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Thermotropic Liquid Crystals and Their Applications

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The structure and the physical and physicochemical properties are discussed, with special attention paid to the relation between the chemical structure and the properties of the mesogens. The influence of external factors on liquid-crystalline phases is examined. Various fields of application of liquid crystals are reported, and requirements to be met by such materials are formulated. A list of 210 references is included.

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I. INTRODUCTION

Many synthetic organic compounds are potentially thermotropic liquid crystals[1]: i.e. over a certain temperature range, on passing into the liquid state, they retain the orientational— and in certain directions sometimes also the translational— long-range order in the disposition of molecules characteristic of crystals. By the end of 1973 more than 5000 organic and organometallic compounds having mesomorphic (liquid-crystalline) properties had been recorded[2], and their number has continually increased. The number of publications on liquid crystals has also grown rapidly during recent years. Thus, according to the publishers LOCUS, about 180 papers in this field appeared during 1968, but in 1973 this had already reached 700. During 1975 about 900 papers and patents were covered in the new journal *Liquid Crystals Abstracts*. Such intensifying interest in liquid crystals is not accidental: just recently the use of thermotropic liquid crystals has made it possible to observe visually changes in temperature[3] of 0.01-0.001 deg, and liquid-crystalline indicators, requiring hardly any energy, have enabled electronic wrist-watches to be placed on the market with an accuracy of a few seconds in a year, as well as pocket electronic calculators. Every year new effects are discovered in liquid crystals, promising great possibilities in science and technology.

The present Review has the aim of acquainting a wide circle of chemists with the fundamental ideas developed during recent years in this interesting and practically important branch of the physics and chemistry of the condensed phase. The greatest attention is paid to the chemical and physical properties of thermotropic liquid crystals that are directly related to their application in

electro-optical devices, although related problems, concerning the fundamental properties of liquid crystals and other fields of application, will be touched on. For further details on individual aspects of thermotropic liquid crystals we may recommend Chistyakov's well known book[4], which gives detailed information on structure, monographs and reviews on the chemistry[5-9], physics, and theory[10,11], electro-optical phenomena[12,13], spectroscopy[14], and thermography[15]. A whole series of short surveys on the most diverse problems of the liquid-crystalline state has been published in a special issue of the *Berichte der Bunsengesellschaft für physikalische Chemie*[16].

II. STRUCTURE AND GENERAL PROPERTIES

1. Classification and Structure

It is now usual to divide thermotropic liquid crystals into three groups—nematic (filamentous), cholesteric, and smectic (soaplike)—although Friedel[17], one of the founders of the nomenclature, not without justification regarded cholesteric as a variety of nematic liquid crystals. The term "smectic" is not specific: this group comprises all liquid crystals that are neither nematic nor cholesteric.

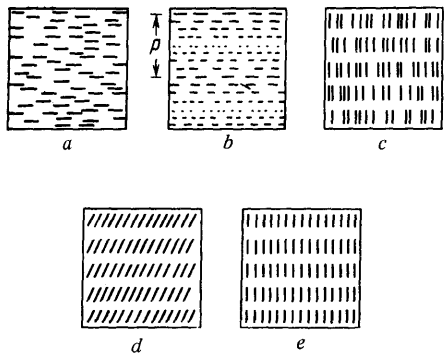


Figure 1. Types of thermotropic liquid crystals: *a*) nematic; *b*) cholesteric; *c*)–*e*) smectic; *P*) pitch of helix.

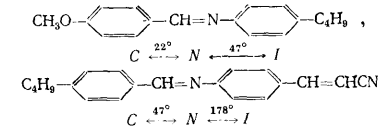
Fig. 1 shows diagrammatically, as rigid rods, the packing of molecules in the various types of liquid crystals.

Formation of the liquid-crystalline state can be observed visually from the melting of the crystalline substance in a capillary. Transition to a homogeneous turbid liquid is then evident, followed at a different temperature by transition from the liquid-crystalline state to an isotropic liquid. A better method is to observe by means of a polarising microscope the change in the phase state of specimens when heated (or cooled). Magnifications of 100–300 are mostly used. The patterns (textures) observed can be used to identify the type of mesophase. The latter method combined with differential scanning calorimetry provides reliable identification of phase transitions, their temperatures, and the heats of transition. Phase transition points can be determined also from the temperature variation of mechanical, optical, electrical, and other properties. The types of mesophases are most reliably determined by X-ray diffraction, but the textures of individual compounds or mixtures are also used for their identification.

Nematic liquid crystals

Only orientational order is present in nematic liquid crystals: i.e. the long axes of the molecules forming a unit structure are approximately parallel, with the molecules able to move freely in three directions and rotate about the long axis. A large volume appears as a strongly scattering turbid liquid; in unoriented layers exceeding 0.1 mm in thickness filamentous structures (disinclinations) can be observed under crossed Polaroids; in thinner layers a schlieren texture is evident with characteristic nodes or points of intersection of disinclinations[1]. Marbled, pseudoisotropic, and homogeneous textures are encountered, as well as the filamentous (schlieren) type†. On oriented specimens ("single crystals") homotropic (pseudoisotropic) and homogeneous (planar) textures can be observed according to the direction of the long axes of the molecules (perpendicular or parallel to the walls of the cuvette).

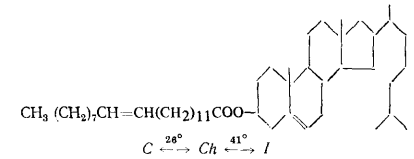
Examples of nematic liquid crystals are *p*-butyl-*p'*-methoxybenzylidenaniline[18] and *p*-*p'*-butylbenzylidenaminocinnamonitrile[19]



Here and subsequently *C*, *N*, and *I* denote respectively crystalline, nematic, and isotropic liquid phases, and the numerals above the arrows indicate the temperatures (°C) of the corresponding phase transitions.

Cholesteric liquid crystals

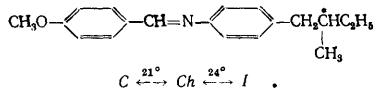
Cholesteric liquid crystals are formed by optically active molecules (until recently almost exclusively by esters of cholesterol). Their distinguishing feature is that the direction of the long axes of the molecules in each successive layer, consisting of molecules oriented in parallel and moving freely in two directions, forms a certain angle with the direction of the molecular axes in the preceding layer. A helix is thus formed, whose pitch *P* depends on the nature of the molecules and on external factors (Fig. 1*b*). Such twisting of the molecular axes leads to selective reflection of light, and the wavelength of maximum reflection changes with variation in the pitch of the helix, e.g. owing to slight temperature variation. The oriented layers form a confocal and planar (homogeneous) texture. An example that is colourless in the crystalline and isotropic liquid states, but changes colour (selective reflection) with change in temperature in the liquid-crystalline state, is cholesteryl erucate[20]



(*Ch* denotes the cholesteric phase).

†Detailed descriptions and photographs of textures will be found in e.g. Refs. 4 and 9.

Cholesteric liquid crystals include also the so-called "chiral" nematics, which have the structure of typical nematic liquid crystals but exhibit optical activity, e.g. *D*(or *L*)-*N*-*p'*-methoxybenzylidene-*p*-(2-methylbutyl)aniline [21]

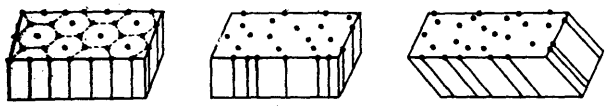


(IV)

$$C \xleftrightarrow{21^\circ} Ch \xleftrightarrow{24^\circ} I \ .$$

Smectic mesophase *A* (S_A)

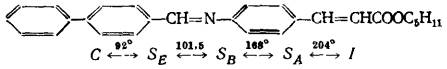
This form comprises layers moving freely relative to one another, whose surfaces are formed by the ends of parallel molecules normal to the surface (Fig. 2*a*). Within a layer the molecules have no translational order: they can move freely in two directions, and rotate about the long axis. The S_A mesophase is the least "organised" among smectic liquid crystals, and may apear in confocal (of fan or polygonal type), homogeneous, or pseudoisotropic textures or as stepped drops. An attempt [22] at a more detailed classification based on crystallographic properties included in particular a variety of the S_A mesophase in which the thickness of the layer was less than the length of a molecule, i.e. in which the molecules were inclined to the plane of the layer and rotated on a cone. The absence of correlation between molecular rotations in different layers leads to a uniaxial crystal as an average structure, in contrast to the biaxial inclined smectic *C*.



a *b* *c*

Figure 2. Structure of a layer of a smectic liquid crystal: *a*) S_A; *b*) S_B; *c*) S_C.

The S_A modification occurs at the highest temperature among smectic phases: when heated, it passes into a nematic or a cholesteric mesophase, or else into an isotropic liquid. An example of a liquid crystal of this type is pentyl *p*-*p'*-phenylbenzylidenaminocinnamate [23] at 168–204°C



(V)

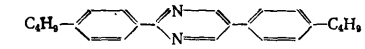
$$C \xleftrightarrow{92^\circ} S_E \xleftrightarrow{101.5} S_B \xleftrightarrow{168^\circ} S_A \xleftrightarrow{204^\circ} I$$

Smectic mesophase *B* (S_B)

This is a more ordered phase than S_A. The molecules in S_B layers, while remaining mutually parallel and normal to the plane of the layer, form a hexagonal type of packing [24] within the layer (Fig. 2*b*).

Smectic mesophase *C* (S_C)

This is analogous to the S_A mesophase, but the mutually parallel long axes of the molecules are inclined at an angle to the surfaces of the layer (Fig. 2*c*). Such a mesophase is formed e.g. by 2,5-di-*p*-butylphenylpyrazine [25]



(VI)

$$C \xleftrightarrow{161.9^\circ} S_C \xleftrightarrow{166.4^\circ} N \xleftrightarrow{181.9^\circ} I \ .$$

As with S_A, different varieties of S_C mesophases may exist, differing in the slope of the molecules (>40° for S_{C1} and ≤26° for S_{C2}), its temperature dependence, and also the ability to pass into other modifications [22].

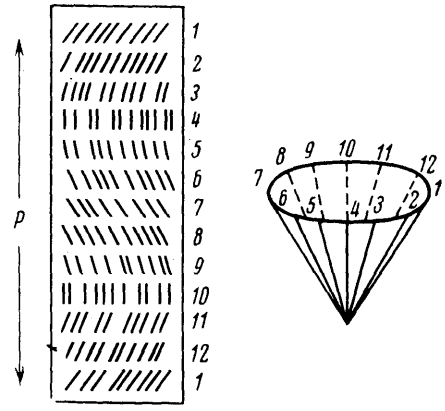
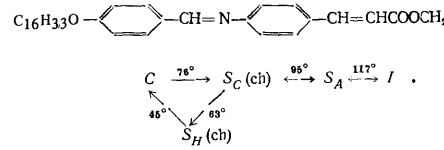


Figure 3. Structure of a ferroelectric *C* smectic, where *P* is the pitch of the "twist". Corresponding numerals on the cone and on the "section" through the layers correspond to the same angle of slope of the molecules.

Liquid-crystalline compounds exhibiting optical activity, e.g. *D*(or *L*)-2-methylbutyl *p*-*p'*-hexadecyloxybenzylidenaminocinnamate [26], are able to form a chiral *C* smectic mesophase S_C(ch), in which each successive layer of molecules is turned to a certain angle relative to the preceding layer, so that a twisted structure of pitch *P* is formed (Fig. 3), which with a definite orientation of molecular dipoles possesses ferroelectric properties [26], e.g.



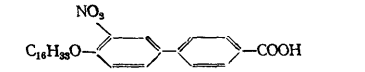
(VII)

$$C \xrightarrow{76^\circ} S_C(ch) \xleftrightarrow{95^\circ} S_A \xleftrightarrow{117^\circ} I \ .$$

$$S_C(ch) \xleftarrow{45^\circ} \quad \xrightarrow{63^\circ} S_H(ch)$$

Smectic mesophase *D* (S_D)

This mesophase is optically isotropic. X-Ray diffraction reveals no layer structure, but indicates a quasi-cubic lattice. Smectic liquid crystals of this type have been found with only a few compounds, e.g. 4'-hexadecyloxy-3'-nitrobiphenyl-4-carboxylic acid [27]



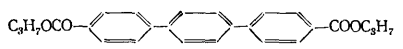
(VIII)

$$C \xleftrightarrow{126.8^\circ} S_C \xleftrightarrow{171.0^\circ} S_D \xleftrightarrow{197.2^\circ} S_A \xleftrightarrow{201.9^\circ} I \ .$$

The S_D mesophase can exhibit not only an isotropic but also a mosaic texture [1].

Smectic mesophase *E* (S_E)

The degree of three-dimensional order is extremely high. The molecules in the layers form an orthorhombic lattice [28,29], from which free rotation about the long axis is absent. The S_E mesophase may appear in mosaic and pseudoisotropic textures. Besides the above example (V), a detailed study has been made of the S_E mesophase of dipropyl *p*-terphenyl-4,4″-dicarboxylate [28]

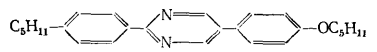


(IX)

$$C \xrightarrow{122.0^\circ} S_E \xrightarrow{137.1^\circ} S \xrightarrow{239.2^\circ} I .$$

Smectic mesophases *F* and *G* (S_F and S_G)

These mesophases have been studied very little. They both have a layer structure, with an ordered arrangement of molecules in the S_G layers. Schlieren and disrupted confocal textures have been observed for S_F, and S_G exhibits a mosaic texture. An example of smectic liquid crystals having both types of mesophase is 5-*p*-pentyloxyphenyl-2-*p*′-pentylphenylpyrimidine [30]



(X)

$$C \xrightarrow{79^\circ} S_G \xrightarrow{103^\circ} S_F \xrightarrow{114^\circ} S_C \xrightarrow{144^\circ} S_A \xrightarrow{210^\circ} I .$$

Smectic mesophase *H* (S_H)

This is analogous to the S_B mesophase, but the long axes of the molecules are inclined at an angle to the planes of the layer. As with the S_C mesophase an S_H mesophase formed by optically active molecules has a chiral structure S_H(ch) (VII), capable of spontaneous polarisation under the influence of external factors [23].

Plastic crystals

Plastic crystals constitute a special class of mesophase, not included among liquid crystals but sometimes met in the search for liquid-crystalline compounds. They were first characterised by Timmermans [31] in 1935. The molecules forming a plastic crystal were located permanently at the points of a cubic [32] (more rarely a hexagonal) lattice, but are orientationally disordered, with consequent isotropy of the optical properties, so that this type of mesophase was for a long time overlooked by research workers, who used a polarising microscope to define a mesophase. Several plastic crystals (e.g. perfluorocyclohexane) flow under their own weight, but most of them are less plastic, although they can be cut with a knife or extruded through small orifices. A plastic mesophase is formed by several compounds—tetrahedral (tetrachloromethane, silicon tetrafluoride, neopentane), octahedral (tetramethylbutane, hexabromoethane, pivalic acid), cyclic (cyclobutane, cycloheptatriene), bridged (camphor, borneol, tricyclo[2,2,2,2]decane) [33]—as well as several "classical" smectic liquid crystals, e.g. 4′-hexadecyloxy-3′-nitrobiphenyl-4-carboxylic acid [27].

In spite of the considerable number of studies on the structure and the interconversion of liquid crystals, these problems are still far from a final solution; systematic investigations on the typing of smectic liquid crystals have been undertaken only during recent years [34]. New phenomena are continually being discovered, requiring detailed investigations, e.g. the observation by Vainshtein, Chistyakov, and their coworkers that a smectic mesophase is formed when nematic liquid crystals are mixed [35].

2. Molecular–Statistical Description of the Liquid-crystalline State

The statistical distribution of molecules among orientations is described quantitatively by a series of parameters, the most important of which is that of orientational order (or degree of ordering)

$$S = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle, \qquad (1)$$

introduced by Tsvetkov [36], where θ is the angle between the axis of an individual molecule in a liquid crystal and the prepared direction of the whole ensemble, and averaging is made over the whole ensemble of molecules (thermal mean). The preferred direction coincides with the optical axis of the liquid single crystal (for nematic liquid crystals, *A* smectics, or a thin layer of a cholesteric liquid crystal) or else with one of the optical axes (sloping smectics *C* and *H*). According to definition $S = 1$ for solid crystals in which the molecules are arranged in parallel, and $S = 0$ for an isotropic liquid phase. In a liquid crystal $0 < S < 1$, and *S* decreases with rise in temperature, as the isotropic phase is approached. The value of the parameter *S* is that it can easily be determined experimentally [37] (from diamagnetic measurements, dichroism, nuclear magnetic resonance spectra, etc.).

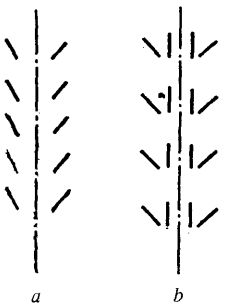


Figure 4. Hypothetical distribution of molecules with preservation of cylindrical symmetry and the same parameter *S*: *a*) dispersion absent; *b*) dispersion takes place.

A more complete statistical description of the molecular distribution is obtained by introducing also the dispersion *D*—a function of $\cos^4\theta$—and additional parameters defined in terms of higher even powers $\cos^n\theta$. The meaning of the parameter *D* can easily be understood by comparing two cylindrical distributions of molecules having the same parameter *S* (Fig. 4). The mean value of $\cos^2\theta$ is the same, but in one case the scatter (dispersion) of the molecules varies relative to the "mean" position shown in Fig. 4*a*.

The question as to which properties molecules should possess for long-range orientational order to be established in a substance occupies a central position in the theory of the liquid-crystalline state. Many attempts have

been made to derive thermodynamic characteristics of liquid crystals from the electronic structure of the molecules. A classification has been given [38] for the levels at which the structure of liquid crystals has been investigated: (*a*) at the simplest level molecules are regarded as rigid rods; (*b*) at the second level molecules are regarded as flat plates, rods with dipoles at an angle to them, or combinations of these two forms; and (*c*) the actual structure of the molecules is considered at the third level. Even at level (*a*) many questions remain unsettled, in particular the evaluation of S for nematic and smectic liquid crystals, the angles of inclination of molecules in smectic C, the degree of bonding detween smectic layers, etc. The main problems at level (*b*) are concerned with the ability of molecules to rotate, the ordering of dipoles, etc. Level (*c*) involves the investigation mainly of the conformations of alkyl chains, the orientation of some molecular residues relative to others, internal rotations, etc.

The inadequacy of regarding molecules as rigid rods follows from the extremely graphic experiments on the probing of smectic liquid crystals by means of spin labels [10,39]. If the label belongs to the aromatic skeleton, the degree of ordering S of the molecule is large. For the same label in the alkyl tail $S \rightarrow 0$ in effect. Thus the alkyl "tails" seem to be "molten", labile, which explains the "soapiness" of smectic liquid crystals (i.e. the ease of slippage of some layers relative to others).

Even at the first level (*a*), however, extremely important qualitative results have been obtained, mainly for nematic liquid crystals, which in some measure constitute a model system even for other liquid-crystal phases. It was shown in particular [40] that dispersion (van der Waals) forces of attraction between molecules play a decisive part in the organisation of nematic order [41]. The anisotropy of electron polarisability is the most important molecular characteristic governing the tendency of a specific substance to form a liquid-crystalline state. Long rodlike molecules with aromatic and heteroaromatic rings arranged in series are to be preferred in this respect. A favourable factor is the presence of a chain of conjugation along the molecular skeleton, since it will increase the longitudinal component of the polarisability. There is probably no correlation between the presence of a permanent dipole moment in the molecule and the ability of the substance to form nematic liquid crystals [5,41]. The steric factor (the length and the structure of the terminal groups) is also very significant. Theory [40] agrees with experiment in predicting a phase transition of the first kind between nematic and isotropic liquid states, as well as a regular temperature dependence of the parameter of orientational order.

An interesting criterion of the ability of a substance to form a mesomorphic state has been suggested by Ogorodnik [42] on the basis of experiments on the Raman scattering of light. He considers that only compounds that in the solid state form more than one crystalline modification (sometimes metastable) can have a nematic phase. Structural order in the mesomorphic state is then due to the superposition of "solid-crystalline clusters" of a different modification. The general applicability of this principle still lacks experimental verification.

Although the "twistedness" of the structure of cholesteric liquid crystals is due to the chirality (mirror-image asymmetry) of its component molecules, there is no clear correlation between the direction of rotation of the cholesteric helix and the sign of rotation of the individual molecules [43]. Goossens [44] attempted to explain the tendency of these liquid crystals to form a twisted structure in terms of electric dipole–quadrupole interaction between molecules on the basis of the Maier–Saupe approach‡. His calculated value for the pitch of the helix agrees with experiment. The theory of Goossens will explain also the temperature variation of the pitch if the temperature dependence of the degree of order is taken into account [45].

Another explanation of the structural twistedness and the temperature dependence of the helical pitch is based on the anharmonicity of the forces of molecular interaction [46]. However, this will explain only the increase in pitch with fall in temperature, which occurs only in the vicinity (on the temperature scale) of smectic phases, a fact that can in principle be attributed to the formation of nuclei (clusters) of a smectic in the cholesteric phase.

Yet another explanation [47] of the appearance of a cholesteric phase attributes it to long-range van der Waals forces of interaction between molecules. On this model such a phase may even be formed by molecules having mirror-image symmetry (optically inactive). This extremely untrivial case has not yet found experimental confirmation.

The first attempts at extending the Maier–Saupe approach [40] to an A smectic phase involved [48,49] introducing two parameters of order, orientational (as in nematic liquid crystals) and translational. A molecular-statistical theory of more complicated types of smectic (C, B, and H) has been developed quite recently [50]. Here molecules are regarded as rigid rods, interactions between permanent dipoles of individual segments of the molecules must be taken into account, and the repulsion potential of the molecules within a single smectic layer must be written in explicit form. Interaction between layers is neglected. The molecular field approximation predicts theoretically [50] phase transitions of the second kind between phases A and C, as well as between B and H, whereas transitions between any other pairs of mesophases are of the first kind. In conformity with theory [50] smectics A and B are characterised by free rotation of molecules about the long axes; free rotation is absent from smectics C and H, in which molecules are tilted relative to the smectic axes, and the dipoles are oriented in definite fashion. The suggested pattern has been subjected to criticism [38,51]. Insufficient experimental data are yet available either to support or to disprove the theoretical view [50].

III. ANISOTROPY OF PROPERTIES

1. Orientation of Molecules

A liquid crystal run into a test-tube is a macroscopically homogeneous "polycrystalline" specimen (a turbid liquid). A "single crystal" must be prepared in order that the anisotropy of properties of a liquid crystal can be studied. This can be accomplished by orienting the whole molecular ensemble either by means of an external field or by the boundary conditions at the walls of the microcuvette. In the latter case planar orientation is distinguished from homotropic orientation (Section II, 1). As soon as the orientation of the molecules at the boundary has been

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‡It must be noted that the optical activity of individual molecules is due to intramolecular interactions of the "electric dipole–magnetic dipole" type, so that it is different in nature.

firmly established, alignment of the remaining molecules parallel to the former is energetically most favourable (departure from the specified orientation increases the elastic energy).

The microrelief of a glass surface (or of electrodes) having a characteristic dimension[52] of the order of 10 Å is usually employed for the planar orientation of liquid crystals. The walls are rubbed with a cloth or polished in a definite direction (Chatelain's method[53]) or else layers of metals or dielectrics sputtered askew are used[54]. Homotropic orientation is usually effected by means of monolayers of surface-active agents such as lecithin, alkoxybenzoic acids, polyamide resins, or organosilicon compounds[55]. Fig. 5 illustrates diagrammatically the two chief modes of orientation of liquid crystals—(*a*) planar orientation due to the microrelief of a metal film sputtered askew and (*b*) homotropic orientation due to a film of a surface-active agent—where it can be demonstrated rigorously that both configurations correspond to minimum elastic energy of the liquid crystal[52].

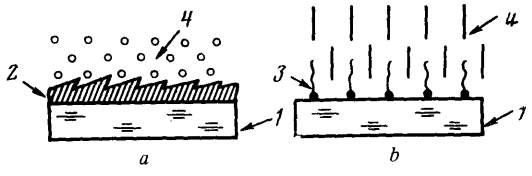


Figure 5. Orientation of a liquid crystal by a surface: *a*) planar; *b*) homotropic: 1) support; 2) obliquely sputtered metal film; 3) surface-active molecules; 4) rodlike liquid-crystal molecules.

If the liquid is a single crystal, almost all its properties are anisotropic, with the anisotropy more marked the greater the degree of ordering S. This quantity S has meaning only for a single crystal, and is a thermodynamic function depending on the properties of the substance and the temperature, but independent to a first approximation of the orienting agent[11]. Thus, if a single crystal having a certain value of S could be obtained by means of a magnetic field of 1 kG, increasing the field to 20 kG will not lead to an increase in S.[56] Incomplete orientation of a specimen (in the absence of a single crystal) can in principle be described by a different parameter—the degree of orientation—but this is not a fundamental characteristic of the substance. We cre compelled to consider this aspect in some detail, for until recently many studies were published in which the physical characteristics of the substance had been determined on unoriented specimens. This involves loss of information to the same extent as in the replacement of a solid single crystal by a polycrystalline powder.

2. Electrical and Magnetic Properties

Fig. 6*a* illustrates a typical temperature dependence of the degree of ordering of a nematic liquid crystal. The temperature variation of the anisotropy of the diamagnetic susceptibility $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ §, and also that of the electronic portion of the dielectric susceptibility $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$, are completely determined by the temperature dependence of S and can be calculated from the anisotropy of these parameters in the solid phase:

$$\Delta\chi_{nlc} = S\,\Delta\chi_s; \quad \Delta\alpha_{nlc} = S\,\Delta\alpha_s \qquad (2)$$

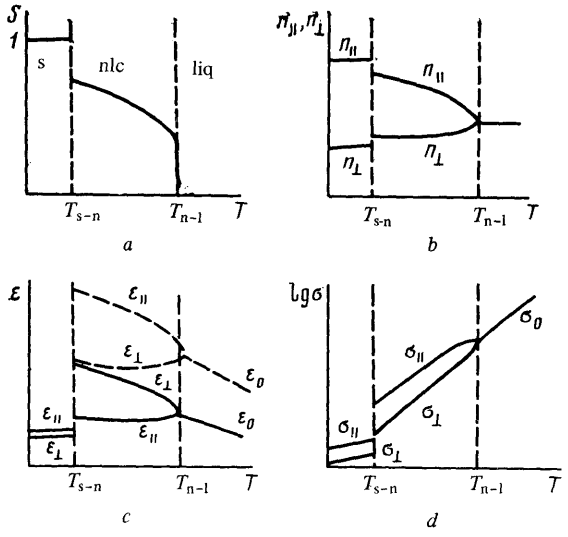


Figure 6. Typical temperature dependence for nematic liquid crystals (nlc) of: *a*) degree of ordering; *b*) refractive indices; *c*) dielectric constant; *d*) electrical conductivity. Here T_{s-n} and T_{n-l} are the solid-nematic and nematic–isotropic liquid phase transition temeratures.

The mean values $\bar{\chi}$ and $\bar{\alpha}$ in the liquid-crystalline phase are equal to the values χ_i and α_i for the isotropic phase (apart from the temperature variation of χ and α). In view of the cylindrical symmetry of distribution of molecules in a nematic liquid crystal, these average values are given by the formulae

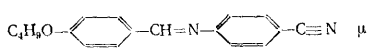
$$\bar{\chi} = \frac{1}{3}(\chi_{\parallel} + 2\chi_{\perp}) \approx \chi_i; \quad \bar{\alpha} = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp}) \approx \alpha_i \qquad (3)$$

More complicated equations hold for the anisotropy of the refractive indices $\Delta n = n_{\parallel} - n_{\perp}$, connected with $\alpha_{\parallel}$ and $\alpha_{\perp}$ by the Lorentz–Lorenz relations[57], for the total dielectric susceptibility $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$, including the orientational component[58], and for the anisotropy of electrical conductivity $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$. However, the general rule of a monotonic fall is maintained for all these quantities: Δn, $\Delta\epsilon$, $\Delta\sigma \to 0$ as $S \to 0$. Typical temperature variations of longitudinal and transverse components of refractive indices, dielectric constants, and electrical conductivities of a nematic liquid crystal are illustrated in Fig. 6*b–d*.

§The subscripts denote directions parallel and perpendicular to the long molecular axes (to the "director" of the nematic liquid crystal).

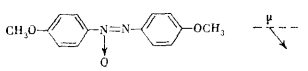
It is noteworthy that $\Delta\chi$, $\Delta n > 0$ in all known nematic and smectic liquid crystals, in conformity with the anisotropy of the magnetic and electronic components of the electric polarisability of oblong molecules. Nevertheless, the sign of $\Delta\sigma$ is different in the two types of mesophases: in the nematic type $\Delta\sigma > 0$ (except for the temperature range in the vicinity of the smectic phase, when nuclei of smectic order are present), since the charge carriers (ions) move more readily in the direction of the long axes of the molecules; in smectic liquid crystals the mobility of the ions is greater along the smectic layers, i.e. normal to the molecular axes, so that $\Delta\sigma < 0$.

The dielectric anisotropy of a nematic liquid crystal may be either positive (Fig. 6*c*, full curves) or negative (broken curves in Fig. 6). This is determined by the components of the orientational polarisability and depends on the relation between the anisotropy of the electronic polarisability of a molecule and the permanent dipole moment μ, as well as the angle β between the dipole moment and the long axis of the molecule[58]. The quantity $\Delta\epsilon > 0$ is characteristic of molecules having a longitudinal dipole moment (i.e. with $\beta \to 0$), e.g.



(XI)

When the angle β is sufficiently large, the case $\Delta\epsilon < 0$ is realised, e.g. in *pp'*-dimethoxyazoxybenzene



(XII)

where $\beta \simeq 60°$. As the frequency of the electric field is raised, the quantities $\epsilon_\parallel$ and $\epsilon_\perp$ exhibit dispersion in different frequency ranges[59]. Dispersion is developed by $\epsilon_\perp$ at frequencies comparable with the frequency of rotation of molecules about the long axis ($f_D^\perp \simeq 10^8$ Hz); that of $\epsilon_\parallel$ occurs at significantly lower frequencies. With long molecules[60] such as



(XIII)

the frequency $f_D^\parallel \simeq 10^4$ Hz, and is determined by hindered rotation of molecules about the short axis. Owing to the dispersion of $\epsilon_\parallel$ and $\epsilon_\perp$ the sign of $\Delta\epsilon$ may change from positive to negative in different frequency ranges[12]. This property can be used in electro-optical devices based on field effects in order to diminish the disconnection time. The dielectric anisotropy of smectic liquid crystals may change sign depending on the temperature, which is explained by pair correlations of neighbouring dipoles[61].

The local anisotropy of electrical properties of cholesteric liquid crystals (within a layer thickness, much smaller than the pitch of the helix) is characterised by the same rules as for the nematic type (e.g. there may be substances having $\epsilon_\parallel - \epsilon_\perp < 0$ and $\epsilon_\parallel - \epsilon_\perp > 0$). Sometimes, of course, anisotropy parameters are introduced to describe a macroscopic specimen having a helical structure. The components of ϵ_h and σ_h parallel and perpendicular to the axis of the helix are then related with the components $\epsilon_\parallel$, $\epsilon_\perp$ and $\sigma_\parallel$, $\sigma_\perp$ by the self-evident formulae

$$\varepsilon_{\parallel h} = \varepsilon_\perp;\ \varepsilon_{\perp h} = \frac{1}{2}(\varepsilon_\parallel + \varepsilon_\perp);\ \sigma_{\parallel h} = \sigma_\perp;\ \sigma_{\perp h} = \frac{1}{2}(\sigma_\parallel + \sigma_\perp)\ . \quad (4)$$

3. Elastic Properties

The elastic properties of an ordinary liquid can be characterised by a single parameter, its compressibility. The elastic energy of a "liquid rod" is unaffected by bending, shearing, or twisting. The situation is different with an anisotropic liquid. For example, three quite different deformations—bending, splaying, and torsion, denoted for brevity *B*, *S*, and *T* deformations—can be imagined for a nematic liquid crystal[12]. Fig. 7 illustrates these three types of deformation, characterised by the respective moduli of elasticity K_{33}, K_{11}, and K_{22}, whose order of magnitude is 10^{-7}–10^{-6} dyn. The elastic force required for a deformation is proportional to that deformation, i.e. to the gradient of the angle of rotation of some molecules relative to others:

$$F_{\text{elast}} = K_{ii}\frac{\partial\varphi}{\partial z}, \quad (5)$$

The elastic energy is expressed in quadratic form:

$$g_{\text{elast}} = \frac{1}{2}K_{ii}\left(\frac{\partial\varphi}{\partial z}\right)^2 \quad (6)$$

A rigorous expression can be obtained for the elastic energy of combined deformation[62]. Elastic coefficients are usually determined from an electro-optical experiment[63]. Attempts have also been made to deduce the temperature dependence of moduli of elasticity from the molecular-statistical theory[64]. The same moduli of elasticity are introduced for cholesteric as for nematic liquid crystals.

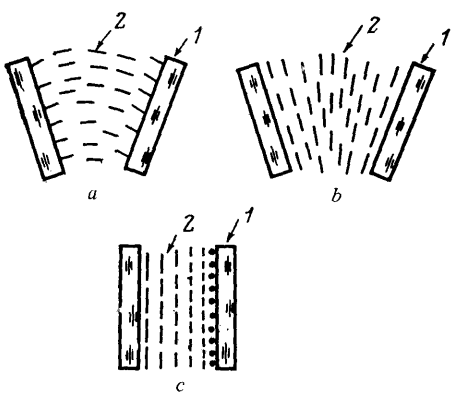


Figure 7. Types of deformation of nematic liquid crystals: *a*) bending; *b*) splaying; *c*) twisting: 1) oriented support; 2) liquid-crystal molecules.

A different situation is found with smectic liquid crystals[65]. In the simplest type—an *A* smectic—the moduli of elasticity for bending and torsional deformations tend to infinity, with only K_{11} remaining finite. The explanation is that an *A* smectic "resists" any deformation in which the distance between the smectic layers changes. Comparing splaying and bending (Fig. 8), for example, we note that in the former case the smectic layers are curved, but the molecules remain normal to them as before, and the distance *d* between the layers is unchanged.

The deformation is described by a finite modulus K_{11}. In the second case the distance between the layers must change for the deformation to occur. The impossibility of such change is expressed by the condition $K_{33} \to \infty$. Torsional deformation is also difficult, as can easily be realised on trying to screw in imagination a pile of thin plates. On the other hand, in contrast to a nematic liquid crystal, it makes sense for an A smectic to introduce a compressibility coefficient $\bar{B}$ representing the increase or decrease in the interlayer distances. This type of deformation does not involve the position of a "director", and the elastic energy is given by a term

$$g_{\text{elast}} = \frac{1}{2}\bar{B}\left(\frac{\partial U}{\partial z}\right)^2, \qquad (7)$$

where U is the displacement of the smectic layer along the coordinate z normal to the layer. The parameter $\bar{B}$ has the same dimensions and order of magnitude as the compressibility coefficients of ordinary liquids. It is interesting that in nematic phases adjacent on the temperature scale to an A smectic a fall in temperature is accompanied by divergence between the moduli of bending and torsional deformations (K_{33}, $K_{22} \to \infty$) as these phases approach the point of transition into the A smectic, a phenomenon explained by a mechanism of formation of nuclei of smectic order in the nematic phase. The modulus K_{22} in a cholesteric liquid crystal also tends to infinity as a neighbouring smectic phase is approached (with change in temperature)[66].

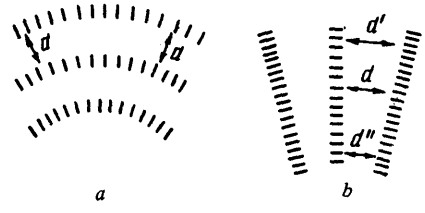


Figure 8. Deformation of an A smectic: *a*) splaying; *b*) hypothetical bending.

Elasticity theory for other types of smectic is very complicated. For example, the simplest description of a C smectic requires the introduction of ten elasticity coefficients (the coefficient $\bar{B}$ and nine moduli[10] are related to the orientation of the "director" and of order of magnitude 10^{-6} dyn).

4. Viscosity Characteristics

The viscosity of a liquid crystal depends on how the "director" is situated relative to the gradient of the rate of flow. This was known long ago[67], but only recently it has been shown by Leslie and by Ericksen[68] that the viscous properties of a nematic liquid crystal can be described completely by five independent coefficients α_i ($i = 1-5$), the Leslie coefficients. Sets of coefficients α_i have been determined for *pp'*-dimethoxyazoxybenzene[69] (XII) and for *p*-butyl-*p'*-methoxybenzylidenaniline (I)[70] from experiments on the Rayleigh scattering of light and on the discharge of a nematic liquid crystal from a capillary. Especially clear experiments were made by Gähwiller, who examined the rate of discharge of a nematic liquid crystal from a capillary of rectangular cross-section (50 × 40 × 0.4 mm) placed in a magnetic field (up to 4 kG) governing the orientation of the liquid-crystal molecules (this applies only at very low rates of flow, when the orienting effect of the flow is insignificant in comparison with the action of the field). Fig. 9 shows the geometry of the experiment. The corresponding viscosity coefficients η_1, η_2, and η_3 were respectively 103, 23.8, and 41.6 cP. These coefficients, together with results of an additional experiment to measure the angle of orientation of the molecules by the flow ($\tan^2\theta = \alpha_3/\alpha_2$), were used to determine all the Leslie coefficients. The great anisotropy of the viscosity of a nematic liquid crystal (e.g. $\eta_1/\eta_2 \simeq 4$) leads to appreciable anisotropy of the mobility of impurity ions, and hence to anisotropy of the electrical conductivity[71] ($\sigma_{\parallel}/\sigma_{\perp} \simeq 1-2$).

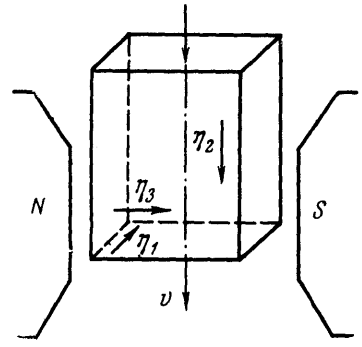


Figure 9. Geometry of Gähwiller's experiment. The "director" direction corresponding to the measured viscosity coefficients η_1 and η_3 is determined by the magnetic field; that corresponding to the measured coefficient η_2 by the material flux v with the field switched off and with an increased rate of discharge; directions of orientation of molecules are denoted by arrows.

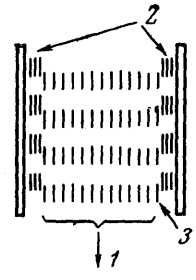


Figure 10. Outflow of A smectic from a capillary: 1) outflowing liquid column; 2) layer fixed adjacent to wall; 3) site of rupture of smectic layers.

Cholesteric and smectic liquid crystals exhibit abnormally large viscosity coefficients (from measurements in capillaries), although their Leslie coefficients are of the same order as those for nematic liquid crystals (from the scattering of light). This increase in the observed

(apparent) viscosity coefficients was attributed by Helfrich[72] to a "penetration" effect (the flowing liquid crystal penetrates through the helical or layer "construction" specified by the boundary conditions at the walls of the capillary). This can be illustrated vividly for a cholesteric liquid crystal by imagining that we are trying to remove a well lubricated screw of large pitch from a threaded orifice, which may be effected by turning the screw. The force of the pressure is consumed in rotating the screw, whose rate of translational motion is small. Thus the "director" of a cholesteric liquid crystal, for which the boundary conditions determine the helical orientation of molecules on the wall of a circular capillary, is also compelled to rotate as material is discharged from the capillary. Here friction may increase the effective viscosity coefficient by factors of 10^5. In the case of smectic liquid crystals discharge should involve the "extrusion" of smectic layers (Fig. 10), whose position is fixed on the wall of the capillary. This is an example of non-Poiseuille and non-Newtonian liquid flow. With indefinite orientation of cholesteric and smectic liquid crystals relative to the capillary (as in most experiments) the apparent viscosity coefficients are almost arbitrary (over a range of 10^5).

IV. INFLUENCE OF EXTERNAL FACTORS

1. General Considerations

Molecules of substances that form liquid crystals themselves exhibit no abnormal properties. At temperatures appreciably above the clear point of nematic liquid crystals, for example, we are dealing with ordinary liquids, whose Kerr constants are no larger than for nitrobenzene (except in the temperature range of the isotropic phase near the transition point, where the Kerr constant may either increase, decrease, or even change sign owing to the short-range order in the arrangement of the molecules[73]). Similarly, esters of cholesterol in the isotropic phase have the same specific optical rotation as have optically active liquids (alcohols, sugar, etc.), but do not form liquid-crystalline phases. The dipole moments and the components of the electrical and magnetic susceptibilities of the molecules also have the same order of magnitude for mesogenic and non-mesogenic substances.

The uniqueness of the properties of liquid crystals—their high sensitivity to external factors—is due to the extremely delicate intermolecular interactions governing the long-range orientational order in the arrangement of molecules. Which specific molecular characteristics are responsible for the tendency of molecules to form an ordered state is the main problem of a molecular-statistical theory of liquid crystals, which is still far from solution. But as soon as long-range order has been established, with the degree of order depending on external factors, the latter influence the anisotropy of almost all the parameters of the liquid crystals. Examples are the dependence of the pitch of the helix of a cholesteric liquid crystal on the temperature or the field and the pressure dependence of the optical anisotropy of a nematic liquid crystal.

Furthermore, many electro- and magneto-optical phenomena are based on reorientation of the "director" (without change in the degree of order). This process of change in optical properties can be divided into three stages. (*a*) Owing to the large anisotropy (as in solid crystals) of the electrical parameters ($\Delta\epsilon$, $\Delta\sigma$, and $\Delta\chi$) the "director" of a liquid crystal "interlocks" with an external field: an orienting moment acts on the molecules of the liquid crystal. In a magnetic field, for example, the axes of the molecules tend to arrange themselves parallel to the field. (*b*) Since a liquid crystal is liquid, the molecules actually undergo reorientation under conditions of competition with elastic forces (in some cases this reorientation is accompanied by mass transfer of liquid—by a flow). (*c*) Change of orientation is easily recorded optically owing to the great anisotropy of optical properties (refractive indices and absorption).

2. Examples of Electro-optical and Magneto-optical Effects

In order to simplify discussion of the three most characteristic effects—the Fréedericksz transition in nematic liquid crystals, uncoiling of the helix in cholesteric liquid crystals, and wavelike instability in smectic liquid crystals—we shall regard a liquid crystal as a pure dielectric, through which an electric current does not flow. In reality this is impossible of achievement, since even with the most careful purifications some quantity of ionic impurities will remain in the liquid crystal, and given appreciable *ionic conductivity* $\sigma \simeq 10^{-12}$–10^{-14} ohm^{-1} cm^{-1}). With perfect purification ions may still be generated by the injection of electrons from the electrode followed by their "capture" by neutral molecules of the substance. In some publications current–voltage characteristics on liquid crystals have been interpreted in terms of an electronic mechanism of conduction. Such views are incorrect, since the electronic conductance of a liquid crystal is extremely small; it should be comparable in order of magnitude with the intrinsic conductivity of impurity-free organic dielectrics such as anthracene and naphthalene. At the present time it is impossible even to state definitely what these values are; calculations give $\sigma < 10^{-19}$ ohm^{-1} cm^{-1}. Electron currents can be observed experimentally in liquid dielectrics only under the abnormal conditions of pulse photoconduction on substances of very low electron affinity[74]. Under normal conditions we are always dealing with an ionic current, although the current carriers (ions) may not be intrinsic, but generated near the electrodes by the injection or exclusion of electrons. In this case an electrochemical process takes place on the electrode.

(*a*) Fréedericksz transition in a nematic liquid crystal

Considering now the simplest example of the reorientation of a nematic liquid crystal in an electric or magnetic field—the Fréedericksz transition[75]—we suppose that the microcuvette illustrated in Fig. 11*a* is filled with a liquid crystal of *p*-*p*′-butoxybenzylidenaminobenzonitrile (XI) and maintained at a temperature corresponding to the nematic range of this compound (64–103°C). Because of the presence of the cyano-group the molecule of (XI) has a dipole moment $\mu \simeq 4.5$ D directed along its long axis[76], so that the longitudinal component (in the direction of the axis of orientation of the molecules) of the static dielectric constant exceeds significantly the transverse component: $\epsilon_{\parallel} \simeq 25$ and $\epsilon_{\perp} \simeq 7$. Let the glasses of the microcuvette be so treated that the molecules of the adjacent layer of the liquid crystal are rigidly fixed parallel to the glass (planar orientation) and do not change their orientation in any circumstances. When an electric

field is applied, a turning moment will act on the molecules of the liquid crystal, tending to reorient them with the direction of the maximum component of the dielectric constant coinciding with that of the field. The reason is that the polarisation induced in the dielectric (the dipole moment of unit volume) is proportional to the dielectric constant; hence the polarisation is greater for the direction of $\epsilon_{\parallel}$. As a consequence, interaction of the induced moment with the external field leads to rotation of the optical axis of the single crystal, with the exception of molecules adjacent to the wall. The proportion of oriented dipoles is $\sim\exp(-\mu E/kT) \simeq 10^{-4}$–$10^{-2}$ for typical field strengths. The "director" of the ensemble of interacting molecules, i.e. the longitudinal axis of their cylindrical distribution, is oriented parallel to the field. Rotation of the molecular ensemble is opposed by the elastic energy of interaction of the molecules (Eqn.6).

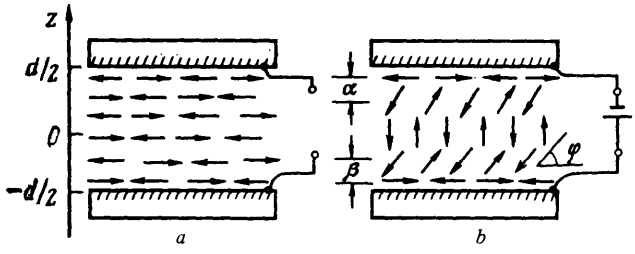


Figure 11. Illustration of the Fréedericksz effect in nematic liquid crystals: *a*) initial orientation of molecules: *b*) orientation of molecules at voltages exceeding the threshold value.

Fig. 11*b* shows regions α and β, in which the molecules are forced to detach themselves from their neighbours, although they "would have preferred" to remain parallel to the latter. As a result of competition between dielectric and elastic moments ($\Delta\epsilon E^2/4\pi$ and $K_{11}\partial^2\varphi/\partial z^2$), deformation has a threshold character. The threshold voltage is

$$v_0 = \pi\sqrt{4\pi K_{11}/\Delta\varepsilon} \quad . \qquad (8)$$

Deformation begins from the middle of the layer ($z = 0$), and extends to the electrode with increase in the field strength, embracing more and more new layers of molecules. With the maximum field almost all molecules other than those adjacent to an electrode are reoriented perpendicular to the electrodes, which can easily be observed optically from the disappearance of double refraction by the liquid-crystal layer. Expressions for the reaction and relaxation times can be obtained[12] from the kinetics of this process taking into account the moment of viscous friction for the "director" (in addition to dielectric and elastic components).

Roughly the same pattern is observed for the twisted structure of a nematic liquid crystal (with mutually perpendicular directions of the "director" on the opposite electrodes), as well as for nematic crystals with $\epsilon_{\parallel} < \epsilon_{\perp}$, if the initial orientation was homotropic.

(*b*) Cholesteric–nematic phase transition

Fig. 12*a* represents the planar texture of a cholesteric liquid crystal when the molecules are oriented parallel to the glasses of the cuvette (in the absence of electodes), while the axis of the cholesteric helix is correspondingly perpendicular to them. Such a texture reflects circularly polarised light selectively[77] if the polarisation corresponds in sign to the twist of the helix, while the wavelength (in a vacuum) satisfies the relation $\lambda = \frac{1}{2}P\bar{n}$ (where P is the pitch of the helix and $\bar{n}$ the mean refractive index of the liquid crystal). The selective reflection is caused by the diffraction of light on the cholesteric planes (analogous to the Wulf–Bragg diffraction of X-rays on ordinary crystals). Measurements of the wavelength of the selective reflection provides a method for determining the pitch P of the helix.

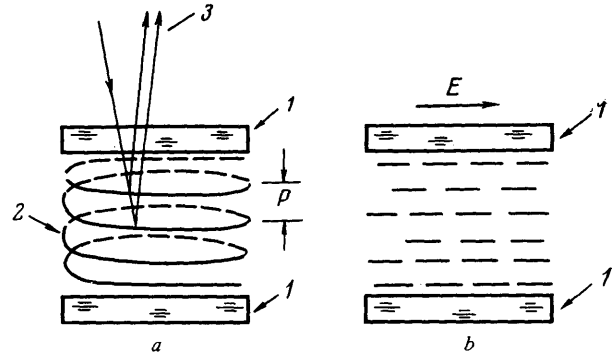


Figure 12. Cholesteric → nematic phase transition, with electric field applied along the surface of the glasses: *a*) planar cholesteric texture in absence of field; *b*) nematic phase with $E > E_0$: 1) glasses (in absence of electrodes); 2) cholesteric helix of pitch P; 3) diffracting light rays.

We now imagine that the dielectric anisotropy of the cholesteric liquid crystal is positive, i.e. that $\epsilon_{\parallel} > \epsilon_{\perp}$ with respect to the "director"), and that the substance is located in a field E perpendicular to the axis of the helix. It is clear that all molecules will tend to orient themselves parallel to the field, which is incompatible with a helical structure and requires an increase in the elastic energy of the liquid crystal. With a sufficiently strong field the helix begins to uncoil (as is evident from the shift to longer wavelengths in the selective reflection maximum), and ultimately a phase transition takes place from cholesteric to nematic liquid crystals (Fig. 12*b*). The threshold field strength for the transition is inversely proportional to the pitch of the helix[78]:

$$E_0 = \frac{\pi^2}{P_0}\sqrt{4\pi K_{22}/\Delta\varepsilon} \quad . \qquad (9)$$

(*c*) Instability of smectic liquid crystals

Formally a Fréedericksz transition occurs also with an *A* smectic, as with a nematic mesophase, and the same formula gives the threshold voltage (Eqn.8). However,

the deformation itself is too small to be recorded ("illusory" transition[79]). As already discussed in Section III, 3, the weakness of the deformation is due to the tendency of an *A* smectic to maintain unchanged the distance between the layers (whereas reorientation requires such change). Since the reorientation of molecules forms the basis of several other, more complicated electro-optical phenomena, e.g. electrohydrodynamic, the properties of smectic liquid crystals are on the whole far less subject to the influence of fields than are those of nematic and cholesteric mesophases¶.

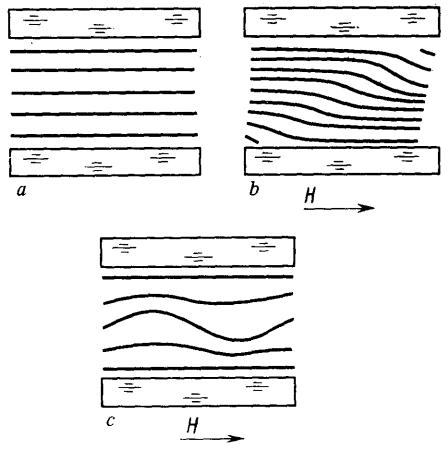


Figure 13. Instability of smectic liquid crystals in a magnetic field with $\Delta\chi > 0$: *a*) initial orientation (the lines represent smectic layers); *b*) hypothetical Fréedericksz transition leading to deformation of smectic structure with change in interplanar spacing; *c*) wavelike deformation with interplanar spacing almost unchanged.

Perhaps the most characteristic instability of a smectic liquid crystal in an external field is its wavelike deformation, which requires almost no change in the interlayer distance[10]. If $\Delta\chi > 0$ and the magnetic field is parallel to the layers, i.e. perpendicular to the axes of the molecules (Fig. 13*a*), the molecules will tend to reorient parallel to the field, which would have led to crumpling of the layers near the glasses, which is energetically disadvantageous (Fig. 13*b*). A compromise is provided by wavelike deformation, with which a minimum is reached in the total (electrical and elastic) energy (Fig. 13*c*). The period *b* of such deformation is the geometric mean of the layer thickness *d* and the "depth of penetration" $\lambda = (K_{11}/B)^{\frac{1}{2}} \simeq 20$ Å: i.e. $b = 2(\pi\lambda d)^{\frac{1}{2}}$ (~5μm for $d = 0.1$ cm), and the critical field is

$$H_c^2 = 2\pi K_{11}/\lambda\, d\,\Delta\chi \quad (\approx 60 \text{ kG}) \,. \tag{10}$$

¶This makes it difficult to measure the anisotropy of the electrical and other parameters of smectic liquid crystals.

(*d*) Electrohydrodynamic instability of nematic liquid crystals

The notion of a liquid crystal as an ideal dielectric must be rejected in considering this problem: electrohydrodynamic processes in a liquid crystal involve currents. A physical description of electrohydrodynamic instabilities is fairly complicated. The main cause of periodic liquid flows is the spatial separation of ions and consequent nonuniform distribution of ionic current in the specimen owing to the anisotropy of electrical conductivity. Because of friction the fluxes of matter break down the "monocrystallinity" of the specimen and the initial uniform distribution of the "director", causing three-dimensionally periodic deformation of this distribution. As the field becomes stronger, the periodic motion of the liquid is replaced by turbulence, which is accompanied by local changes in optical anisotropy and hence by intense scattering of light[80,81] (dynamic scattering). This effect usually develops in nematic liquid crystals having negative dielectric anisotropy (with $\Delta\sigma > 0$), but may occur even when $\Delta\epsilon > 0$, in particular when $\Delta\sigma < 0$,[82] as well as with $\Delta\epsilon = 0$.[83]

3. Effects of Temperature and Other Factors

Such factors as pressure, temperature, and optically inactive additives exert a relatively weak influence on the ordered character of nematic liquid crystals, and hence on the anisotropy of their properties. A different situation obtains with cholesteric mesophases, the helical pitch of which is extremely sensitive to the above factors. The explanation is that the energy of intermolecular interaction responsible for the helical structure is only 10^5 of that determining the nematic order[45]. A sharp change in pitch is accompanied by marked changes in optical properties, precisely at the spectral positions of maximum selective reflection[15] and the point of inversion of the sign of optical activity[84]. For example, the temperature of a layer of a cholesteric liquid crystal can be recorded optically to better than 0.02 deg.[84]

In most cases (for an exception see e.g. Ref. 85) the pitch of the helix *P* increases with fall in temperature, the relative change $P^{-1}|\,dP/dT|$ reaching 100 deg^{-1} (cholesteryl nonanoate at 75°C). The reason for the variation in pitch with temperature has not been finally elucidated[44-46]. With cholesteric liquid crystals formed by optically active molecules not derived from cholesterol, such as compound (IV),[21] the temperature dependence of the pitch is very slight, and such substances are of the greatest interest for electro-optical applications. With increase in pressure from 1 to 2000 bars a considerable change has been observed[86] in the wavelength of maximum selective reflection (from the violet to the red part of the spectrum) by a cholesteric liquid crystal. The pitch of the helix can be changed also by adding optically inactive impurities to cholesteric mesophases[87].

Optically active additions to nematic liquid crystals lead to the formation of a cholesteric structure[88]. At low concentrations *c* of the additives the pitch of the helix is inversely proportional to the concentration:

$$P = (2\beta c)^{-1}, \tag{11}$$

where β is the twisting power of a specific additive. The same effect is obtained on addition of an optically active impurity to a compensated mixture (with $P = \infty$) of cholesteric liquid crystals.

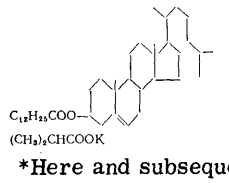
The property of twisting a nematic into a cholesteric structure is in general inherent in any chiral macroscopic species (possessing no plane of mirror-image symmetry), and the pitch of the helix is inversely proportional to the concentration c of these species in the mesophase [10]. At higher concentrations c the relation (11) breaks down. The twisting power β cannot be regarded as exclusively a property of the additive [89], but depends also on the solvent. Anomalous results—such as (*a*) the production of nematic–cholesteric mixtures with the same sign of rotation (dextrorotatory) on the addition to a nematic liquid crystal of cholesteric components with a different sign of rotation [90] and (*b*) the production of a laevorotatory mixture from two dextrorotatory components [91]—can be explained by taking into account not only β but also the twisting power of the solvent induced by the solute [92].

V. CHEMICAL STRUCTURE AND PROPERTIES

1. Chemical Classes

The >5000 liquid-crystalline compounds known at the present time include representatives of various classes—acyclic, isocyclic, aromatic, heterocyclic, organometallic compounds, steroids, and salts of organic acids (Table 1)[2].

Table 1.

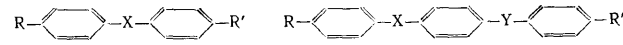
Formula	Transition temperatures*				
	$T_{s\text{-}sm}$	$T_{s\text{-}n}$	$T_{sm\text{-}n}$	$T_{sm\text{-}c}$	T_{cl}
$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	11.7	—	—	—	15.5
C_5H_{11}–C$_6$H$_4$–COOH	—	54	—	—	105
CH_3O–C$_6$H$_4$–CH=N–C$_6$H$_4$–C_4H_9	—	22	—	—	47
C_2H_5OCO–(C$_6$H$_4$)$_4$–$COOC_2H_5$	284	—	—	—	367
C_9H_{19}–C$_6$H$_4$–(N=N)$_2$–C$_6$H$_4$–C_9H_{19}	140	—	146	—	151.5
(CH$_3$O–C$_6$H$_4$–CH=N–C$_6$H$_4$–)$_2$Hg	—	209	—	—	285
	63.5	—	—	78.8	84.8
$(CH_3)_2CHCOOK$	240	—	—	—	335

*Here and subsequently the following subscripts are used to denote phases in the symbols for phase transition temperatures: c = cholesteric; i = isotropic; n = nematic; s = solid; and sm = smectic. As an example $T_{s\text{-}sm}$ is the temperature of transition from the solid to the smectic state. All transitions from solid to mesomorphic and from mesomorphic to the isotropic state are also denoted as melting points T_m and clear points T_{cl} respectively.

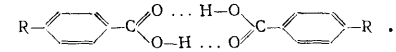
A small group comprises acyclic liquid crystals, mainly unsaturated aliphatic acids and their derivatives. In it may be included a few esters of carbonylbisamino-acids of general formula ROCOCHR'NHCONHCHR'COOR. These compounds are obtained from optically active esters of valine and leucine, and form a smectic phase [93].

A more representative group consists of isocyclic liquid crystals (~200 compounds [2]). Among them only 4,4″-dialkyltercyclohexanes and *trans*-4-alkylcyclohexanecarboxylic acids do not contain benzene rings. They are characterised by formation of a plastic mesophase. The remaining liquid crystals of this group contain aromatic rings together with the isocyclic residue. These are mainly 2,6-di-*p*-R-benzylidenecyclohexanones, where R = Alk, AlkO, or AcylO. Analogous derivatives of cyclopentanone and cycloheptanone have also been obtained.

More than 50% of known liquid crystals are benzene derivatives, a considerable proportion of which can be represented by the formulae



where R, R′ = Alk, AlkO, AcylO, AlkOCOO, AlkOCO, Hal, NO_2, or CN, while X and Y represent single bonds or the groups N:N, N:NO, CH:CH, CH:N, CH:NO, COO, C:C, etc. *para*-Substituted benzoic and cinnamic acids are also mesomorphic, forming in the liquid-crystalline state dimers, e.g.



Certain derivatives of naphthalene [2,94], 2,7-disubstituted derivatives of fluorene and fluorenone, and also 4,4‴-disubstituted *p*-quaterphenyls possess the properties of liquid crystals. This applies also to unsubstituted *p*-quinque-, *p*-sexi-, and *p*-septi-phenyls.

Most known heterocyclic liquid crystals (~700) have an analogous structure to the benzene derivatives, but with one of the benzene rings replaced by pyridine, pyrimidine, pyrazine, pyridazine, or 1,2,4,5-tetrazine. Liquid-crystalline compounds are known also in other classes of heterocycles, e.g. quinolines [95] and benzazoles [96].

Cholesteric liquid crystals are formed by cholesterols, thiocholesterols, stigmasterols, ergosterols, and certain other sterols substituted in the hydroxy-group. Chloro-, bromo-, and iodo-cholesterols are also mesomorphic.

Around 200 liquid-crystalline compounds are salts of aliphatic or aromatic acids with alkali or alkaline-earth metals, or hydrohalides of substituted pyridines and quinolines.

2. Structure and Transition Temperatures

The demand by technology for liquid-crystalline materials has been the main stimulus to the establishment of rules between structure and mesogenicity and to the prediction of transition temperatures. The first requirement to be met by such materials is the occurrence of a mesophase over a wide temperature range including room temperature. Mixtures of liquid-crystalline compounds provide the best means of achieving this aim, since individual substances rarely have melting points below 40°C. However, individual liquid crystals are required to have melting points as low as possible and a wide temperature range of existence of the mesophase.

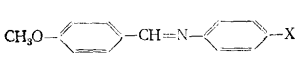
Examination of experimental data on transition temperatures and especially study of these temperatures in various homologous series have yielded several empirical conclusions on the relation between structure and mesogenicity. These rules apply to temperatures of transitions from one mesophase to another and from a mesophase to an an isotropic state, whereas temperatures of transition from the crystalline state to mesophase vary irregularly.

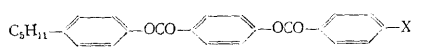
Only observations of a general character have been made on the latter, applicable also to melting points of non-mesomorphic compounds and consisting in a rise in such temperatures with increase in molecular weight, polarisability, polarity, and molecular symmetry, as well as on formation of intermolecular hydrogen bonds.

The occurrence of regularities in the transition points between one mesophase and another or the isotropic liquid is due primarily to the fact that the structure of a given mesophase and the relative arrangement of molecules in it are common to compounds having different structures. Yet such compounds may form solid crystals differing in structure and with different relative arrangements of the molecules in the crystal lattice. Small variations in molecular structure may lead to packing in a different three-dimensional lattice with markedly different intermolecular distances and a different arrangement of the molecules, which will produce significantly different intermolecular interactions and hence melting points. Furthermore, transition from the crystalline to the mesomorphic state will be accompanied by a greater change in energy of intermolecular interaction than in transitions between mesophases or from a mesophase to an isotropic liquid. This rule is apparent in the heats of transition: thus for *pp'*-dialkoxyazoxybenzenes the heats of transition crystal–mesophase, smectic–nematic, nematic–isotropic, and smectic–isotropic liquid are respectively 11.7–28.0, 0.02–2.30, 0.27–2.30, and 6.97–7.90 kJ mole^{-1}.[97] A detailed account has been given[98] of the thermodynamic properties of liquid crystals.

In investigations of the correlation between molecular structure and mesogenicity the greatest attention has hitherto been paid to transition points between mesophases and especially to the temerature T_{cl} of transition from a mesophase to an isotropic liquid. At the clear point the energy of thermal motion of the molecules becomes equal to the energy of intermolecular interaction ensuring long-range orientational order. The clearing temperature is thus a measure of the mesogenicity of a compound or of the thermal stability of the mesophase (if a compound A exists as a mesophase from 70 ot 200°C, and a compound B over the range 200–201°C, the mesophase of B has the greater thermal stability). In comparisons of this kind it is unimportant whether the clear point lies above or below the melting point of the solid crystal (enantiotropic or monotropic liquid crystals respectively).

Two conclusions concerning transition temperatures follow from the Maier–Saupe theory of nematic liquid crystals (Section II, 2), which is based on dispersion forces of attraction between molecules: firstly, molecules possessing anisotropy of polarisability are necessary for establishment of the liquid-crystalline state, and the transition temperature rises with increase in such anisotropy; secondly, permanent dipoles can exert only a weak influence on transition temperatures. A comparison has been made of the variation in the anisotropy of polarisability of the substituent X and the clearing temperatures of azomethines (XIV) and esters (XV) [99]


(XIV)


(XV)

X = F, Cl, Br, CH_3, CH_3O, C_2H_5O, NO_2, CN.

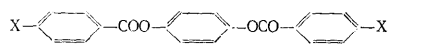
According to the Maier–Saupe theory the clear point is given by

$$T_{cl} = A/4.54\,kV^2, \qquad (12)$$

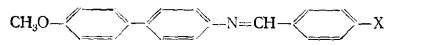
where k is Boltzmann's constant, V is the molar volume at T_{cl}, and A is proportional to the square of the anisotropy of polarisability of the molecule[40]. Expressing the anisotropy in terms of the sum of the polarisabilities $\Delta\alpha_M$ of the main part of the molecule and $\Delta\alpha_X$ of the substituent, we obtain

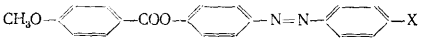
$$T_{cl} \propto (\Delta\alpha_M)^2 + 2\,\Delta\alpha_M \cdot \Delta\alpha_X + (\Delta\alpha_X)^2 \ . \qquad (13)$$

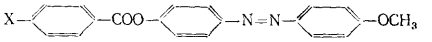
Neglecting the last term (since $\Delta\alpha_M \gg \Delta\alpha_X$), we obtain a linear relation between T_{cl} and $\Delta\alpha_X$. Experimental data on esters (XV) are well represented by a straight line, and those on azomethines (XIV) also reveal a well defined tendency for T_{cl} to rise with increase in $\Delta\alpha_X$. Examples for several other series


(XVI)


(XVII)


(XVIII)


(XIX)


(XX)

(Table 2) confirm this tendency, although the methoxy-derivatives may exhibit regular deviations.

Table 2. Effect of terminal substituents X on clear points.

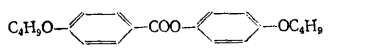
X	$(\Delta\alpha_X)$, Å^3	Clearing temperature T_{cl}, °C						
		(XIV)[99]	(XV)[100]	(XVI)[101]	(XVII)[101]	(XVIII)[5]	(XIX)[2]	(XX)[2]
F	0.5	26	180	199	—	265	198	—
CH_3	1.2	38	199	236	265	279	271	281
Cl	2.5	47	212	246	275	295	250	293
CH_3O	3.1	102	223	300	300	318	316	316
Br	3.9	—	213	252	277	294	275	292
NO_2	4.0	82.5	—	281	—	308	317	310
C_2H_5O	4.2	122	—	287	295	304	300	—
CN	4.4	119	249	353	—	—	322	327

Extension of the above equations to other classes is restricted both by the scarcity of data on the quantity A and molar volume V and by the discrepancies found sometimes between calculated and experimental values, probably resulting from the postulates made in the theory. It must be borne in mind also that a substituent introduced into a molecule not only changes the polarisability but may produce several other effects, e.g. by changing the molecular geometry, which will have a significant influence on the clearing temperature. As a consequence it is difficult to make an unambiguous interpretation of many experimental results on transition points in liquid-crystalline compounds. Clearly, however, increase in the anisotropy of polarisability should lead to a rise in the clear point. The quantity V should be regarded probably as a factor representing the effect of steric forces of repulsion between molecules in the mesophase. The increase in intermolecular distance caused by these forces leads to a weakening of intermolecular forces of attraction and hence to a fall in the clearing temperature.

The anisotropy of electronic polarisability is determined to a first approximation by the geometrical anisotropy. As a consequence, mesomorphic properties are present in the *trans*-forms of *pp'*-disubstituted stilbenes

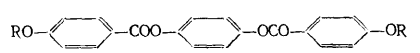
and *p*-substituted cinnamic acids, but absent from the *cis*-analogues. Among alkoxybenzoic acids only the *para*-isomers are mesomorphic, whereas the *ortho*- and *meta*-isomers are not. These facts can be used in determining molecular structure when it is necessary to choose between linear and branched configurations of isomers.

The introduction of additional benzene rings has a greater effect on the clearing temperature than have terminal substituents. In a series of esters, for example, the transition points vary as follows with increase in the number of benzene rings [102,103]:



(XXI)

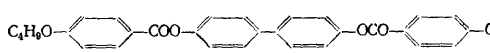
$T_{s-n} = 86°$, $T_{n-i} = 91°$



(XXII)

a) R = Me: $T_{s-n} = 213°$, $T_{n-i} = 297°$;

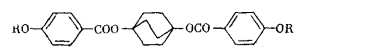
b) R = Bu: $T_{s-n} = 153°$, $T_{n-i} = 241°$



(XXIII)

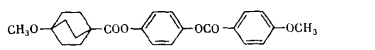
$T_{s-sm} = 171°$, $T_{sm-n} = 184°$, $T_{n-i} = 358°$.

Replacing the *p*-phenylene rings in (XXII) by the rigid but less polarisable bicyclo[2,2,2]octane rings leads to fall in the nematic–isotropic transition point [104]:



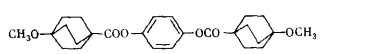
(XXIV)

a) R = CH_3; T_{s-n} = 185°, T_{n-i} = 269°;
b) R = C_4H_9; T_{s-n} = 152°, T_{n-i} = 221°



(XXV)

T_{s-n} = 189°, T_{n-i} = 221°



(XXVI)

T_m = 209°, T_n = 130°

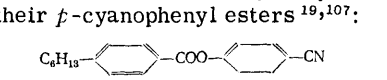


(XXVII)

T_m = 197°, T_n = 195°.

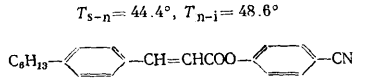
The width of the bicyclo-octane ring is comparable with that of the benzene ring (5.0 and 4.9 Å), but the latter is more planar (2.7 instead of 4.5 Å thick). In view of the possibility of rotation of molecules in liquid crystals about the long axis, the effect of the latter factor is neglected. The probable reason for the considerable fall in thermal stability of the mesophase (by 100 deg) on passing from (XXIV) to (XXVII) is that the cyclohexane fragment is less rigid than the bicyclo-octane ring. The diminished molecular rigidity results in disruption of linearity and thereby diminished anisotropy of polarisability of the molecule. A fall in the clear point is observed also on passing from esters of biphenyl-4,4′-diol to those of bicyclohexyl-4,4′-diol. [105]

The role of an additional double bond in a molecule of a liquid crystal has been examined in *p*-alkylbenzenzoic acids [106] and their *p*-cyanophenyl esters [19,107]:



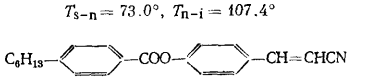
(XXVIII)

$T_{s-n} = 44.4°$, $T_{n-i} = 48.6°$



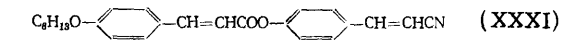
(XXIX)

$T_{s-n} = 73.0°$, $T_{n-i} = 107.4°$



(XXX)

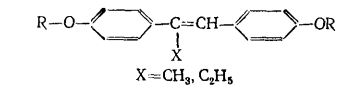
$T_{s-n} = 97.5°$, $T_{n-i} = 147.7°$



(XXXI)

$T_{s-n} = 93.8°$, $T_{n-i} = 226.5°$

The rise in the clearing temperature in this case can also be treated as a consequence of increased anisotropy of polarisability of the molecule. The higher values for (XXX) than for (XXIX) can be explained by the longer conjugated chain containing the double bond in the former. This reflects the fact that the anisotropy of polarisability is influenced not only by the overall linear configuration of the molecule and the presence of readily polarisable structural units but also by the possibility of conjugation between various parts of the molecule (terminal and central groups, benzene rings, double bonds). Introduction of the α-alkyl group in the stilbene derivatives



(XXXII)

disrupts conjugation in the molecule, with a consequent fall in the clear point for the methyl homologue from 176 to 95°C and for the ethyl homologue [108] from 189 to 121°C. Data on the variation of the clearing temperature due to the substitution of azomethines [109] and of biphenyl derivatives [5] can be interpreted similarly.

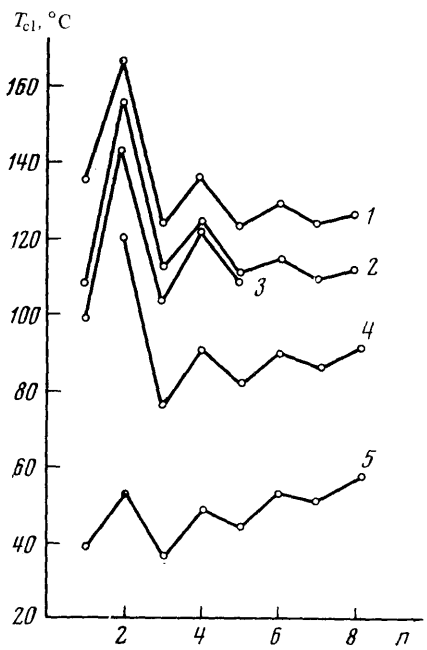
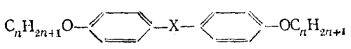
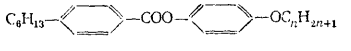


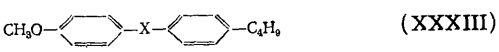
Figure 14. Clear points of the compounds [2]



where X represents: 1) N:NO; 2) N:N; 3) CH:N; 4) COO; 5) and of



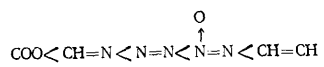
A closely related problem is the influence of the central group on the thermal stability of the nematic phase (Fig.14). Data are available also for alkylalkoxy-derivatives with one pair of substituents [110]:



(XXXIII)

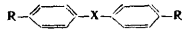
X =	CH=CH	N=N	N=N	N=CH	CH=N	N=N	N=CH	CH=N	C≡C	COO	OCO
T_{cl}, °C	121	77	74	70	53	49	49	46	37	24	22

With an unsymmetrical central group the isomers in the series (XXXIII) (excluding nitrones) have closely similar clear points. As appears from the above data, the central groups X can be arranged in the sequence



of increasing thermal stability of the mesophase. On passing from non-conjugated esters to partly conjugated azomethines and to planar and conjugated azo-compounds and stilbenes the anisotropy of polarisability tends to increase in the same sequence.

Table 3. Calculated parameters of central groups for determining clear points of [111]



X	Temperature parameter, deg	X	Temperature parameter, deg
N=N	0	CH=N	−9
CH=CH	+51	COO	−35
N→O	+21	C=C	−33*
		CH=CCl	−32
CH=N→O	+8		

*Taken from Ref. 112.

Statistical treatment of a large quantity of experimental data [111] on the clearing temperatures of nematic liquid crystals led to suggested parameters defining the influence of central and terminal groups (Tables 3 and 4). An unknown clear point is determined as the sum of the parameters of central and terminal groups. Thus for *p*-butyl-*p'*-methoxystilbene [110]

$$T_{cl} = 55° (OCH_3) + 15° (C_4H_9) + 51° (CH=CH) = 121°;$$

$$T_{cl}^{exp} = 121° .$$

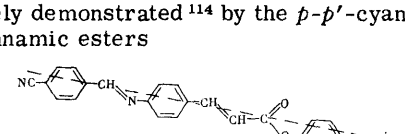
However, considerable discrepancies between calculated and experimental values are found for the same substituents in an azomethine (61 and 47°C), an azo-compound (70 and 47°C), and an azoxy-compound (91 and 71°C). The additive approach is evidently of limited application to the determination of clear points.

The variation of the clearing temperature with growth of the alkyl chain also exhibits several peculiarities—(i) alternation, i.e. a rise in the clear point on passing from a liquid crystal having an even number of atoms (including oxygen) in the chain to a liquid crystal with an odd number of atoms, followed by a fall on subsequently passing from an odd to an even number of atoms, (ii) a fall in the case compounds whose clear points lie above 80°C, and (iii) a rise in compounds having clear points below 80°C—which can be explained by the Maier–Saupe theory [112]. For an odd atom the increment of polarisability along the long axis of the molecule is about double the increment transverse to the axis, but for an even atom in the chain the contributions to the polarisability parallel and transverse to the axis are roughly equal, which leads to the alternation in clearing temperature. The overall anisotropy of polarisability increases with growth of the alkyl chain, which causes a rise in the clear point for compounds having low clear points (increase in A in Eqn.12). In compounds having high clearing temperatures the increase in mobility of the alkyl chain begins to have an effect, which increases as the chain becomes longer, with growth in the steric forces of repulsion (increase in V in Eqn.12) and fall in the clear point.

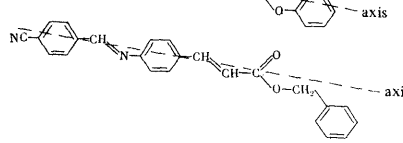
Table 4. Calculated increments of terminal groups for determining clear points of [111]

R	Temperature parameters, deg					
	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$
C_nH_{2n+1}	−2	5	12	15	14	2
$C_nH_{2n+1}O$	55	75	56	61	55	58
$C_nH_{2n+1}COO$	65	67	63	54	50	45
$C_nH_{2n+1}OCOO$	68	61	42	41	43	35

The above examples of the relation between clearing temperature and structure were concerned with the variation of the anisotropy of the molecular polarisability, i.e. with the quantity A in Eqn.(12). No reliable data are available on the dependence on the molar volume V. However, it is known that increasing the width of the molecule (defined as the diameter of the smallest cylinder into which the molecule can be placed), e.g. by introducing a side-chain, leads to a fall in the clear point [5,113]. Broadening the molecule increases the interaxial distances in the mesophase, which weakens intermolecular interactions and lowers the clear point. The influence of this factor is effectively demonstrated [114] by the *p-p'*-cyanobenzylidenaminocinnamic esters



(XXXIV)



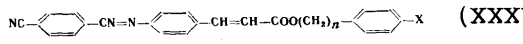
(XXXV)

The explanation of this effect is that, when n is even (e.g. in compound XXXIV), the benzene ring of the ester group fits along the long axis of the molecule, but when n is odd (as in XXXV) it fits across this axis, thereby increasing the width of the molecule. A similar observation has been made on phenylalkanoates of sterols [115].

The clear points of substituted derivatives (XXXVI) vary with n and the location of the substituent (Table 5). When n is even, substitution at position 4″ increases the anisotropy of the molecule and hence raises the clearing temperature, but 3″-substitution widens the molecule and

lowers this temperature. When n is odd, 4″-substitution also has the latter effects. With 3″-substitution conformers may apear in which the substituent widens the molecule and lowers the clear point, but the substituted benzene ring may occupy a position in which the substituent has no broadening effect ($n = 1$, X = Cl). The change in clearing temperature with the parity of n in unsubstituted compounds (XXXVI) reaches 240 deg, and in 4″-substituted derivatives >360 deg (Table 5).

Table 5. Clear points for the compounds



(XXXVI)

X	Clear points, °C			
	$n = 0$	$n = 1$	$n = 2$	$n = 3$
H	280.2	38.5	187.7	36.4
4″-Cl	338	—30*	217.8	13
4″-CH_3	290—331	—30*	226.5	7
3″-Cl	231.5	47.5	150.6	32.8
4″-CH_3	219.4	26	154.5	9

*Mesophase not observed on cooling to −30°C.

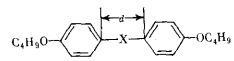
Introduction of a side-chain into the molecule of a liquid crystal lowers not only the clear point but often also the melting point, which provides a method for obtaining low-temperature liquid crystals [100]. However, melting-point depression is not observed in all cases [5,116].

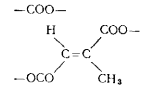
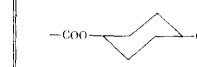
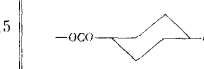
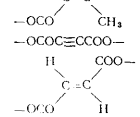
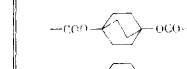
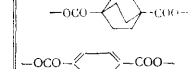
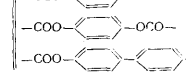
Thus the Maier–Saupe theory is useful in a qualitative discussion of the relation between structure and clear point. However, there are also other approaches to the theory of nematic liquid crystals. As a generalisation of the Maier–Saupe approach the molecular-statistical theory of such mesophases [41,117] takes into account not only dispersion forces but also interactions between permanent dipoles, induced dipole–dipole and dipole–quadrupole interactions, and also steric forces of repulsion. It has been suggested [118] that the agreement between experimental and theoretical values [41,117] is a consequence of the introduction of correcting parameters into the theory, and a general form of interaction potential between rodlike molecules is proposed.

The geometrical anisotropy of molecules is a decisive factor in the formation of nematic phases in solutions of macromolecules and viruses [119], but its role is not so obvious for thermotropic liquid crystals. Unambiguous conclusions cannot be reached from a direct comparison of the clearing temperatures with the length of the latter (Table 6). There is undoubtedly a tendency for the thermal stability of the mesophase to improve as the molecule becomes longer, but it is further influenced by the considerable differences in electronic structure and geometry of the central groups. Increase in the geometrical anisotropy of the molecule can be regarded as a factor favouring formation of a mesomorphic state, regardless of the presence of anisotropy of the π-electron polarisability.

The cholesteric liquid crystals known at the present time contain one or more asymmetric carbon atoms, although a cholesteric mesophase can probably be formed by molecules containing other chiral units. These liquid crystals are formed not only by steroids but also by compounds containing an asymmetric carbon atom in an alkyl chain, e.g. (IV). As racemates such compounds form nematic liquid crystals, but in optically active form give a cholesteric mesophase. The thermodynamic properties of the nematic (racemic) phase are identical with those of the cholesteric phase. Ideas developed for nematic liquid crystals can be applied to the relation between structure and cholesteric mesogenicity.

Table 6. Clear points of esters of *p*-n-butyoxyphenol [120]



X	d, Å	T_{cl}, °C	X	d, Å	T_{cl}, °C
	3.5	92		10.0	157
	7.8	94		10.0	220
	8.15	99.5		9.6	221
	7.8	144		9.75	226
				9.6	235
				9.75	241
				13.95	358

The general demands on structure of potentially smectic substances are the same as for nematic compounds. A specific aspect is that smectic liquid crystals consist of molecules having a longer terminal substituent. Thus in homologous series [2] the lower members are nematic, intermediate members possess smectic and nematic properties, and the higher members form smectic liquid crystals. Another feature of smectic mesophases is the significant role of permanent dipole moments in ensuring smectic ordering, as is evident both from theory (Section II, 2) and from dielectric data (Section III, 2). Specific comparisons of chemical structure and properties (in particular transition temperatures) require accurate knowledge of the structure of the smectic mesophase. Although smectic liquid crystals have been found in many classes of compounds, precise identification of the mesophase (S_A, S_B, S_C, etc.) has been accomplished only in rare cases, and conclusions on the relation between structure and properties cannot be correct at the present time.

3. Dielectric Properties of Liquid Crystals

Dielectric properties are an important characteristic of liquid crystals, determining in the case of nematics the possibility of their use in electro-optical devices. Thus those having a small negative dielectric anisotropy $\Delta\epsilon$ are used in instruments based on the dynamic scattering effect, whereas liquid crystals having a large positive or negative anisotropy $\Delta\epsilon$ are employed in devices based on field orientational effects. Threshold voltages (Eqn.8)

and connection times of field orientational effects depend on this anisotropy[12]:

$$\tau_{conn} = \frac{4\pi\gamma_1 d^2}{\Delta\varepsilon U^2 - 4\pi^3 K_i}, \quad (14)$$

where K_i is the coefficient of elasticity, γ_1 the coefficient of viscosity, and d the thickness of the layer of liquid crystals.

The dielectric constants of liquid crystals are determined in flat cells on specimens oriented by the walls or by an external magnetic field. Owing to the difficulties of obtaining uniformly oriented specimens of smectic liquid crystals, their dielectric properties have been studied less fully.

Application of an external electric field to an isotropic liquid causes a static polarisation P equal to the sum of the orientational, electronic, and atomic polarisations and depending on the strength E of the applied field and the dielectric constant ϵ of the liquid[121]:

$$P = P_o + P_e + P_a = \frac{\varepsilon - 1}{4\pi} \cdot E \quad (15)$$

The orientational polarisation P_O is determined by the magnitude and direction of the permanent dipole moment, and for non-polar molecules $P_O = 0$. The electronic polarisation P_e depends on the ease of displacement of the electron orbitals relative to the nuclei under the influence of the electric field, i.e. on the electronic polarisability α:

$$P_e = \frac{4}{3}\pi N\alpha . \quad (16)$$

For organic molecules the atomic polarisation is usually taken to be $P_a = 0.1 P_e$.[121]

The dielectric constants of liquid crystals are related to the degree of ordering S, the mean polarisability $\bar{\alpha}$, the anisotropy of polarisability of the molecule $\Delta\alpha$, the dipole moment μ, and its angle β relative to the long axis of the molecule[58]:

$$\frac{\varepsilon_\parallel - 1}{4\pi} = NhF\left[\bar{\alpha} + \frac{2}{3}\Delta\alpha S + F\frac{\mu^2}{3kT}\{1 - (1 - 3\cos^2\beta)S\}\right] \quad (17)$$

$$\frac{\varepsilon_\perp - 1}{4\pi} = NhF\left[\bar{\alpha} - \frac{1}{3}\Delta\alpha S + F\frac{\mu^2}{3kT}\left\{1 + \frac{1}{2}(1 - 3\cos^2\beta)S\right\}\right] \quad (18)$$

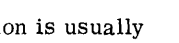
$$\frac{\Delta\varepsilon}{4\pi} = NhF\left\{\Delta\alpha - F\frac{\mu^2}{2kT}(1 - 3\cos^2\beta)S\right\} \quad (19)$$

where N is the number of molecules in unit volume, T K is the temperature, k is Boltzmann's constant, and h and F are factors representing the field in space and the Onsager reaction field. It follows from Eqns.(17)–(19), deduced from Onsager's theory of dielectrics, that the dielectric properties of liquid crystals are determined by the molecular parameters, the parameter S characterising the liquid-crystalline state, and the temperature, where S is strongly dependent on temperature, but the other parameters vary little. Equation (19) indicates that, for molecules having $\mu = 0$ and for those having $\mu \neq 0$ with $3\cos^2\beta = 1$ (i.e. with $\beta = 55°$), the anisotropy $\Delta\epsilon$ is determined by the value of $\Delta\alpha$.

Equations (17)–(19) have been tested quantitatively on *pp'*-dimethoxyazoxybenzene[122]. Comparison of the angles β determined by three different methods gave values of 65°, 62°, and 75° obtained from dielectric measurements, the Kerr constant, and group dipole moments respectively. The first two methods yield similar values, but the high value obtained by the third method is attributed[122] to the absence of accurate data on the angle of the dipole moment of the azoxy-group. Use of these formulae to determine dielectric constants is restricted by the lack of accurate data on molecular polarisabilities, dipole moments, and the angles β. Nevertheless, Eqns.(17)–(19) can be used for a qualitative and semi-quantitative interpretation of experimental results.

Table 7. Dielectric constants of nematic liquid crystals of



No.	R	R'	X	$\varepsilon_\parallel$	$\varepsilon_\perp$	$\Delta\varepsilon$	Reduced* temp. T/T_{cl}, K	Ref.
1	C_5H_{11}	C_5H_{11}	N=N	2.82	2.38	+0.44	0.97	124
2	C_7H_{15}	C_7H_{15}	N=N ↑ O	2.71	2.31	+0.4	0.97	124
3	C_5H_{11}	C_5H_{11}	N=N	3.74	3.50	+0.24	0.97	124
4	$C_6H_{13}O$	OC_6H_{13}	N=N	3.26	3.22	+0.04	0.97	122
5	$C_6H_{13}O$	CN	N=N	22.3	11.2	+11.1	0.97	122
6	C_5H_7	C_5H_{11}	COO	4.56	4.28	+0.28	0.98	123
7	$C_5H_{11}O$	C_4H_9O	COO	5.12	5.32	−0.20	0.98	123
8	$C_5H_{11}O$	CN	COO	27.80	11.66	+16.14	0.98	123
9	CN	OC_5H_{11}	COO	11.60	6.04	+4.56	0.98	123
10	CH_3O	$OCOCH_3$	CH=N	5.68	6.60	−0.92	0.98	123
11	C_5H_7O	$OCOCH_3$	CH=N	5.54	5.94	−0.40	0.98	123
12	$C_7H_{15}O$	$OCOCH_3$	CH=N	5.08	5.33	−0.25	0.98	123
13	$C_5H_{11}O$	CN	CH=N	22.63	9.82	+12.81	0.98	123
14	CN	OC_5H_{11}	CH=N	17.23	7.87	+9.36	0.98	123
15	C_7H_{15}	CN	COO––COO	37.7	7.8	+29.9	125° C	122
16	C_2H_5O	OC_6H_{13}	C(CN)=CH	6.4	11.3	−5.3	60° C	125

*Reduced temperatures are used to eliminate the implicit dependence of ϵ on T involved in the parameter S in Eqns.(17)–(19).

The measured dielectric constants of liquid crystals (Table 7) clearly indicate the significant part played by permanent dipole moments in determining the dielectric properties. Non-polar molecules (No.1 and 2) have small values of ϵ and $\Delta\epsilon$, which increase somewhat on introduction into the molecule of weakly polar substituents (alkoxy-groups) or a polar central bond (azoxy, azomethine, or ester groups). The greatest effect is exerted by the nitrile group ($\mu = 4.18$), which, depending on the position at which it is introduced, may produce either a large positive anisotropy $\Delta\epsilon$ (No. 4, 8, 13, and 15) or a large negative value (No. 16).

A quantitative assessment of the role of group dipole moments in determining dielectric constants was obtained by comparing calculated molecular dipole moments with the effective values determined from dielectric measurements[123]. Calculation, which took into account the degree of order S, was based on projections of the dipole moment of each group on the long and short axes of the molecules ($\mu_{i\parallel}$ and $\mu_{i\perp}$):

$$\mu_\parallel^{theor} = \left[\sum \mu_{i\perp}^2 \cdot (1 - S) + (1 + 2S) \cdot \left(\sum \mu_{i\parallel}\right)^2\right]^{1/2} \quad (20)$$

$$\mu_\perp^{theor} = \left[\sum \mu_{i\perp}^2 \cdot \left(1 + \frac{S}{2}\right) + (1 - S) \cdot \left(\sum \mu_{i\parallel}\right)^2\right]^{1/2} . \quad (21)$$

The μ_i values used in the calculations are given in Table 8. Dipole moments were determined from dielectric measurements by means of formulae analogous to those proposed by Onsager for isotropic dielectrics [123]:

$$\mu_{\parallel}^{exp} = \frac{9kT}{4\pi N} \frac{(\varepsilon_{\parallel} - \bar{n}^2) \cdot (2\varepsilon_{\parallel} + \bar{n}^2)}{\varepsilon_{\parallel} (\bar{n}^2 + 2)^2} \quad (22)$$

$$\mu_{\perp}^{exp} = \frac{9kT}{4\pi N} \frac{(\varepsilon_{\perp} - \bar{n}^2)(2\varepsilon_{\parallel} + \bar{n}^2)}{\varepsilon_{\parallel} (\bar{n}^2 + 2)^2}, \quad (23)$$

where $\bar{n}$ is the mean refractive index of the liquid crystal. Measurements of the dielectric constant were made at a temperature of 0.98 T_{cl} K, with the degree of order taken to be $S = 0.4$. In all the examples cited [123] μ^{theor} exceeds μ^{exp} usually by at most 30%. Thus data on group dipole moments can be used to determine the sign of $\Delta\epsilon$ and to estimate dielectric constants.

Table 8. Group dipole moments μ_i. [123]

Group	μ_i	μ_i	$\mu_{i\parallel}$	$\mu_{i\perp}$
Ph—C(=O)—O—Ph	↗	1.90	0.89	0.68
Ph—C(=H)—N—Ph	↘	1.57	0.40	1.51
Ph—CH_3	←	0.37	−0.37	0
Ph—CN	→	4.18	4.18	0
Ph—O—CH_3	↙	1.28	−0.40	1.22
Ph—O—C(=O)—CH_3	↖	1.69	−0.69	1.54

Introduction into the molecule of a nitrile group with a dipole moment directed along the long axis leads to increases not only in $\epsilon_{\parallel}$ but also in $\epsilon_{\perp}$ (Table 7). This is a consequence of the imperfect orientation of molecules in the liquid-crystalline phase ($S \neq 1$).

Changing the sites of substituents has different effects on $\epsilon_{\parallel}$ in azomethines (Table 7, No. 13 and 14, $\epsilon_{\parallel} = 22.6$ and 17.2) and in esters (No. 8 and 9, 27.8 and 10.6). In both cases $\epsilon_{\parallel}$ is determined mainly by the group dipole moment of the nitrile group, to which is added (No. 8 and 13), or from which is subtracted (No. 9 and 14), the parallel component of the ester ($\mu_{\parallel} = 0.89$) or azomethine ($\mu_{\parallel} = 0.40$) the central group. Since the component $\mu_{\parallel}$ of an ester group is more than double that of an azomethine group, the observed effects are also more pronounced in the esters. In the case of liquid crystals having slight anisotropy $\Delta\epsilon$ transposition of substituents may lead to change not only in the dielectric constant but also in the sign of $\Delta\epsilon$. This has been observed in isomeric phenyl benzoates [126] and 4(4′)-butyl-4′(4)-methoxyazoxybenzene [127] (incidentally, our results indicate that the characteristics measured in Ref. 126 do not apply to the same isomer).

The dielectric constants of liquid crystals depend not only on molecular structure, degree of order, and temperature but also on the frequency of the applied electric field (Section III, 2).

VI. LIQUID-CRYSTALLINE MATERIALS

1. General Requirements

The practical utilisation of thermotropic liquid crystals requires a set of properties that individual liquid-crystalline componds do not usually possess. For example, the working substance in indicator devices operating on the dynamic scattering effect should be in a liquid-crystalline state throughout the temperature range in which the device functions (laboratory and domestic instruments require liquid crystals melting at or below 0°C and clearing at or above 50°C). The electrical conductivity should be sufficient for an effect to appear ($\geq 10^{-10}$ ohm^{-1} cm^{-1}) but at the same time not too high ($< 10^{-7}$ ohm^{-1} cm^{-1}), so that electrolytic processes that would lower the operating resources of the instrument are slowed down and the consumption of energy is diminished. The working substance should have a slight negative dielectric anisotropy ($\Delta\epsilon$ from −0.2 to −0.6), with definite viscosity characteristics to ensure acceptable durability (until the appearance of scattering) and relaxation times (around 100 ms), it should be photochemically stable, and it should be oriented in the cell in a specified manner. Several less fundamental requirements (stability in moisture, atmospheric oxygen, etc.) may be satisfied by the technique of filling and hermetically sealing the indicator cell.

For indicators operating on orientational effects the working substance should usually have positive dielectric anisotropy, but the conductivity requirement is significant only in the sense that diminishing the conductivity (to $< 10^{-12}$ ohm^{-1} cm^{-1}) may considerably increase the operating resources and decrease the consumption of current.

Cholesteric liquid crystals for thermographic purposes should operate in a specified temperature range (sometimes very narrow, < 1 deg), have high thermal sensitivity, and be resistant to light and chemical attack by the atmosphere.

As a consequence of the above and several other requirements, individual compounds are not used for practical application, but more or less complicated compositions or liquid-crystalline materials.

2. Liquid-crystalline Mixtures

Mixtures of two or more liquid crystals are used to achieve the required temperature range for a nematic mesophase. Attempts are made to find a eutectic composition, at which the melting point passes through a well defined minimum for a given combination of individual components, whereas the variation of the clear point is approximately linear. Fig. 15 shows the phase diagram for a binary mixture of *p*-cyanophenyl *p*-hexylbenzoate (A) and *p*-heptylbenzoate (B). [128] The maximum temperature range of existence of the mesophase (~30 deg) evidently corresponds to the eutectic mixture, containing ~50% of component B. The problem of finding the eutectic of binary and ternary mixtures can be solved by simple trial and error, although this is quite laborious in the latter case. With four or more components trial and error is unsuitable, and the thermodynamic constants of the components and mathematical methods must be employed to find the optimum composition.

On the assumption that mixtures of structurally similar components are nearly ideal solutions the composition and

the melting point of the eutectic of an i-component mixture can be calculated from a set of i le Châtelier–Schröder–van Laar equations [129,130] containing i unknowns

$$\begin{cases} \ln X_1 = \frac{\Delta H_1}{R} \cdot \left(\frac{1}{T_m} - \frac{1}{T_{m1}}\right) \\ \cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \ln X_i = \ln(1 - X_1 - \ldots - X_{i-1}) = \frac{\Delta H_i}{R} \cdot \left(\frac{1}{T_m} - \frac{1}{T_{mi}}\right), \end{cases} \quad (24)$$

where X_i, $T_{m,i}$, and ΔH_i are respectively the mole fraction, the melting point, and the heat of fusion of the ith component, and $R = 8.314$ J mole^{-1} deg^{-1}. The clear point of such systems can be calculated with sufficient accuracy by means of the equation [131]

$$T_{cl} = \sum X_i T_{cl\,i}, \quad (25)$$

in which $T_{cl,i}$ is the clear point of the ith component.

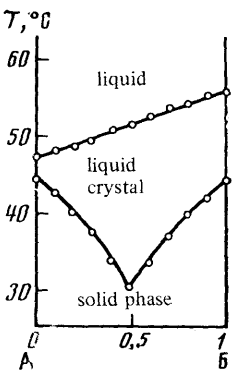


Figure 15. Diagram of phase transitions of p-cyanophenyl: A) p-hexylbenzoate; B) p-heptylbenzoate.

In several cases (biphenyls, azoxy-compounds) the calculated values agree well with experiment, but this method is not universally applicable. Thus clearing temperatures calculated for liquid-crystalline p-cyanophenyl p-alkylbenzoates differ considerably (by up to 20 deg) from the experimental values [132]. In these cases the problem of finding the eutectic composition can be solved by a simplex method of experiment design [133] consisting in an initially arbitrary (approximate) choice of composition and "step" for its variation, experimental determination of the melting points of $i + 1$ mixtures (where i is the number of components), and mathematical treatment of the results [133], followed by choice of a new initial composition and interval of variation until a eutectic with specified properties is attained.

Even the first experiments on the use of this method have shown [128] that good results can be obtained with a comparatively small number of experiments. Thus it was necessary to measure the melting points of only eight mixtures in order to find the eutectic composition of the ternary system of mixed carbonates p-$C_4H_9C_6H_4COO$-p'-C_6H_4OCOOR (R = C_6H_{13}, C_7H_{15}, C_8H_{17}), and the calculated melting point (68.5°C) coincided with the value determined from the thermogram. Calculation based on Eqn.(24) gave too low a melting point (63°C) for the eutectic mixture [128].

Even more complicated problems than lowering the temperature of formation of the mesophase and extending the temperature range of its existence are solved by trial-and-error selection of the component composition of liquid-crystalline mixtures. For example, materials with a relatively small positive dielectric anisotropy $\Delta\epsilon$ and a wide temperature range of the mesophase can be used in indicator devices operating on the field effect. Yet the large majority of liquid-crystalline compounds of this type are benzonitrile derivatives [134] having a large dielectric anisotropy [19] and high melting points. By mixing liquid crystals having a large positive dielectric anisotropy with low-temperature liquid crystals having a small negative dielectric anisotropy we can select a composition satisfying the above requirements. Thus mixing in different ratios p-p'-butoxybenzylidenaminobenzonitrile (BBABN) ($\Delta\epsilon = +19$ at 63°C, [135] m.p. 64°C, T_{cl} = 105°C) with a 2 : 1 mixture of p-butyl-N-p'-methoxybenzylidenaniline (BMBA) and p-butyl-N-p'-ethoxybenzylidenaniline (BEBA) ($\Delta\epsilon = -0.46$ at 25°C, m.p. −12°C, T_{cl} = 48°C) we can obtain the mixtures listed in Table 9 [136,137].

Table 9. Effect of additions of BBABN on phase transition temperatures and sign of dielectric anisotropy of mixtures of BMBA and BEBA.

Mixture, mass %		T_m, °C	T_{cl}, °C	$\Delta\epsilon$ at 24°C
⅓BEBA + ⅔BMBA	BBABN			
100	0	−12	+48	−0.5
99.1	0.9	−13	+49	−0.3
98.2	1.8	−13	+50	−0.1
95.5	4.5	−10	+52	+0.7
92.0	8.0	−2	+55	+1.5
85	15.0	+2	+60	+3.2
69	31.0	+22	+74	+6.5
0	100	+64	+105	+18.0 (64° C)

Admixture of non-mesophasic compounds having a large dipole moment and compatible with the liquid crystal can be used to control the sign and the magnitude of the dielectric anisotropy. Thus additions of 2% and 7% of p-dimethylaminobenzonitrile [138] to a mixture of azoxy-compounds (Merck, m.p. = −5°C, T_{cl} = +75°C, $\Delta\epsilon = -0.2$) yields respectively $\Delta\epsilon = +1.1$ and +3.8 with a fall in the clear point (67 and 48°C).

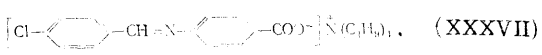
3. Additions for a Specified Conductivity

As already remarked above, liquid-crystalline materials in devices using dynamic scattering should have a definite electrical conductivity. Well purified liquid crystals are considerably less conducting than is required, and do not exhibit dynamic scattering of light. Unpurified substances, although scattering light on application of an electric field, cannot be used technically, since the nature and the content of their impurities are practically uncontrollable, depend on the quality and the "previous history" of the raw material, are sensitive to slight changes in the conditions of production and purification, etc.

In practice materials of specified conductivity and threshold voltage are obtained by the use of ionic additives or electron donors and acceptors [139], which probably form charge-transfer complexes with the components of the liquid-crystalline material. In the latter case the increase

in conductivity is caused by dissociation of the charge-transfer complexes into ions [71]. Acceptor additives [139] (tetracyanoquinodimethane, tetracyanoethylene, dichlorodicyanobenzoquinone), when introduced into mixtures of liquid-crystalline azoxy-compounds, effectively increase the conductivity with slight anisotropy (i.e. the ratio $\sigma_{\parallel}/\sigma_{\perp}$) and raise the threshold of dynamic scattering in an alternating current [83]. The conductivity of *p*-butyl-*N*-*p*′-methoxybenzylidenaniline was greatly increased by introduction of the charge-transfer complex of benzoquinone and quinol [142].

Tetra-alkylammonium halides can be used as ionic additives for nematic liquid crystals [140], with the anisotropy of the conductivity increasing with decrease in the ionic radius of the halogen. Choice of ions that are "compatible" with the structure of a given liquid crystal enables us to diminish such undesirable side-effects as fall in the temperature of transition to an isotropic liquid and decrease in the degree of ordering of the liquid crystals. Thus the use has recently been proposed [141] of additions of tetrabutylammonium salts of substituted benzoic acids p-$RC_6H_4COON(C_4H_9)_4$ (where R = NO_2, Cl, NH_2, CH_3, etc.) or threadlike compounds, e.g.



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4. Orienting additions

As already noted above, liquid crystals in electro-optical cells should be oriented parallel or perpendicular (homotropically) to the walls. Such orientation can be attained by chemical or mechanical treatment of the surfaces, as well as by introducing into the liquid crystals orienting additives that are adsorbed on the surface [143], the orienting effect being determined in the latter case by the chemical nature of the additive, the surface, and the liquid crystal, as well as by the topology of the surface.

An example of an orienting addition is 0.5% of polyamide resin introduced into *p*-butyl-*N*-*p*′-methoxybenzylidenaniline and Schiff bases of similar structure to ensure their homotropic orientation [144,145]. Lecithin [146] and silicone oil [146,147] applied to glass have a similar effect. Addition of 0.25–2.5% of hexadecylammonium bromide to nematic liquid crystals [148] also leads to their homotropic orientation, whereas smaller quantities of the additive produce planar orientation [149], since the additive molecules are then able to "lie" on the electrode surface.

Orienting additives of various classes—amines, carboxylic acids, etc.—are known, most of which change chemically during operation of the cell, so that their orienting influence becomes weaker. At the present time, therefore, silane surface-bonding agents have found application [150]; they react chemically with the glass or quartz, which improves considerably their reliability. Various types of orientation can be obtained depending on the geometry chosen for the additive. Thus homotropic orientation of liquid crystals is ensured by $C_{18}H_{37}N^{+}(CH_3)_2 \cdot [CH_2]_3Si(OCH_3)_3Cl^{-}$ hydrolysed on glass, with vertical octadecyl groups, and planar orientation by $CH_3NH[CH_2]_3 \cdot Si(OCH_3)_3$ molecules.

It is clear from the above that the production of liquid-crystalline materials is a quite complicated scientific and technical problem. No materials have yet apeared that satisfy all the technical requirements [151]. Improvement of the chemical and electrochemical stability of liquid crystals, extension of the temperature range of existence of the mesophase (especially to lower temperatures), decrease in the threshold and working voltages, improvement of the temporal characteristics, and other aspects are still urgent problems.

VII. FIELDS OF APPLICATION

The main peculiarity of liquid crystals is their ability to change their optical properties under the influence of almost any external factor. Therefore the number of applications suggested by various workers is immense. However, restricting consideration to those liquid crystals whose characteristics enable them to compete with traditional materials, we can distinguish the most important uses as electro-optical devices, thermography, spectroscopy, and certain others. Below we shall briefly examine several examples, with literature references only to the most typical papers, without any claim to completeness.

1. Electro-optical Devices

Because of the extremely low power consumption by the exciting source (10^{-4}–10^{-6} W cm^{-2} layer surface) nematic liquid crystals have already found wide application in indicators of numerical and graphic information for such electronic devices as wrist-watches and pocket calculators [152]. These instruments are autonomic (i.e. not connected to the mains), and in effect only liquid-crystalline "dials" are able to ensure that their batteries will function for a long time. Here it is important that not only the power input but also the supply voltage should be small (the latter a few volts), which makes it possible to use integral circuits as radio units. Indicators usually operate either on the dynamic scattering effect or on the twist effect, the latter similar to the Fréedericksz effect. The required numerals are displayed e.g. by feeding a voltage to a definite combination of segments of transparent electrodes formed into a typesetting "eight" (similar to that indicated by the postmark on envelopes). The range of possible application of indicators is, clearly, not restricted to watches and calculators. They can be used whenever information is to be displayed to human beings, e.g. in calculating machines, advertising panels, measuring instruments [153], control devices [154], etc. In all these cases the rapidity of response of the liquid crystals need not be better than 0.1 s (since the inertia of the human eye is almost the same), and liquid crystals can provide this with a symbol of high contrast range. Next is the production of coloured information indicators either by the use of dye molecules incorporated into liquid-crystalline matrices [155] or on the interference principle.

Another important trend in the electro-optics of liquid crystals is the attempt to produce a flat television screen for the reproduction of moving images [156]. Here the demands on the time characteristics of liquid crystals are far more severe, and success depends both on the development of liquid-crystalline materials with more rapid response and a more sharply defined threshold dependence of contrast on voltage and on the level of semiconductor technology necessary for the production of complicated mosaic devices for controlling the liquid-crystalline units. The preparation of new liquid crystals having diminished viscosity coefficients and increased elastic coefficients (to improve rapidity of response), is now the most important but hardly the most easily solved problem in the chemistry of nematic liquid crystals.

A third line of advance is the application of liquid crystals to optics[157], quantum electronics, holography, and equipment for the optical processing of information[158]. Here they are used to control the degree of coherence of a laser beam, for the phase modulation and deflection of beams with response in the millisecond range, for transforming an image from a cathode-ray tube (incoherent) to an image in coherent beams with subsequent registration on holograms, etc. Equipment has also been suggested for pictorial logic on liquid crystals[159].

Finally, electro-optical liquid-crystalline materials have been used to make X:ray, ultraviolet, and infrared images visible[160]. A film of the liquid crystals is placed in contact with a film of a photoconductor sensitive to the given spectral range. Variation of the electrical resistance of the photoconductor leads to variation in the voltage on the liquid-crystalline film with a corresponding change in its optical properties. The received (invisible) image can be made visible by means of an external liquid-crystalline intensifer. Procedures have also been proposed for visualisation of the emission of lasers without the use of photoconductors—by thermal effects in nematic[161], cholesteric[162], or smectic[163] liquid crystals. Defects in integral circuits can be visualised[164] by means of liquid crystals. A very complete survey of the most recent fields of application of liquid crystals has appeared[165].

2. Thermography

In virtue of the ability to reflect light selectively cholesteric liquid crystals find wide application in laboratories and in industry for the convenient visualisation of thermal fields and the measurement of temperature. Thermography by means of such mesophasss can be widely used also for detecting external factors leading to change in temperature, such as optical, X-ray, microwave, and radioactive emissions, currents of air, etc.

Portions of the human skin lying over malignant tumours and certain other seats of inflammatory processes have a rather higher temperature, and the use of cholesteric liquid crystals in polymer films (or applied directly to the skin) provides an effective method for locating foci of disease[4,166-168].

The high resolving power of cholesteric liquid crystals (of the order of the thickness of a layer, i.e. 20–90 μm) permits their use in microelectronics to reveal technical defects in microcircuits[171,172], the thermography of the thermal fields of transistors[173], which will reveal the "hottest" sites, so that cooling can be provided for in advance, in order to improve the reliability of the circuit.

The possible use of cholesteric liquid crystals in aerodynamic experiments[174] can be based on differences in the rate of cooling of the preheated mesophase depending on the rate of flow around the model.

Devices enabling the distribution of light flux across the diameter of a laser beam have been based on cholesteric liquid crystals[175]. The latter can be used also to determine internal stresses and defects in metals and alloys[176].

Further details of the thermographic applications of cholesteric liquid crystals can be found in Ref. 14. A detailed bibliography has been published[177] on the application of liquid crystals.

3. Spectroscopy

Use in spectral investigations may provide information either on the properties of the liquid crystal itself or on those of molecules dissolved in it. When liquid crystals are used as solvents, the spectra of oriented molecules can be obtained, since the long axes of dissolved molecules are oriented on the average parallel to the "director" of a nematic liquid crystal. The dissolving power of liquid crystals is almost equivalent to that of ordinary isotropic solvents, and an appropriate liquid-crystalline solvent can be selected for any substance. Such investigations are restricted by the absorption of light by the liquid crystal itself. For example, the use in ultraviolet spectroscopy of nematic mesophases containing aromatic or heteroaromatic rings is limited by the intrinsic absorption at wavelengths shorter than 350 nm. This limit can be shifted to 250 nm by using a compensated cholesteric phase as solvent[178,179] or a nematic liquid crystal based on cyclohexane. The ultraviolet or infrared spectra of oriented liquid crystals can be used to determine the polarisation of the moments of electronic or vibrational transitions in the molecules forming the liquid crystals[40,180,181], by the application of polarised radiation (parallel or perpendicular to the "director").

Examination of the dichroism of the electronic absorption by impurity molecules of dyes (or related compounds) in oriented liquid crystals and matrices[182] permits determination of the direction of the electron oscillators in these molecules, leading in several cases to conclusions on the geometrical configuration of the molecule. For example, determination of the directions of the oscillators of two long-wavelength bands due to symmetrical biscyanine dyes shows that these oscillators are mutually perpendicular[183]. The directions of oscillators in molecules of aromatic hydrocarbons have been determined by the same method[184]. Analysis of the dichroism of liquid crystals of solutions of autocomplexes of 1,4-naphthaquinone and 1,3,5-trinitrobenzene provides indications on the molecular geometry of the complexes and in several cases refinement of the specific mechanism of intramolecular charge transfer in these compounds[185]. By measuring the dichroism of rod-shaped impurity molecules, we can also investigate the structure of the liquid-crystalline matrices themselves[57].

Even at concentrations of 1–2% the dissolution of chiral compounds in a nematic liquid crystal converts the latter into a cholesteric phases (induced cholesteric liquid crystals[186,187]). Since the specific rotation of a cholesteric phase is a thousandfold that of any isotropic solution, it has been proposed to use this effect as a method of proving the chirality of molecules possessing very small specific rotations or present in small quantities. The helical pitch of an induced cholesteric liquid is in most cases so large that the selective reflection lies in the infrared[188]. The pitch and the direction of the helix have been determined from the dispersion curves of optical rotation in the infrared[189].

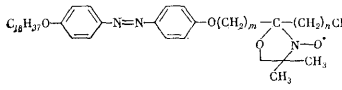
The addition of chiral molecules to a C smectic also produces a twist in its structure, the pitch in this case being about the same as for nematic–cholesteric mixtures[190].

Optically inactive molecules dissolved in a cholesteric liquid crystal exhibit in an absorption band circular dichroism induced by the liquid crystal[191,192]. This dichroism is caused not simply by the helical ordering of the dissolved molecule in the cholesteric matrix but by electronic or magnetic interactions of the chromophore of the solute molecule with the solvent[193]. The molar amplitude of the induced dichroism ($\sim 10^7$ deg cm^2) is tenfold that of the circular dichroism in chiral hexahelicene (8.62×10^5 deg cm^2).[194] The directions of polarisation

of the moments of optical transitions have been determined for the dissolved molecule from the sign of the induced dichroism [191-193].

The largest number of spectroscopic investigations using liquid crystals have been made in the nuclear magnetic resonance range. Several reviews have been published on this aspect [14,195,199,210]. The n.m.r. spectra of a liquid-crystalline phase contain considerably more lines than do the spectra of an isotropic liquid. This is due to the presence of direct interactions between protons, which vanish in the isotropic state because of the high rotational mobility of the molecules. The degree of ordering of a liquid crystal can be determined from the n.m.r. spectra, and measurement of relaxation times will give information on the dynamics of orientational fluctuations in these systems. The fine structure of n.m.r. spectra may disappear with liquid crystals whose molecules contain many interacting protons. Such liquid crystals can be used as solvents; the resonance lines of a dissolved molecule are then observed on a smooth background. The n.m.r. spectra of simple molecules in anisotropic matrices are used to determine bond angles and lengths in the molecules.

Quite a large number of studies have been made on the use of liquid crystals in electron spin resonance spectroscopy [14,197,198]. Nematic, smectic, and compensated cholesteric liquid crystals are used as solvent. Employment of a liquid-crystalline solvent will give more complete information on the e.s.r. spectra of polyradicals. An interesting example of the use of e.s.r. spectroscopy to investigate the structures of liquid crystals is an examination of the mobility of the alkyl chains in *pp'*-dioctadecyloxyazoxybenzene [199]. Compounds of the type


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well miscible with the liquid crystal, were added (0.3%) as spin label. Transition from the solid phase of the azoxybenzene derivative to the smectic *B* phase was shown to be accompanied by increase in the mobility of the alkyl chains, and on passing from smectic *B* to smectic *C* the angle between the long axes of the molecules and the smectic plane increased.

Mössbauer spectroscopy has been used to determine the structural parameters of smectic phases [200]. The possibility has been demonstrated [201] of determining the ordering tensor of the Mössbauer label from its γ-resonance spectra in nematic and cholesteric mesophases.

4. Other Examples

Here we shall mention only those new trends in the application of liquid crystals on which information has appeared quite recently and which appear to be especially interesting. It has been proposed to use liquid crystals for the visualisation of ultrasonic fields and to record acoustic holograms [202], for visualisation of the distribution of mechanical stresses in various rigid objects, and to analyse gases and vapours [15].

Owing to the ordered character of a mesophase, rodlike impurity molecules dissolve in it better than do branched molecules. Ths forms the basis for the use of liquid crystals as stationary phase for the separation of isomers in gas–liquid chromatography [203,204]. Their use as anisotropic solvents in chemical reactions also is extremely promising. Both the mechanism and the kinetics of the reaction may be changed. Examples are molecular rearrangements [205,206] and polymerisations in the liquid-crystalline state [207,208].

Among important practical results may be cited the discovery of ferroelectricity in a chiral *C* smectic [26,209]. Liquid ferroelectrics may be extremely useful in nonlinear optics (e.g. for regenerators of the second harmonic of light with high resistance to laser emission); they can be used in new forms of piezo- and pyro-transducers, memory devices, etc.

REFERENCES

1. G. H. Brown and J. W. Doane, Appl. Phys., 4, 1 (1974).
2. D. Demus, H. Demus, and H. Zaschke, "Flüssige Kristalle in Tabellen", VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1974.
3. R. D. Ennulat, L. E. Garn, and J. D. White, Mol. Cryst. Liq. Cryst., 26, 245 (1974).
4. I. G. Chistyakov, "Zhidkie Kristally" (Liquid Crystals), Nauka, Moscow, 1966.
5. G. W. Gray, "Molecular Structure and Properties of Liquid Crystals", Academic Press, New York, 1962.
6. G. H. Brown, G. W. Doane, and V. D. Neff, "A Review of the Structure and Physical Properties of Liquid Crystals", Butterworths, London, 1971.
7. G. H. Brown and W. G. Shaw, Chem. Rev., 57, 1049 (1957).
8. J. Castellano, RCA Rev., 33, 296 (1972).
9. G. W. Gray and P. A. Winsor (Editors), "Liquid Crystals and Plastic Crystals", Ellis Horwood Ltd., Chichester, 1974.
10. P. G. de Gennes, "The Physics of Liquid Crystals", Clarendon Press, Oxford, 1974.
11. M. Y. Stephen and J. P. Straley, Rev. Mod. Phys., 46, 617 (1974).
12. L. M. Blinov, Uspekhi Fiz. Nauk, 114, 67 (1974).
13. A. P. Kapustin, "Elektroopticheskie i Akusticheskie Svoistva Zhidkikh Kristallov" (Electro-optical and Acoustic Properties of Liquid Crystals), Nauka, Moscow, 1973.
14. S. Chandrasekhar and N. V. Madhusudana, Appl, Spectroscopy Rev., 6, 189 (1972).
15. D. Ferguson, Fiz. Tverd. Tela, No. 7 (1972).
16. Ber. Bunsenges. phys. Chem., 78, 811–968 (1974).
17. M. G. Friedel, Ann. Phys., 18, 273 (1922).
18. H. Kelker, B. Scheurle, R. Hatz, and W. Barsch, Angew. Chem., 82, 984 (1972).
19. V. V. Titov, E. I. Kovshev, A. I. Pavluchenko, V. T. Lazareva, and M. F. Grebenkin, J. Phys. (France), 36, Colloq. Cl, C-387 (1975).
20. I. H. Page and H. Rudy, Biochem. Z., 20, 304 (1930).
21. D. Dolphin, Z. Muljiani, J. Cheng, and R. B. Meyer, J. Chem. Phys., 58, 413 (1973).
22. A. de Vries, Fifth International Liquid Crystal Conference, Abstracts, Stockholm, 1974, p. 150.
23. D. Coates, K. J. Harrison, and G. W. Gray, Mol. Cryst. Liq. Cryst., 22, 99 (1973).
24. K. Herrmann and A. H. Krummacher, Z. Krist. Kristallgeom. Abt., A81, 317 (1932).
25. H. Schubert, R. Hacker, and K. Kindermann, J. prakt. Chem. [4], 37, 12 (1968).
26. R. B. Meyer, L. Liébert, L. Strzelecki, and R. Keller, J. Phys. Letters, 36, L-69 (1975).
27. D. Demus, G. Kunicke, J. Neelsen, and H. Sackmann, Z. Naturforsch., 23a, 84 (1968).
28. S. Diele, Phys. Stat. Sol. (*a*), 25, K183 (1974).

29. J. Doucet, A. M. Levelut, M. Lambert, L. Liebert, and L. Strzelecki, J. Phys. (France), 36, Colloq. Cl, C-13 (1975).
30. G. Kraus, K. Seifert, H. Zaschke, and H. Schubert, Z. Chem., 11, 22 (1971).
31. J. Timmermans, Bull. Soc. chim. belg., 44, 17 (1935).
32. H. Sackmann and D. Demus, Fortschr. chem. Forsch., 12, 349 (1969).
33. W. J. Dunning, J. Phys. and Chem. Solids, 18, 21 (1961).
34. D. Demus, G. Kunicke, J. Neelsen, and H. Sackmann, Z. phys. Chem. (Leipzig), 255, 71 (1974).
35. B. K. Vainshtein, I. G. Chistyakov, G. G. Maidachenko, L. A. Gusakova, V. D. Belilovskii, V. M. Chaikovskii, L. K. Vistin', and S. P. Chumakova, Dokl. Akad. Nauk SSSR, 220, 1349 (1975).
36. W. Zwetkoff, Acta Physicochim, URSS, 16, 132 (1942).
37. A. Saupe and W. Maier, Z. Naturforsch., 15a, 287 (1960).
38. A. de Vries, J. Phys. (France), 36, Colloq. Cl, C-1 (1975).
39. M. Dvolaitzky, F. Poldy, and C. Taupin, see Ref. 22, p. 154.
40. W. Maier and A. Saupe, Z. Naturforsch., 14a, 882 (1959).
41. S. Chandrasekhar and N. V. Madhusudaha, Acta Cryst., A27, 303 (1971).
42. K Z. Ogorodnik, Fiz. Tverd. Tela, 17, 2761 (1975).
43. H. Baessler and M. M. Labes, J. Chem. Phys., 52, 631 (1970).
44. W. J. A. Goossens, Phys. Letters, 31A, 413 (1970).
45. H. Stegemeyer, Ber. Bunsenges. phys. Chem., 78, 861 (1974).
46. P. N. Keating, Mol. Cryst. Liq. Cryst., 8, 315 (1969).
47. I. E. Dzyaloshinskii, S. G. Dmitriev, and E. I. Kats, Zhur. Eksper. Teor. Fiz., 68, 2335 (1975).
48. K. K. Kobayashi, J. Phys. Soc. Japan, 29, 101 (1970).
49. W. L. McMillan, Phys. Rev., A4, 1238 (1971); A6, 936 (1972).
50. R. J. Mayer and W. M. McMillan, Phys. Rev., A9, 899 (1974).
51. A. de Vries, J. Chem. Phys., 61, 23 (1974).
52. D. Berreman, Phys. Rev. Letters, 28, 1683 (1972).
53. P. Chatelain, Bull. Soc. franc. Minér., 66, 105 (1943).
54. J. L. Janning, Appl. Phys. Letters, 21, 173 (1972).
55. F. J. Kahn, Appl. Phys. Letters, 22, 386 (1973).
56. P. Chatelain, Bull. Soc. franc. Minér., 50, 280 (1937).
57. L. M. Blinov, V. A. Kizel', V. G. Rumyantsev, and V. V. Titov, Kristallografiya, 20, 1245 (1975).
58. W. Maier and G. Meier, Z. Naturforsch., 16a, 262 (1961).
59. G. Meier and A. Saupe, in "Liquid Crystals" (Edited by G. Brown, G. Dienes, and M. Labes), Gordon–Breach Sci. Publ., New York, 1967, p. 195.
60. W. H. de Jeu and T. H. W. Lathouwers, Mol. Cryst. Liq. Cryst., 26, 225 (1974).
61. W. H. de Jeu, T. H. W. Lathouwers, and P. Bordewijk, Phys. Rev. Letters, 32, 40 (1973).
62. F. C. Frank, Discuss. Faraday Soc., 25, 19 (1958).
63. H. Gruler, Z. Naturforsch., 28a, 474 (1973).
64. S. Chandrasekhar, N. V. Madhusudana, and K. Shuba, Acta Cryst., A28, 28 (1972).
65. P. G. de Gennes, J. Phys. (France), 30, Colloq. C4, C4-65 (1969).
66. L. Cheng, R. B. Meyer, and H. Gruler, Phys. Rev. Letters, 31, 349 (1973).
67. V. N. Tsvetkov and G. M. Mikhailov, Zhur. Eksper. Teor. Fiz., 7, 1398 (1937).
68. J. Ericksen, "Liquid Crystals", Gordon and Breach, New York, 1969, Vol. 2, Part 1, p. 117.
69. Orsay Liquid Crystal Group, in "Liquid Crystals and Ordered Fluids" (Edited by J. Johnson and R. Porter), Plenum Press, New York, 1970, p. 195.
70. C. Gähwiller, Phys. Letters, 36A, 311 (1971).
71. M. I. Barnik, L. M. Blinov, and M. F. Grebenkin, "III Vsesoyuznaya Konferentsiya po Zhidkhim Kristallam, Tezisy" (Third All-Union Conference on Liquid Crystals—Abstracts), Ivanovo, 1974, p. 95.
72. W. Helfrich, Phys. Rev. Letters, 23, 372 (1969).
73. V. N. Tsvetkov and E. I. Ryumtsev, Kristallografiya, 13, 290 (1968).
74. W. F. Schmidt and A. O. Allen, J. Chem. Phys., 52, 4788 (1970).
75. V. Fréedericksz and V. Zolina, Trans. Faraday Soc., 29, 919 (1933).
76. V. G. Rumyantsev, P. D. Berezin, L. M. Blinov, and I. N. Kompanets, Kristallografiya, 18, 1104 (1973).
77. I. G. Chistyakov and V. N. Aleksandrov, Uch. Zap. Ivanovsk. Gos. Pedinst., 77, 34 (1970).
78. P. G. de Gennes, Solid State Comm., 6, 163 (1968).
79. A. Rapini, J. Phys. (France), 33, 237 (1972).
80. V. K. Fréedericksz and V. N. Tsvetkov, Dokl. Akad. Nauk SSSR, 9, 123 (1935).
81. G. N. Heilmeier, L. A. Zanoni, and L. A. Barton, Proc. IEE, 56, 1162 (1968).
82. L. S. Chou and E. F. Carr, Phys. Rev., A7, 1639 (1973); W. T. Flint and E. F. Carr, Mol. Cryst. Liq. Cryst., 22, 1 (1973).
83. M. I. Barnik, L. M. Blinov, M. F. Grebenkin, S. A. Pikin, and V. G. Chigrinov, Zhur. Eksper. Teor. Fiz., 69, 1080 (1975).
84. C. W. Smith, D. G. Gisser, M. Yong, and S. R. Powers, Appl. Phys. Letters, 24, 453 (1974).
85. T. Harada and P. Crooker, Mol. Cryst. Liq. Cryst., 30, 79 (1975).
86. P. Pollman and H. Stegemeyer, Chem. Phys. Letters, 20, 87 (1973).
87. J. Voss and E. Sackmann, Z. Naturforsch., 26, 1496 (1973).
88. H. Stegemeyer and K. J. Mainusch, Chem. Phys. Letters, 16, 38 (1972).
89. A. Wulf, J. Chem. Phys., 60, 3994 (1974).
90. H. Kozawaguchi and M. Wada, Japan. J. Appl. Phys., 15, 651, 657 (1975).
91. H. Stegemeyer and H. Finkelman, Chem. Phys. Letters, 23, 228 (1973).
92. J. Adams and W. Haas, Mol. Cryst. Liq. Cryst., 30, 1 (1975).
93. C. A. Lochmüller and R. W. Souter, J. Phys. Chem., 77, 3016 (1973).
94. L. A. Karamysheva, E. I. Kovshev, and V. V. Titov, Zhur. Org. Khim., 12, 2648 (1976).
95. V. V. Titov, E. I. Kovshev, L. A. Karamysheva, G. V. Purvanetskas, and V. K. Daukshas, Khim. Geterotsikl. Soed., 1364 (1975).
96. A. I. Pavluchenko, N. I. Smirnova, E. I. Kovshev, and V. V. Titov, "I Flüssigkristall. Konf. sozialist. Länder", Halle, 1976, Kurzref., 24.
97. J. van der Veen, W. H. de Jeu, M. W. M. Wanninkof, and C. A. M. Tienhoven, J. Phys. Chem., 77, 2153 (1973).
98. I. Haller, Progr. Solid state Chem., 10, Part 2, 103 (1975).

99. W.H. de Jeu, J. van der Veen, and W. J. A. Goosens, Solid State Comm., 12, 405 (1973).
100. J. P. Van Meter and B. H. Klanderman, Mol. Cryst. Liq. Cryst., 22, 285 (1973).
101. J. P. Schroeder and D. W. Bristol, J. Org. Chem., 38, 3160 (1973).
102. R. Steinsträsser, Z. Naturforsch., 27b, 774 (1972).
103. M. J. S. Dewar and J. P. Schroeder, J. Org. Chem., 30, 2296 (1965).
104. M. J. S. Dewar and R. S. Gobverg, J. Amer. Chem. Soc., 92, 1582 (1970).
105. L. A. Karamysheva, E. I. Kovshev, and V. V. Titov, Zhur. Org. Khim., 12, 1508 (1976).
106. A. I. Pavlyuchenko, E. I. Kovshev, V. V. Titov, and G. V. Purvanetskas, Zhur. Org. Khim., 12, 375 (1976).
107. A. I. Pavlyuchenko, E. I. Kovshev, and V. V. Titov, see Ref. 71, p. 195.
108. W. R. Young, A. Aviram, and R. J. Cox, J. Amer. Chem. Soc., 94, 3976 (1972).
109. J. van der Veen and A. H. Grobben, Mol. Cryst. Liq. Cryst., 15, 239 (1971).
110. R. E. Rondeau, M. A. Berwick, R. N. Steppel, and M. P. Serve, J. Amer. Chem. Soc., 94, 1096 (1972).
111. L. E. Knaak, H. M. Rosenberg, and M. P. Serve, Mol. Cryst. Liq. Cryst., 17, 171 (1972).
112. D. Demus, Z. Chem., 15, 1 (1975).
113. V. A. Usol'tseva and I. G. Chistyakov, Uspekhi Khim., 32, 1124 (1963) [Russ. Chem. Rev., No. 9 (1963)].
114. D. Coates and G. W. Gray, J. Phys. (France), 36, Colloq. C-1, C1-365 (1975).
115. R. D. Ennulat and A. J. Brown, Mol. Cryst. Liq. Cryst., 13, 357 (1971).
116. A. I. Pavlyuchenko, N. I. Smirnova, E. I. Kovshev, and V. V. Titov, Zhur. Org. Khim., 12, 1511 (1976).
117. S. Chandrasekhar and N. V. Madhusudana, Acta Cryst., A27, 303 (1971).
118. R. L. Humphries, P. G. James, and G. R. Luckhurst, J. Chem. Soc., Faraday Trans. II, 68, 1031 (1972).
119. A. Saupe, Ber. Bunsenges. Phys. Chem., 78, 848 (1974).
120. L. Verbit and R. L. Tuggey, "Liquid Crystals and Ordered Fluids", (Edited by J. Johnson and R. Porter), Plenum Press, New York, 1973, Vol. 2, p. 307.
121. V. I. Minkin, O. A. Osipov, and Yu. A. Zhdanov, "Dipol'nye Momenty v Organicheskoi Khimii" (Dipole Moments in Organic Chemistry), Khimiya, 1968.
122. W. H. de Jeu, Adv. Liquid Crystal Research, in the press.
123. R. T. Klingbiel, D. G. Genova, T. R. Criswell, and J. P. Van Meter, J. Amer. Chem. Soc., 96, 7651 (1974).
124. W. H. de Jeu and T. W. Lathouwers, Z. Naturforsch., 29a, 905 (1974).
125. W. H. de Jeu and J. van der Veen, Phys. Letters, 44A, 277 (1973).
126. W. H. de Jeu and T. W. Lathouwers, Z. Naturforsch., 30a, 79 (1975).
127. W. H. de Jeu and T. W. Lathouwers, Chem. Phys. Letters, 28, 239 (1974).
128. A. V. Ivashchenko and V. V. Titov, Zhur. Fiz. Khim., in the press.
129. E. C.-H. Hsu and J. F. Johnson, Mol. Cryst. Liq. Cryst., 20, 273 (1973).
130. D. S. Hulme and E. P. Raynes, Chem. Comm., 1974, 98.
131. R. L. Humphries, R. G. James, and G. R. Luckhurst, Symp. Faraday Soc., 5, 107 (1971).
132. A. V. Ivashchenko, V. V. Titov, and E. I. Kovshev, Mol. Cryst. Liq. Cryst., 33, 195 (1976).
133. V. G. Gorskii and V. Z. Brodskii, Zavod. Lab., 31, 831 (1965).
134. B. P. 1 273 779 (1972); Chem. Abs., 77, 54 808 (1972).
135. M. Schadt, J. Chem. Phys., 56, 1497 (1972).
136. M. F. Grebenkin, Candidate's Thesis, Scientific Research Institute of Organic Intermediates and Dyes, Moscow, 1976.
137. M. F. Grebenkin, V. A. Seliverstov, L. M. Blinov, and V. G. Chigrinov, Kristallografiya, 20, 984 (1975).
138. R. Steinsträsser and L. Pohl, Fifth International Conference on Liquid Crystals, Abstracts, Stockholm, 1974, p. 249.
139. A. Baise and M. M. Labes, J. Chem. Phys., 59, 551 (1973).
140. R. Chang, "Liquid Crystals and Ordered Fluids" (Edited by J. F. Johnson and R. S. Porter), Plenum Press, New York, 1973, p. 367.
141. T. Wada and F. Mito, see Ref. 138, p. 247.
142. M. Ozutzumi, Appl. Phys. Letters, 24, 213 (1974).
143. F. J. Kahn, G. N. Taylor, and H. Schonhorn, Proc. IEE, 61, 823 (1973).
144. W. Haas, J. Adams, and J. B. Flammery, Phys. Rev. Letters, 25, 1326 (1970).
145. US P. 3 687 515 (1972); Chem. Abs., 77, 146 264 (1972).
146. T. Ushida, H. Watanabe, and M. Wada, Japan J. Appl. Phys., 11, 1559 (1972).
147. French P. 2 165 565 (1972).
148. US P. 3 656 834 (1972); Chem. Abs., 77, 27 336 (1972).
149. J. E. Proust, L. Ter-Minassian Saraga, and E. Guyon, Solid State Comm., 11, 1227 (1972).
150. F. J. Kahn, Appl. Phys. Letters, 22, 111, 396 (1973).
151. L. Creagh, Proc. IEE, 61, 814 (1973).
152. L. A. Goodman, J. Vacuum Sci. Technol., 10, 804 (1973).
153. R. A. Soref, Appl. Opt., 9, 1323 (1970); Proc. IEE, 61, 384 (1973).
154. L. K. Vistin' and I. G. Chistyakov, Pribory Sistemy Upravleniya, 19 (1975); 45, 4718 (1974).
155. G. H. Heilmeier and L. A. Zanoni, Appl. Phys. Letters, 13, 91 (1968).
156. B. J. Lechner, F. J. Marlawe, E. O. Nester, and J. Tuets, Proc. IEE, 59, 1566 (1971).
157. V. I. Lebedev, V. I. Mordasov, and M. G. Tomilin, Opt.-mekh. Prom., 60 (1974).
158. I. N. Kompanets and V. V. Nikitin, Mikroelektronika, 3, 441 (1974).
159. V. A. Tsvetkov, N. A. Morozov, and M. I. Elinson, Kvant. Elektron., 1, 1785 (1974).
160. J. D. Margerum, J. Nimoy, and S. Y. Wong, Appl. Phys. Letters, 17, 51 (1970).
161. L. M. Klyukin, I. D. Samodurova, A. S. Sonin, B. M. Stepanov, and M. I. Epshtein, see Ref. 71, p. 157.
162. T. M. Ponomarenko and V. N. Sintsov, "I Nauchnaya Konferentsiya po Zhidkhim Kristallam, Sbornik Trudov" (First Scientific Conference on Liquid Crystals—Collected Papers), Ivanovo, 1972, p. 291.
163. C. Tani, Appl. Phys. Letters, 19, 241 (1971).

164. K. Thiessen and T. Le Tuyen, Phys. Stat. Sol., 13a, 73 (1972).
165. J. Borel, G. Labrunie, and J. Robert, J. Phys. (France), Colloq. C-1, 36, C1-215 (1975).
166. M. Gautherie, J. Phys. Radium, 30, C4, 122 (1969).
167. O. S. Selawry, H. S. Selawry, and J. F. Holland, Proc. First Internat. Conf. on Liquid Crystals (Edited by G. H. Brown, G. J. Dienes, and M. M. Labes), Gordon and Breach, New York, 1967, p. 175.
168. A. P. Savinov and Yu. M. Gerusov, see Ref. 71, p. 172.
169. R. T. Panchenkov, V. R. Ivanov, I. G. Chistyakov, and I. I. Gorina, see Ref. 71, p. 177*.
170. M. D. Moiseenko, M. V. Mukhina, and V. F. Mus, see Ref. 71, p. 182*.
171. W. E. Woodmansee, Materials Evaluation, 564 (Oct. 1966); see Ref. 9.
172. G. W. Lukianoff, "Liquid Crystals" (Edited by G. H. Brown), Gordon and Breach, New York, 1968, Vol. 2, Part 1, pp. 219, 222.
173. V. A. Golosov, A. I. Dudarchik, and A. E. Burasov, Electron. Tekh., Ser. 12, No. 6 (12), 77 (1971).
174. E. I. Klein, see Ref. 172, p. 225.
175. A. S. Sonin and B. M. Stepanov, Priroda, No. 11, 14 (1974).
176. W. E. Woodmansee, see Ref. 172, p. 228.
177. T. Kallard (Editor), "Liquid Crystals and their Applications", Optosonic Press, New York, 1970.
178. E. Sackmann, S. Meiboom, and L. C. Snyder, et al., J. Amer. Chem. Soc., 90, 3567 (1968).
179. E. Sackmann and D. Rehm, Chem. Phys. Letters, 4, 537 (1970).
180. W. Maier and G. Englert, Z. phys. Chem. (Frankfurt), 12, 123 (1957).
181. M. M. Kusakov, V. L. Khodzhaeva, M. V. Shishkina, and I. I. Konstantinov, Kristallografiya, 14, 485 (1969).
182. E. Sackmann, J. Amer. Chem. Soc., 90, 3509 (1968).
183. L. M. Blinov, G. G. Dyadyusha, F. A. Mikhailenko, I. L. Mushkalo, and V. G. Rumyantsev, Dokl. Akad. Nauk SSSR, 220, 860 (1975).
184. E. Sackmann and H. Möwald, Chem. Phys. Letters, 12, 467 (1972).
185. V. G. Rumyantsev, L. M. Blinov, Ya. F. Freimanis, and Ya. Ya. Dregeris, Zhur. Strukt. Khim., 16, 222 (1975).
186. H. Stegemeyer and K. J. Mainusch, Chem. Phys. Letters, 6, 5 (1970).
187. A. D. Buckingham, G. P. Ceasar, and M. B. Dunn, Chem. Phys. Letters, 3, 540 (1969).
188. E. H. Korte, S. Baulek, and B. Schrader, Ber. Bunsenges. phys. Chem., 78, 876 (1974).
189. Yu. V. Denisov, V. A. Kizel', V. V. Mnev, E. P. Sukhenko, and V. G. Tishchenko, Pis'ma v Zhur. Eksper. Teor. Fiz., 22, 242 (1975).
190. M. Brunet, J. Phys. (France), 36, Colloq. C-1, C1-321 (1975).
191. F. D. Saeva and J. J. Wysocki, J. Amer. Chem. Soc., 93, 5928 (1971).
192. H. Stegemeyer and K. J. Mainusch, Naturwiss., 58, 599 (1971).
193. F. D. Saeva, "Liquid Crystals and Ordered Fluids" (Edited by J. Johnson and R. Porter), Plenum Press, New York, 1974, p. 581.
194. R. Steinsträsser and L. Pohl, Angew. Chem., 85, 706 (1973).
195. A. Saupe, Mol. Cryst. Liq. Cryst., 16, 87 (1972).
196. P. Diehl and P. M. Henrichs, Nucl. Magn. Resonance, 1, 321 (1972)*.
197. G. R. Lukkharst, Uspekhi Khim., 40, 572 (1971) [Russ. Chem. Rev., No. 3 (1971)].
198. G. R. Fryburg, E. Gelerinter, and D. L. Fischel, Mol. Cryst. Liq. Cryst., 16, 39 (1971).
199. F. Poldy, M. Dvolaitsky, and C. Taupin, J. Phys. (France), 36, Colloq. C-1, C1-27 (1975).
200. V. I. Gol'danskii, O. P. Kevdin, N. K. Kivrina, E. F. Makarov, V. Ya. Rochev, and R. A. Stukan, "II Vsesoyuznaya Konferentsiya po Zhidkhim Kristallam, Sbornik Dokladov" (Second All-Union Conference on Liquid Crystals—Collected Papers), Ivanovo, 1973, p. 63.
201. V. I. Gol'danskii, O. P. Kevdin, N. K. Kivrina, V. Ya. Rochev, E. F. Makarov, R. A. Stukan, I. G. Chistyakov, and L. S. Shabyshev, "II Vsesoyuznaya Konferentsiya po Zhidkhim Kristallam, Sbornik Dokladov" (Second All-Union Conference on Liquid Crystals—Collected Papers), Ivanovo, 1973, p. 56.
202. R. K. Mueller, Proc. IEE, 59, 1319 (1971).
203. R. V. Vigalok and M. S. Vigdergauz, Izv. Akad. Nauk SSSR, Ser. Khim., 717, 718 (1972).
204. J. P. Schroeder, "Liquid Crystals and Plastic Crystals" (Edited by G. W. Gray and P. A. Winsor), Ellis Horwood Ltd., Chichester, 1974, p. 356.
205. M. J. S. Dewar and B. D. Nahlovsky, J. Amer. Chem. Soc., 96, 460 (1974).
206. S. I. Torgova, E. I. Kovshev, and V. V. Titov, I Flüssigkristal Konf. sozialist. Länder, Halle, 1976, Kurzref., p. 118.
207. Yu. V. Amerik and B. A. Krentsel', in "Uspekhi Khimii i Fizikokhimii Polimerov" (Advances in the Chemistry and the Physical Chemistry of Polymers), Nauka, 1973, p. 97.
208. L. Liebert and L. Strzelecki, Bull. Soc. chim. France, 1973, 603.
209. P. Pieranski, E. Guyon, and P. Keller, J. Phys. (France), 36, 1005 (1975).
210. A. Saupe, Angew. Chem., 80, 99 (1968).

*Not mentioned in the text—(Ed. of Translation).

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