Blinov, "Electrooptical and Magnetooptical Properties of Liquid Crystals," J. Wiley & Sons Ltd., Chichester e.a., 1983.
81. V. G. Chigrinov, *Kristallografia*, **27**, 404 (1982).
82. P. N. Keating, *Mol. Cryst. Liquid Cryst.*, **8**, 315 (1969).
83. B. Böttcher, *Chem. Ztg.*, **96**, 214 (1972).
84. W. J. A. Goossens, *Phys. Lett.*, **31A**, 413 (1970).
85. W. J. A. Goossens, *Mol. Cryst. Liquid Cryst.*, **12**, 237 (1971).
86. A. Wulf, *J. Chem. Phys.*, **59**, 1487 (1973).
87. L. N. Lisetski, *Fiz. Tverd. Tela*, **24**, 3361 (1982).
88. H. Stegemeyer, *Ber. Bunsenges. phys. Chem.*, **78**, 860 (1974).
89. H. Stegemeyer, H. Finkelmann, *Naturwissenschaften*, **62**, 436 (1975).
90. Y. R. Lin-Liu, Y. M. Shih, C. W. Woo and H. T. Tan, *Phys. Rev. A.*, **14**, 445 (1976).
91. Y. R. Lin-Liu, Y. M. Shih and C. W. Woo, *Phys. Rev. A*, **15**, 2550 (1977).
92. B. W. van der Meer, G. Vertogen, A. J. Dekker and J. G. J. Ypma, *J. Chem. Phys.*, **65**, 3935 (1976).
93. B. W. van der Meer, Thesis, Graningen, 1979.
94. H. Kimura, M. Hoshino and H. Nakano, *J. de Phys. Coll.*, **40**, C3-229 (1979).
95. W. J. Goossens, *J. de Phys. Coll.*, **40**, C3-158 (1979).
96. H. Schröder, "Liquid Crystals of One- and Two-Dimensional Order," Berlin e.a., 1980.
97. B. W. van der Meer and G. Vertogen, *Phys. Lett.*, **59A**, 279 (1976).
98. A. P. Zakhlevnych and M. I. Shliomis, *Zh. Eksp. and Teor. Fiz.*, **86**, 1309 (1984).
99. R. M. Hornreich and S. Shtrikman, *Phys. Rev.*, **A29**, 3444 (1984–).
100. Z. Yaniv, N. A. P. Vaz, G. Cudicino and J. W. Doane, *Phys. Rev. Lett.*, **47**, 46 (1981).
101. P. M. L. O. Scholte and G. Vertogen, *Physica*, **113A**, 587 (1982).
102. V. B. Magalinski and N. A. Glushkov, *Kristallografia*, **25**, 1104 (1980).
103. Vl. K. Pershin, *Zhurn. Tekhn. Fiz.*, **54**, 1833 (1984).
104. M. A. Osipov and S. A. Pikin, *Mol. Cryst. Liquid Cryst.*, **103**, 57 (1983).
105. M. J. Bradshaw, E. P. Raynes, I. Fedak and A. J. Leadbetter, *J. de Phys.*, **45**, 157 (1984).
106. H. Kozawaguchi and M. Wada, *Mol. Cryst. Liquid Cryst.*, **44**, 97 (1978).
107. K. C. Lim and J. T. Ho, *Phys. Rev. Lett.*, **40**, 944 (1978).
108. M. F. Achard, G. Sigaud and F. Hardouin, "Liquid Crystals of One- and Two-Dimensional Order," Springer, Berlin e.a., 1980, p. 149.
109. C. Destrade, H. Gasparoux and F. Guillon, *Mol. Cryst. Liquid Cryst.*, **40**, 163 (1977).
110. C. Clément and J. C. Goulin, *Compt. Rend. Acad. Sci.*, **C286**, 597 (1978).
111. V. G. Tishchenko and R. M. Cherkashina, "Kholestericheskie Zhidkie Kristally," Novosibirsk, 1976, p. 26.
112. J. W. Emsley, R. Hashim, G. R. Luckhurst, G. N. Rumbles and F. R. Viloria, *Mol. Phys.*, **49**, 1321 (1983).
113. L. N. Lisetski, *Ukr. Fiz. Zhurn.*, **27**, 1321 (1982).
114. A. L. Tsykalo, E. E. Nyankina and A. D. Bagmet, *Zhurn. Tekhn. Fiz.*, **50**, 2365 (1980).
115. B. W. van der Meer, F. Postma, A. J. Dekker and W. H. de Jeu, *Mol. Phys.*, **45**, 1227 (1982).

116. V. K. Pershin and S. A. Skopinov, *Kristallografia*, **26**, 178 (1981).
117. A. A. Gerasimov, *Ukr. Fiz. Zhurn.*, **27**, 1314 (1982).
118. L. N. Lisetski and V. G. Tishchenko, *Fiz. Tverd. Tela.*, **19**, 280 (1977).
119. H. Schröder, *Ber. Bunsenges Phys. Chem.*, **78**, 855 (1974).
120. G. Heppke, F. Oestreicher and G. Scherowsky, *Z. Naturforsch.*, **37a**, 1176 (1982).
121. G. W. Gray and D. G. McDonnel, *Mol. Cryst. Liquid Cryst.*, **34**, 211 (1977).
122. B. W. van der Meer and G. Vertogen, *Z. Naturforsch.*, **34a**, 1359 (1979).
123. L. N. Lisetski, A. V. Tolmachev and V. G. Tishchenko, *Pis'ma v Zh. Eksp. and Teor. Fiz.*, **23**, 205 (1978).
124. A. I. Galatina, L. G. Derkach, N. L. Kramarenko, O. M. Tsygulyova and N. M. Shkabara, *Kristallografia*, **29**, 1114 (1984).
125. A. A. Gerasimov and L. N. Lisetski, *Fiz. Teverd. Tela.*, **25**, 872 (1983).
126. M. Nakagawa and T. Akahane, *J. Phys. Soc. Japan*, **52**, 399, 2659 (1983).
127. M. A. Cotter and D. C. Wacker, *Phys. Rev. A*, **18**, 2669 (1978).
128. S. R. Lunt and G. R. van Hecke, *Mol. Cryst. Liquid Cryst.*, **111**, 1 (1984).
129. P. Palffy-Muhoray, D. A. Dunmur and A. Price, *Chem. Phys. Lett.*, **93**, 572 (1982).
130. J. E. Adams, W. E. Haas and J. J. Wisocki, *Bull. Amer. Phys. Soc.*, **14**, 6 (1969).
131. J. E. Adams and W. E. L. Haas, *Mol. Cryst. Liquid Cryst.*, **15**, 27 (1971).
132. D. E. Martire, G. A. Oweimreen, G. I. Agren, S. G. Ryan and H. T. Peterson, *J. Chem. Phys.*, **64**, 1456 (1976).
133. R. L. Humphries and G. R. Luckhurst, *Chem. Phys. Lett.*, **23**, 567 (1973).
134. L. Lei and H. Yun, *Phys. Lett.*, **89A**, 287 (1982).
135. T. Akahane and T. Tako, *Mol. Cryst. Liquid Cryst.*, **70**, 57 (1981).
136. S.-H. Chen and L. S. Chou, *Mol. Cryst. Liquid Cryst.*, **67**, 221 (1981).
137. C. S. Bak and M. M. Labes, *J. Chem. Phys.*, **62**, 3066 (1975); 63, 805 (1975).
138. L. B. Leder, *J. Chem. Phys.*, **54**, 4671 (1971).
139. H. Baessler and M. M. Labes, *J. Chem. Phys.*, **52**, 631 (1970).
140. L. B. Leder, *J. Chem. Phys.*, **58**, 1118 (1973).
141. M. Yu. Rubtsova, Thesis, Moscow, 1980.
142. S. H. Chen and L. S. Chou, *Mol. Cryst. Liquid Cryst.*, **40**, 223 (1977).
143. T. P. Kudryashova, L. N. Lisetski and I. G. Chistyakov, *Kristallografia*, **24**, 998 (1979).
144. I. I. Gorina, M. Yu. Rubtsova and I. G. Chistyakov, *J. de Phys. Coll.*, **40**, C3-229 (1979).
145. M. Tsukamoto, T. Ohtsuka, K. Mormoto and Y. Murakami, *Jap. J. Appl. Phys.*, **14**, 1307 (1975).
146. G. S. Chilaya, Z. M. Elashvili, L. N. Lisetski, T. S. Piliashvili and K. D. Vinokur, *Mol. Cryst. Liquid Cryst.*, **74**, 261 (1981).
147. G. S. Chilaya, Z. M. Elashvili, T. S. Piliashvili, K. D. Vinokur and L. N. Lisetski, "Advances in Liquid Crystal Research and Applications," Ed. L. Bata, Pergamon Press, Oxford-Akadémiai Kiadó, Budapest, 1980, p. 1185.
148. G. S. Chilaya, Z. M. Elashvili, S. P. Ivchenko, L. N. Lisetski and K. D. Vinokur, ibid., p. 1191.
149. G. S. Chilaya, Z. M. Elashvili, S. P. Ivchenko and K. D. Vinokur, *Mol. Cryst. Liquid Cryst.*, **106**, 67 (1984).
150. L. N. Lisetski, G. S. Chilaya, K. D. Vinokur, V. G. Tischenko and V. D. Panikarskaya, *Ukr. Fiz. Zhurn.*, **24**, 1582 (1979).
151. N. L. Kramarenko, L. N. Lisetski and L. G. Derkach, *Fiz. Tverd. Tela*, **24**, 3283 (1982).
152. A. Göbl-Wunsch, G. Heppke and F. Oestreicher, *J. de Phys.*, **40**, 773 (1979).
153. A. Göbl-Wunsch and G. Heppke, *Z. Naturforsch.*, **34a**, 594 (1979).
154. K. D. Vinokur, G. S. Chilaya and G. Solladie, "The Fourth International Liquid Crystal Conference of Socialist Countries," Tbilisi, 1981, p. 407.
155. H. Finkelmann and H. Stegemeyer, *Z. Naturforsch.*, **28a**, 799 (1973).
156. H. Finkelmann and H. Stegemeyer, *Z. Naturforsch.*, **28a**, 1046 (1973).

157. J. Adams and W. Haas, *Mol. Cryst. Liquid Cryst.*, **30**, 1 (1975).
158. H. Hanson, A. J. Dekker and F. van der Woude, *J. Chem. Phys.*, **62**, 1941 (1975).
159. H. Kozawaguchi and M. Wada, *Jap. J. Appl. Phys.*, **14**, 651, 657 (1975).
160. E. I. Katz, *Zh. Eksp. and Teor. Fiz.*, **74**, 2320 (1978).
161. L. N. Lisetski, B. L. Timan, V. G. Tishchenko and O. D. Kolotiy, *Ukr. Fiz. Zhurn.*, **23**, 94 (1978).
162. T. P. Kudryashova, L. N. Lisetski and I. G. Chistyakov, *Zhurn. Fiz. Khim.*, **52**, 2194 (1978).
163. I. G. Chistyakov, T. P. Kudryashova and L. N. Lisetski, *Izv. Akad. Nauk SSSR, ser. Khim.*, p. 1731 (1979).
164. P. Adamski, A. Holwek, A. Dylik-Gromiec and M. Wojciechowski, *Mol. Cryst. Liquid Cryst.*, **60**, 53 (1980).
165. J. Voss and E. Sackmann, *Z. Naturforsch.*, **28a**, 1496 (1973).
166. T. P. Kudryashova and L. N. Lisetski, *Ukr. Fiz. Zhurn.*, **23**, 246 (1978).
167. G. S. Chilaya, L. N. Lisetski and T. P. Kudryashova, "Third Liquid Crystal Conference," Budapest, 1979, p. D-6.
168. L. N. Lisetski and T. P. Antonyan, *Zhurn. Fiz. Khim.*, **54**, 1147 (1980).
169. V. D. Panikarskaya, V. G. Tishchenko and L. N. Lisetski, *Zhurn. Fiz. Khim.*, **54**, 1147 (1980).
170. D. G. Willey and D. E. Martire, *Mol. Cryst. Liquid Cryst.*, **18**, 55 (1972).
171. G. Gottarelli, M. Hibert, B. Samori, G. Solladie, G. P. Spada and R. Zimmermann, *J. Am. Chem. Soc.*, **105**, 7318 (1983).
172. G. Gottarelli, P. Mariani, G. P. Spada, B. Samori, A. Forni, G. Solladie and M. Hibert, *Tetrahedron*, **39**, 1337 (1983).
173. L. A. Kutulya, I. B. Nemchyonok, A. V. Tolmachev and V. G. Tishchenko, "Fifth Liquid Crystal Conference of Socialist Countries," v. I, pt. II, Odessa, 1983, p. 12.
174. L. M. Blinov and L. A. Beresnev, *Usp. Fiz. Nauk*, **134**, 391 (1984).