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LIQUID CRYSTALS

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Abstract: The book describes the progress in the field of liquid crystals from their discovery to the present time. It includes the classification of liquid crystals, their optical properties, the molecular structure of compounds which form liquid crystals, symmetry, x-ray structural analysis, theories of liquid crystal state, thermodynamic properties, magnetic properties, electric properties, ultrasonic effects, viscosity and surface tension. A brief chapter is devoted to the importance of liquid crystals in industrial applications, medicine and biology. In the last section procedures are given for the synthesis of ten compounds which form liquid crystals. The book has a 125 item bibliography.

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# Liquid Crystals

by
I. G. Chistyakov

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U. S. ARMY FOREIGN SCIENCE AND TECHNOLOGY CENTER
Munitions Building
Washington, D. C. 20315

# LIQUID CRYSTALS

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# LIQUID CRYSTALS

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I. G. Chistyakov

## Introduction

The liquid crystal (or mesomorphic) state of a substance is such a state when the substance possesses structural properties intermediate between the properties of a solid crystal and of a liquid.

Many scientific discoveries have an interesting fate, and without a precedent is the existence of a substance in the form of liquid crystals. This was a subject of doubt in the course of approximately twenty years after the discovery of mesomorphism. However, this is not surprising: the term itself "liquid crystals" sounds highly extraordinary. In the minds of many physicists and chemists at the beginning of the century such a combination of words appeared close to absurd.

In the development of science of liquid crystals great contributions were made by the French crystallographers Grandjean, Mauguin, Friedel and Chatelain. Friedel [1], for example, proposed a new classification for the state of matter on the basis of structural differences.

In reality, while according to the laws of thermodynamics three states of matter exist (solid, liquid and gas) such a division does not reflect to any extent the internal structure of the substance or the degree of ordering of its particles. Certain substances (resins, glasses) possess properties which are characteristic of both the solids and of the very viscous, supercooled liquids. Liquid crystals possess properties of liquids and the properties of solid crystalline bodies. On the other hand, looking somewhat ahead, let us say that certain substances which upon cooling do not undergo transition into the solid crystalline form but vitrify, preserve the liquid-crystal structure.

An Austrian botanist Reinitzer [2] was the first who ran across the liquid-crystal state substance. He discovered peculiar properties in cholesteryl benzoate which he synthesized. The crystals of this substance melted at 145° C forming an opaque liquid, which upon further heating to 179° C went through a transition into ordinary clear liquid, displaying no further changes at higher temperatures. If the melt was then cooled, then at 179° C it acquired bluish coloration which rapidly disappeared and the liquid mass became turbid. When 145° C was approached the coloration again appeared and immediately the substance solidified. Being highly intrigued by this behavior, which indicated something similar to double melting, Reinitzer asked a German physicist Lehmann to study his preparations. Having studied the substance by means of a polarizing microscope Lehmann [3] established that the turbid phase was optically anisotropic. The preparation was a combination of a large number of disorderly oriented microscopic regions of spontaneous optical anisotropy. The scattering of light along the boundaries of these regions resulted in the opaque appearance of the preparation.

Subsequently Lehmann discovered that other substances display similar properties, for example p-azoxyanisole, p-azoxyphenatole, ethyl p-azoxybenzoate, ammonium oleate, etc. A characteristic property of all these substances is that in a definite temperature interval they possess at the same time both the properties of a liquid (high fluidity, the ability of existing in a drop form, merging of drops upon contact) and the properties of crystalline bodies (anisotropy). According to Lehmann's proposal this characteristic behavior indicated that the above substances can exist in some newly discovered aggregate state. This state he called without hesitation "liquid crystal." The communications of Lehmann brought about doubts in many scientists in regard to the possibility of the existence of such a state. Apparently, a definite role in this was played by the initial error of Lehmann's hypothesis regarding liquid crystals. He thought that liquid crystals, just as ordinary crystals have a highly mobile three dimensional space lattice. Some scientists attempted to prove that liquid crystals are nothing else but an emulsion with high dispersion of light as a result of which the preparation appears opaque. Others thought that substances form very fine solid crystals, surrounded by a liquid film and adhering to each other upon contact, or on the contrary droplets of ordinary liquid on the surface of which a thin crystalline film is formed. However, many investigations of Lehmann [4,5] Schenk [6] and other scientists have proven undisputably that the liquid crystal state is a discrete thermodynamic state of matter and liquid crystals differ from ordinary liquids not only in their optical properties, but also in electrical magnetic and other properties. Lehmann has established that liquid crystals are of two forms. The crystals of the first type, the viscosity of which is close to the viscosity of water, he called "true liquid crystals" and crystals of the second type -- "fluid crystals." The viscosity of the latter is approximately a factor of two higher than the viscosity of the former type.

In the opinion of the German chemist Zorlander [7], liquid crystals are formed primarily from those organic substances whose molecules have elongated rod-like shapes. By 1908 he and other chemists synthesized approximately 250 such compounds. At present the number of substances which form liquid crystals has increased to 3000.

Both Friedel and Lehmann distinguish two liquid crystalline states. New terms were introduced to designate these states: "smectic" and "nematic" states. Both states are combined by the general term "mesomorphic" state. The word "smectic" was derived from a Greek word "smectos" meaning soap, since this state is characteristic for many soaps and was discovered for the first time in scap forming substances. In the smectic state elongated molecules of substance form layers which slip easily over each other. The term nematic was derived from the Greek word "nematos" meaning threadlike. Under the microscope preparations of substances which are in the nematic state appear as thin mobile threads. In the nematic state molecules are oriented in a definite direction. The term "mesomorphic" ("mesos" -- intermediate) indicate that both nematic and smectic states are characterized by the molecular ordering which is intermediate between ordered molecules in crystals and amorphic substances. In general the classification of the state of the substance according to Friedel appears as follows.

Amorphic state. It is characterized by the disorderly arrangement and random motion of the molecules. Rotation of molecules is possible around any molecular axis.

Nematic state. In the nematic state the center of gravity of elongated molecules is located at random. The prolonged axes of molecules are oriented along a definite direction. Rotation is possible about the longitudinal molecular axis.

Smectic state. In the smectic state the centers of gravity of elongated molecules, equidistant from each plane, are mobile in two directions (along the smectic plane). The rotation of molecules is possible about the longitudinal molecular axis.

Crystalline state. It is characterized by fixed molecular arrangements both in the centers and azimuths in a three dimensional space lattice.

The nature of arrangement of molecules of substance, in different states (according to Friedel) are shown in Figure 1.

Naturally such classification is not definitive. For example, Friedel classes gases and liquids in one structural type (amorphous state). However, the x-ray structural analysis data show [8] that in liquids, and in general in amorphous bodies, the degree of ordering (close order) of molecules may be different than in gases. The variation of ordering of chain molecules in polymer substances is also well known [9]. One more

extremely interesting state of substance which A. I. Kitaygorodskiy [10] named "gas-crystalline" should be mentioned. The centers of gravity of molecules in this state form a crystal lattice, but azimuthal orientation of these molecules is random.

Apparently in the liquid crystal phases different degrees of ordering of the molecules are also possible. The most direct approach to the study of this question is based on the principles of study of symmetry taking into account different types of dislocations which are found in real liquid crystal aggregates. Soviet scientists as A. V. Shubnikov and B. K. Vaynshteyn are primarily responsible for the advances in this area.

In addition the terms "liquid crystal," "fluid crystals," "mesomorphic state" (smectic and nematic), one frequently finds other terms in literature: "anisotropic liquids," "paracrystals." The most widely used terms, however, are "smectic liquid crystals" and "nematic liquid crystals." This terminology shall be used in our book.

Liquid crystals which are obtained by heating solid substances are called thermotropic liquid crystals. This method of obtaining liquid crystals is not the only possible method. Liquid crystals may be formed also by dissolving solid crystals of certain substances in various solvents. Such liquid crystals are called lyotropic.

The liquid state of the substance has been investigated by many Soviet (Yu. V. Vul'f, A. B. Mlodzeyevskiy, A. V. Shubnikov, V. K. Frederiks, B. K. Vaynshteyn, V. N. Tsvetkov, G. M. Mikhaylov, V. A. Marinin, A. P. Kapustin, N. M. Melankholin and others) and foreign (Lehmann, Vorlander, Friedel, Mauguin, Grandjean, Robinson, Lawrence, Bragg, Bernal, Frank, Weyngand, Zocher, Oseen, Maier, Kast, Chatelain, Gray and others) scientists. The results of investigations were discussed at conferences in Germany (1931), in England (1933 and 1958) and in the USA (1965). Approximately one thousand scientific papers were published on the subject of liquid crystals. Nonetheless their nature and properties are far from being completely known. This is [illegible] by the fact that in literature one frequently finds contradictory definitions of the nature of the liquid crystal state itself. At the same time urgency of the investigation of this field is obvious. Liquid crystals begin to acquire an ever increasing importance in different fields of new technology, industry, biology [illegible]

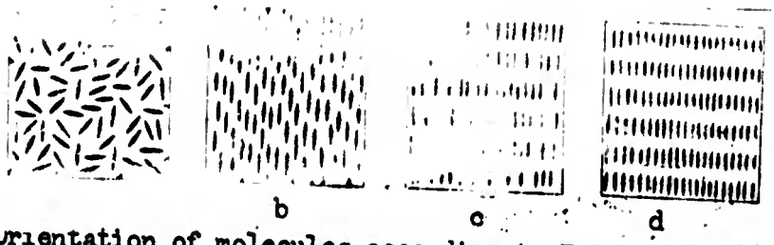


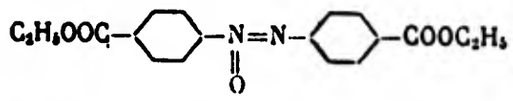

Figure 1. Orientation of molecules according to Friedel. a--isotropic melt; b--nematic liquid crystal; c--smectic liquid crystal; d--solid crystal.

Chapter 1

# TEXTURE AND OPTICAL PROPERTIES OF LIQUID CRYSTALS

## 1. Smectic Liquid Crystals

A classical example of a substance which forms smectic liquid crystals is ethyl p-azoxybenzoate



The solid crystals of this ester melt at 114° C and undergo transition to smectic type liquid crystals, the particles of which are arranged in layers. At 120° C the liquid crystals are converted into ordinary isotropic liquids.

If the molten preparation is placed under a microscope the following picture may be observed. As soon as the temperature of the preparation falls to 120° C liquid crystal nuclei begin to precipitate in the form of rods (Fig. 2). Such a state of nuclei is explained by the fact that the rate of their growth in the axial direction is approximately a factor of five greater than in the radial direction.

When a smectic liquid crystal is viewed in crossed polaroids brightly shining rods on a dark background are clearly visible. This indicates that the crystals are optically anisotropic. Liquid crystals have only one axis. By rotating the microscope stage one can note that light from all rods disappears and reappears again simultaneously as though they were one single unit. When a quartz compensator is introduced they acquire a yellow coloration (lowering of the coloring), if the longitudinal axis of a rod coincides with the $N_p$ axis of the compensator. This indicates that the sign of the elongation of the rods is positive. Liquid crystals have one optical axis, consequently the optical sign of the rods is also positive. Since smectic liquid crystals have layered structure (longitudinal axes of molecules are perpendicular to the layers), it appears

that the layers are perpendicular to the longitudinal axis of the rods. Here we have an example of how optical investigations enable us to determine the structure of objects without any more complex investigations (for example x-ray diffraction).

Upon contact rods merge together. In the state where small rods fuze with larger ones thickening appears. This indicates that smectic liquid crystals possess anisotropic fluidity. The propagation of such a substance along the longitudinal axis of the rod is more difficult. It is much easier to grow smectic layers in the radial direction. Therefore, the substance redistributes mainly in this very direction forming a new rod thickened in the middle.

## Focal-Conic Texture

Upon further growth of the liquid crystal all rods fuze together forming the so-called focal-conic texture which consists of individual sections -- focal-conic domains (Fig. 3). The geometry of each domain is quite complex. Individual molecules of liquid crystal interact with glass (the slide and the cover glass) as a result of which the smectic layers twist, forming a family of surfaces, or the so-called Dupin cyclides [1, 11, 12]. In order to determine the arrangement of layers of substance in the focal-conic domain let us first consider a family of Dupin cyclides. The basis for the formation of such cyclides is focal-conic pair -- an ellipse AB and a hyperbola COD (Fig. 4). These curves possess the following properties: the geometric locus of the vertices of the cones of revolution, the side surfaces of which lie along the ellipse AB, is a hyperbola COD. On the contrary, the ellipse AB is a geometric locus of the vertices of cones of revolution, which pass with their surface along the hyperbola COD; the latter passes through the focus O of the ellipse AB. The planes of the hyperbola and of the ellipse are mutually perpendicular. If surfaces perpendicular to all straight lines which pass through the hyperbola and ellipse are constructed, these surfaces will be Dupin cyclides. On our diagram such straight lines are AC, AK, BK and BC and the cross sections of cyclides are circles whose centers are at points A and B. Cyclides are designated by numbers 1-16. They separate this space into parallel to each other layers of equal thickness.

As the numerical order increases the central opening of cyclides decreases. In cyclid number 10 the opening completely disappears. Both sides of its surface have only pits remaining. The bottom of the pit converges to point O. In subsequent cyclides the pits are smoothed more and more and the cyclide number 16 already has no pit at all. The bottom of the pit (points C and D in Fig. 4) are a significant distance from each other. On the contrary as the number decreases the cross section of cyclides decreases and the opening increases. For cyclide number 8, for example, the corss section is reduced to a point. Subsequent cyclides become incomplete (Fig. 5b). Such a family of surfaces is characteristic

for the confocal smectic texture. The domains, shown in Figure 3, are formed by smectic layers which acquire the shape of Dupin cyclides. If straight lines are drawn through all points of hyperbola CD (see Fig. 4) and ellipse, then a conical space is obtained, bounded by two cones of revolution (Fig. 6). This is in fact the geometric representation of the structure of confocal domains. At any place in it the direction of long molecular axes coincides with the direction of the straight line drawn through three points: the center of a given molecule in the layer, the point on the ellipse and the point on the hyperbola. Such a line may be BC or KC. The direction of the straight lines indicates the arrangement of optical axes in confocal domains.

Figure 2. Smectic nuclei of ethyl p-azoxybenzoate in the form of elongated rods float in the isotropic melt; larger rods have more complex form (300 x).

The structure of confocal domains determines the optical picture which is observed under the microscope (see Fig. 3). The disruption in the optical continuity of the substance occurs along the ellipse and the hyperbola, therefore, they are very well observed in the natural light. In the case when confocal domain is located in the layer of substance the fact that the molecules which are on the ends of the hyperbola are attached to the cover glass and the slide means we can clearly see ellipses. When the domain lies on its "side" one can easily distinguish hyperbolae. The molecular orientation near the ellipses and hyperbolas changes rapidly, i.e., disinclination occur which are analogous to dislocations in crystals.

The ellipses of certain domains may be incomplete. In this case we shall have not two, but four cones of revolution (Fig. 7), which determine the domain. Two of the cones are based on the ellipse (their vertices C and D lie at the ends of the hyperbolae) and two on the hyperbola (vertices A and B lie on the ends of the broken ellipse).

Figure 3. Confocal smectic texture of ethyl p-azoxybenzoate (crossed nicol prisms, 300 x).

Ordinary crystals may occlude droplets of solvent. Upon heating such droplets dissolve the crystal from the inside and upon cooling the dissolved substance is again crystallized out. The droplet etches out inside the crystal an area exactly repeating the shape of the crystal. It is called "negative crystal." Somewhat similar phenomenon takes place in the case of smectic liquid crystals. Upon slow heating of the preparation it is possible to see that bubbles of isotropic melt, formed in confocal domains they have elongated shape and appear as "negative" smectic rods. Bubbles occur on the hyperbola. The position of the bubbles is more stable when their longitudinal axes are directed toward the CBD side. The bubble which develops on the convex side of the hyperbola soon after moves in order to occupy a more stable position. The bubbles of isotropic melt have tails, along which still finer bubbles are located. One may frequently observe how small bubbles slip along the hyperbola to the point O and there they merge into much larger bubbles.

Near the convex surface of the liquid crystal between domains and the surface a vacant space is left, which is filled by smaller confocal domains. Free space is in turn left in the neighborhood of these, where even smaller domains are formed, etc. When one observes the convex surface from the top one can clearly see a hyperbola which conveys to the texture its design.

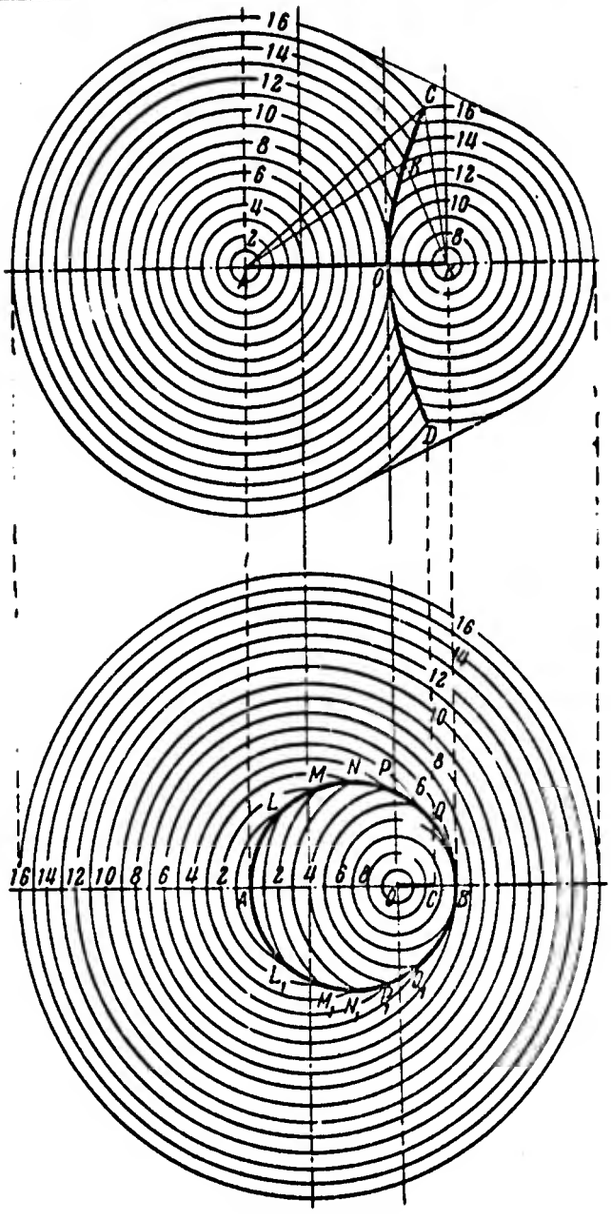



Figure 4. A family of Dupin cyclides in two projections. COD and AB are hyperbola and ellipse respectively which form a confocal pair. The same numbers designate cross sections which refer to the same cyclides.

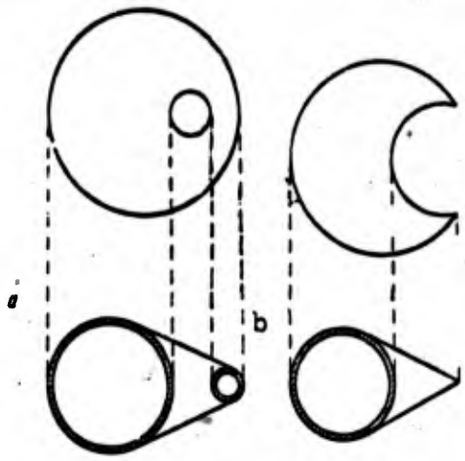



Figure 5. The structure of a layer bounded by Dupin cyclides
a. 8th and 9th
b. 4th and 5th

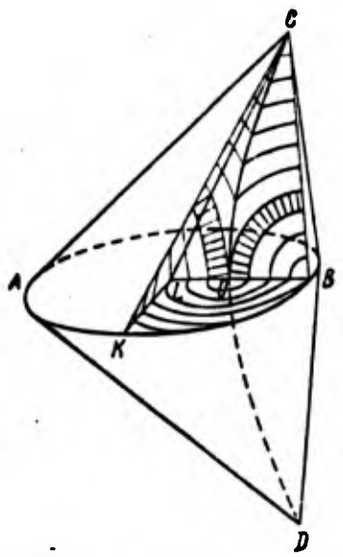



Figure 6. Schematic representation of the structure of confocal domain. Smectic layers form a series of Dupin cyclides. The longitudinal axes of the molecules are perpendicular to the surfaces of layers and parallel to the straight lines which pass through the hyperbola and the ellipse. In one of the layers the position of molecules is indicated.

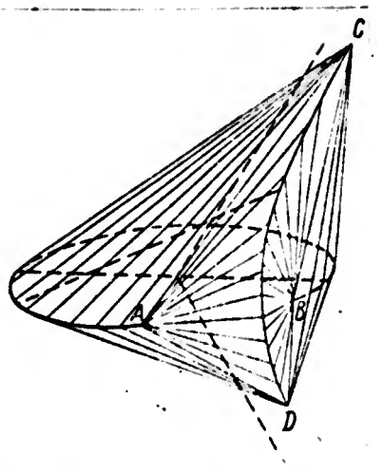



Figure 7. Confocal domain with incomplete ellipse.

## Polygonal Texture

Smectic liquid crystals frequently form the so-called polygonal texture (Fig. 8). This texture is very easily formed when the slide and the cover glass are treated with hydrofluoric acid. It is also recommended to add a small amount of rosin to the preparation. In this case the viscosity of the medium and its thermal properties become most favorable for the occurrence of the polygonal texture. Upon cooling at the moment of occurrence of smectic phase the preparation should be moved by pressing the cover glass with a wooden stick. On the other hand, in isolated sections of the preparation polygonal texture is formed even without these additional measures.

The development of such structure results from binding of the smectic layers in different domains. Each layer belongs at the same time to various domains, and passes from one domain into another (Fig. 9). As a result of such an arrangement the smectic substance between the cover glass and the slide is separated into pyramidal and tetrahedral blocks (Fig. 10). Each pyramidal block contains several confocal domains. Each ellipse of the domain has a hyperbola lying in the vertical plane. All hyperbolas meet at the lower surface at point O, which is the projection of the intersection of main axes of the ellipses onto the lower surface. In tetrahedral blocks smectic layers bind domains into different types of pyramids.

In the smectic liquid crystal the ordinary light is split into two beams -- ordinary and extraordinary. The oscillations of the intensity vector E of the extraordinary beam lies in the plane of the beam itself and the optical axis of the substance, coincident with the direction of the longitudinal axis of the molecule. The direction of the optical axis of the confocal domains varies from point to point due to twisting of the

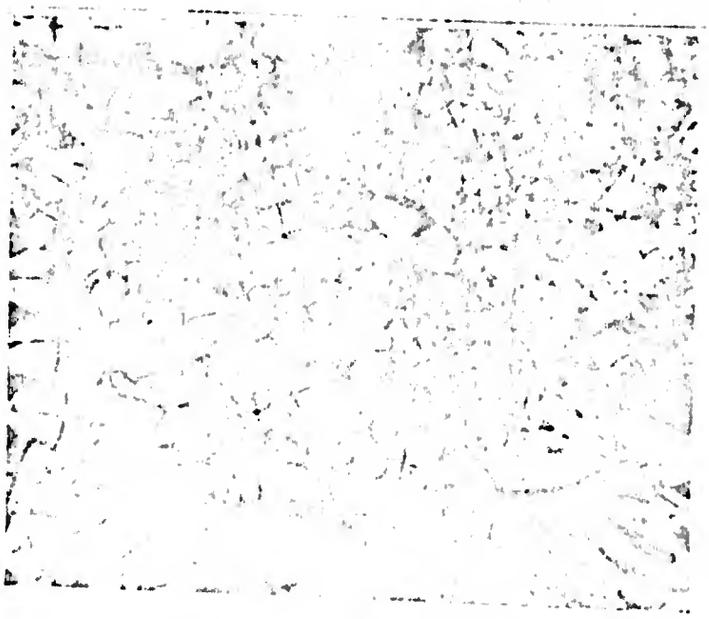


Figure 8. Polygonal texture of the upper surface of the preparation (one analyzer is turned on, polarizer is turned off).

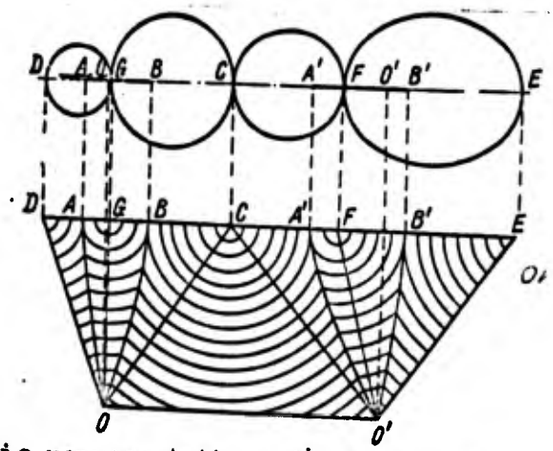



Figure 9. Schematic representation of the association of smectic layers in confocal domains. ODG, OGC, O'CF and O'Fe are conical surfaces which bound the domains; OA, OB, O'A' and O'B' are hyperbolas of different domains.

smectic layers. As a result of this the extraordinary rays are deflected and they do not enter the objective of the microscope. The images, therefore, obtained in this manner will produce only the ordinary nondeflected rays. The direction of their vibration is perpendicular to the optical axis. Part of the rays in which the angle between the direction of the vibration of the intensity vector of the electric field and the direction of the vibration in the analyzer comprises 90° would be attenuated. This

explains the occurrence of the dark branches in each of the ellipses (Fig. 11a). If one observes the lower surface of the preparation (Fig. 11b), having only one polarizer on, then the extraordinary beams will be deflected as usual and the image of the lower surface will produce the ordinary rays, but the dark branches in the ellipses will be rotated through a 90° angle and will coincide with the direction of vibrations in the polarizer.

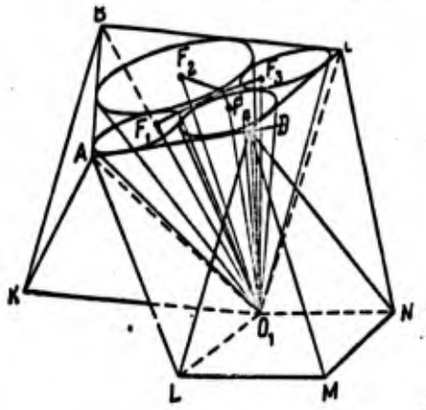



Figure 10. Schematic diagram of blocks in a polygonal texture. The figure shows confocal domains of one of the pyramids. $O_1$ABCD and $DO_1$LMN are pyramids, $ABO_1N$ and $CDO_1N$ are tetrahedra.

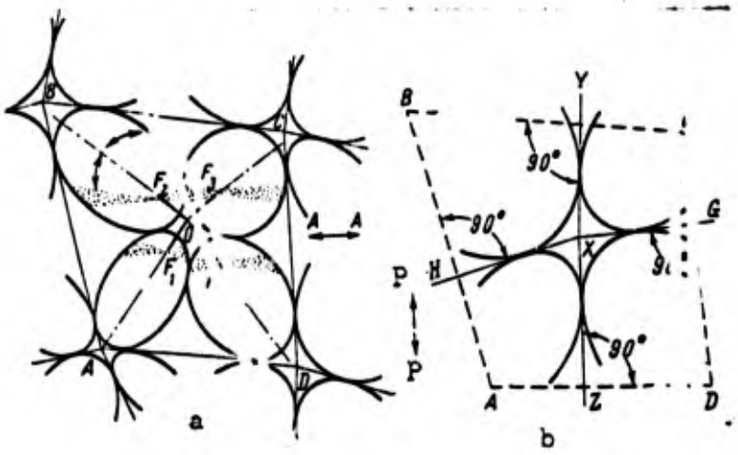



Figure 11. A schematic representation of sections in a polygonal texture. a. upper surface (ABCD -- base of the pyramid, A-A direction of the vibration in the analyzer; b. lower surface directly under the ABCD section (P-P direction of vibration in the polarizer). Part of the ellipses are apparent which are adjacent to pyramids, the bases of which lie on the lower surface of the preparation.

## Surface Texture of Smectic Drops

In preparations formed without a cover glass smectic drops have a dark axial cross when placed on the slide and when the nicol prisms are crossed (Fig. 12). When the quartz plate KR-1 is introduced between the crossed nicol prisms of the microscope the interference coloration of crystals becomes the same as for the spherocrystals with positive sign of elongation [13]. In the case of crossed nicol prisms the large and plain drop is not visible at all. This indicates that the smectic layers are parallel to the glass, and that the optical axis is perpendicular to the surface of the preparation. In small drops, having a convex surface, the layers are somewhat curved, so that molecules perpendicular to the surface (and consequently the optical axis of the layers), are at some angle to the horizontal plane. Thus, the preparation, is transparent and only in those places where the direction of the optical axes coincides with the direction of the oscillation of light in the analyzer and polarizer quenching takes place. This explains the occurrence of the dark cross. On the surface of the large and convex drops a texture is frequently formed which masks the dark axial cross. If the preparation is slowly cooled by means of an air stream, such texture will not occur even on the surface of large drops. Figure 13 shows the occurrence of somewhat smaller droplets which have not merged in the isotropic melt of a large drop of smectic substance. The droplets which float in the isotropic melt do not have the dark cross. In the presence of the quartz plate KR-1 their interference coloration increases or decreases depending in what quadrant of the isotropic drop the smectic drop exists. Upon rapid cooling, along with such homogenious smectic drops smectic rods also occur in the isotropic melt as well as the surface texture of the drop (Fig. 14). Upon contact of a rod with a smectic drop they merge.

It is interesting to note that rods may also occur inside of the large homogenious drop, if its surface is cooled and vibrated by means of an air jet. However, one can hardly assume that here transformation of a section of a homogenious drop into a smectic rod takes place. Apparently, the homogenious liquid-crystal layer in this case exists only on the surface of the drop. The inner layers, however, consist of isotropic melt in which rods are nucleated. When the cooling ceases the rod decreases in size, gradually disappears, or is immediately converted into a surface texture. Generally, during such a rearrangement several domains of surface texture are formed, the number of which depends on the size of the rod. Figure 15 shows the manner in which the rearrangement of several rods into surface texture takes place. The observation of the domains of surface texture in the polarized light showed that they have contrafocal structures.

A group of such domains, if they do not occupy the whole surface of the drop, can move along the surface of the drop. As the temperature is decreased the viscosity of the smectic substance increases and the motion of domains ceases. Domains may be moved by a strong air jet. In this case they are frequently destroyed leaving a trace on the surface of the supercooled smectic drop (Fig. 16).

Figure 12. In a drop of ethyl p-axoxybenzoate the dark axial cross is masked by the domains of surface texture (200 x).

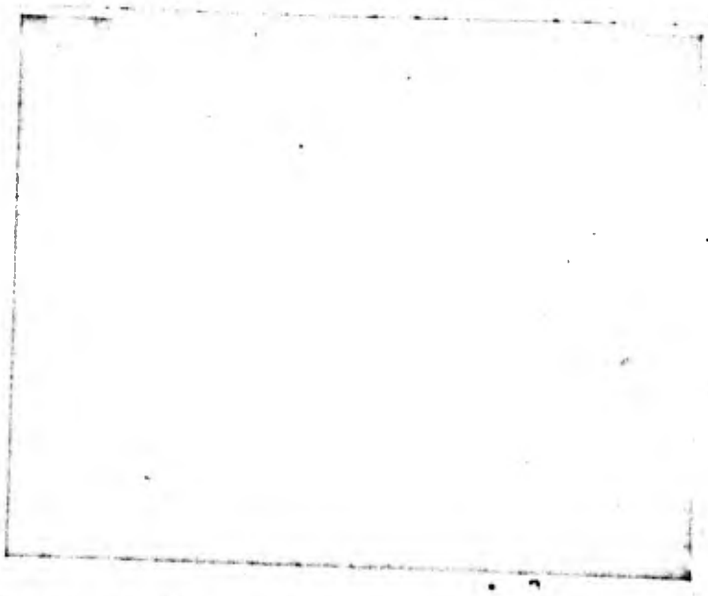


Figure 13. Several homogenious smectic drops at the edge of a large drop (300 x).

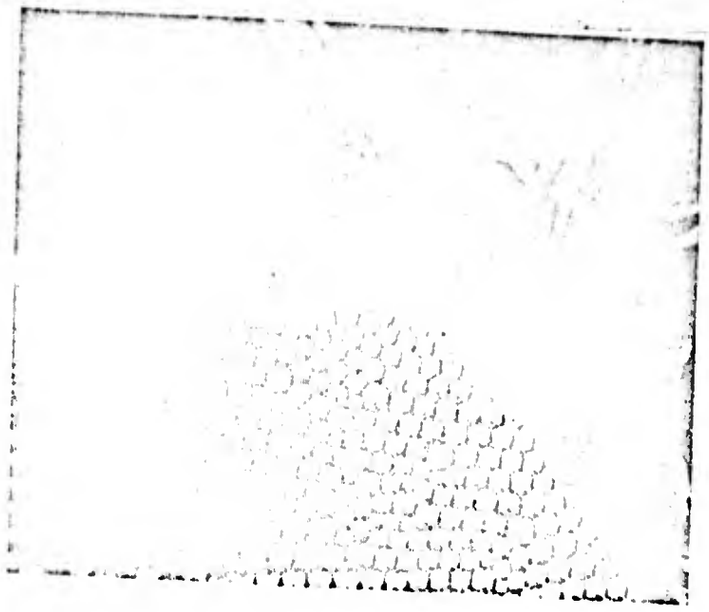


Figure 14. Rods, homogenious drops and surface texture in a crystal of ethyl p-azoxybenzoate (crossed nocol prisms, 150 x).

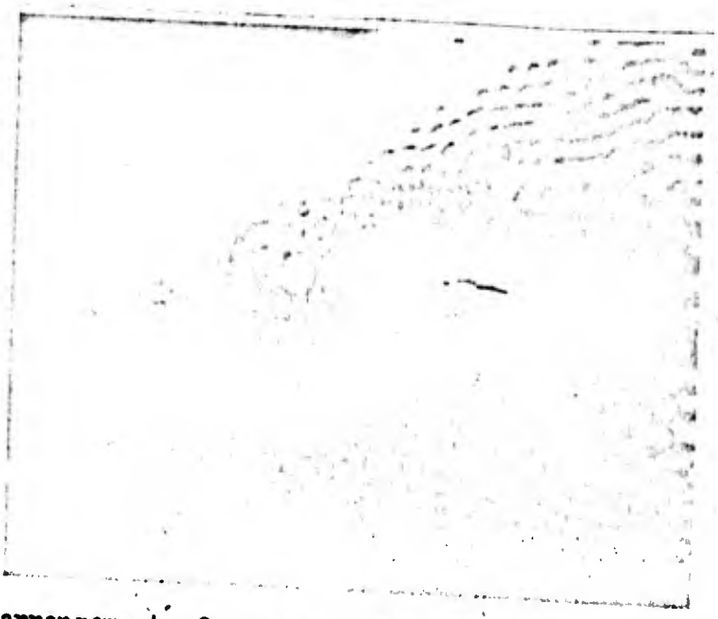


Figure 15. Rearrangement of rods into a surface texture. The newly formed domains are inside the circles (crossed nicol prisms, 200 x).

Figure 16. Traces left by domains which were moved on the surface of a supercooled smectic drop (crossed nicol prisms; 450 x).

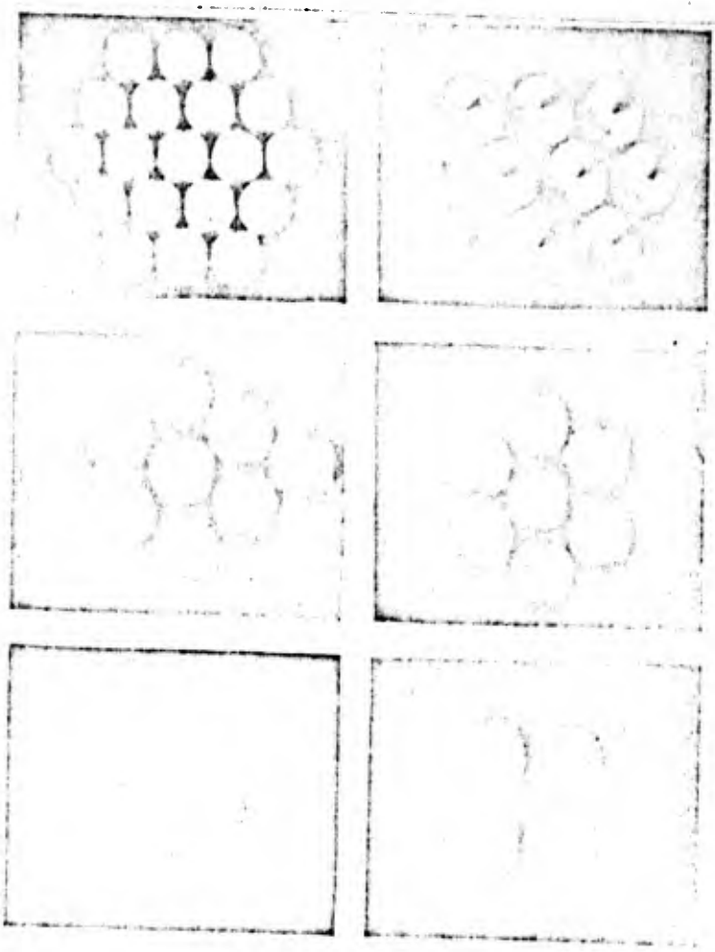


Figure 17. Symmetric figures formed by domains of surface texture.

One may frequently observe an extremely curious phenomenon on the drops with surface texture. Several freely floating domains of the surface texture are spontaneiously arranged symmetrically (Fig. 17) which highly resembles the symmetric arrangements of floating magnets.

## Multistep Droplets

On the glass surface smectic drops generally have spherical convex shape, but if the substance is placed on a very clean and smooth surface (for example freshly cleaved along the cleavage plane mica sheet) extremely characteristic multistep drops are formed (Fig. 18). The occurrence of such drops is a result of multilayer smectic liquid crystals. The thickness of each step is equal to a multiple of the thicknesses of individual smectic layers (equal to the length of the molecule). The edges of each step are generally not smooth, but they contain very fine confocal domains. During mechanical vibration of the surface of the drop one may observe the smooth slippage of individual layers over each other. The motion of the layers is apparent also when the drop is permitted to flow along the mica surface when solid crystals are melted and smectic drops are formed.

The splitting of the drop into individual steps results, apparently, due to the presence of impurities which are accumulated on the surfaces, thus separating one step from the other.

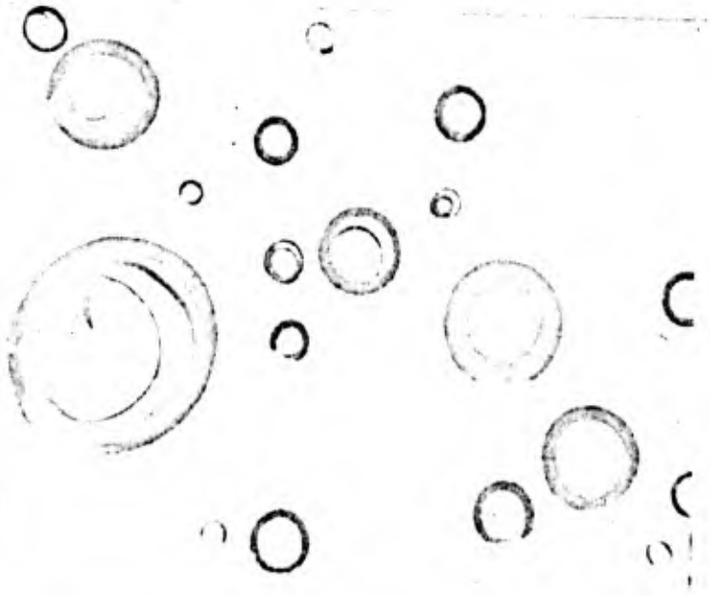


Figure 18. Multistep drops of the smectic phase on a clean mica surface.

## Orientation of Smectic Mesophase by the Crystalline Surfaces

Frequently smectic liquid crystals are oriented in a definite direction along the cleavage plane of certain crystals. This happens, however, only in the case when a definite relationship exists between the period of the crystal lattice and the period of layers of the smectic liquid crystals. The distances between the smectic layers must be approximately equal to one of the lattice parameters, exposed at the cleavage of the solid crystal. For example, the orientation is possible during the melting of ethyl p-azoxycinnamate along the (010) plane of the cleavage of a talcum crystal (Fig. 19). In this case the streams of smectic melt are rectangular and they flow along the directions which produce 60° angles between them, so that the ends of the streams are always parallel to crystallographic direction, and optical axis of the stream is parallel to (100) direction of talcum [1].

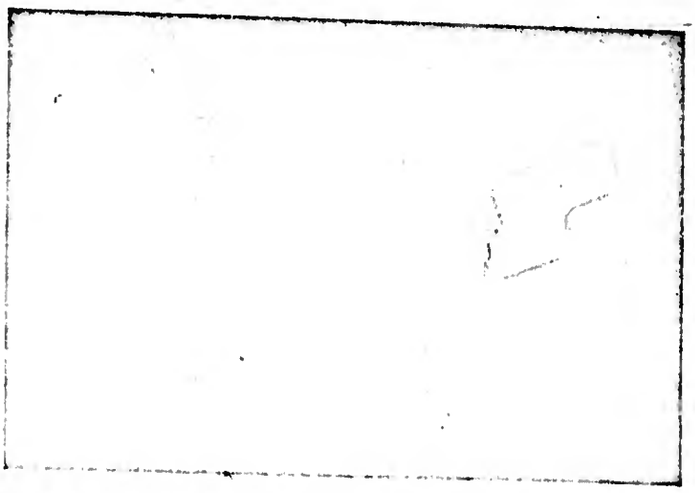


Figure 19. A scheme by means of which the rectangular stream of a smectic liquid crystal is formed during melting of solid crystals of ethyl p-azoxycinnamate at the cleavage plane of the talcum crystal.

## Smectic Single Crystals

Large homogenious sections of smectic substance may be formed between the slide and the cover glass. In each of these sections the optical axis has constant direction (homeotropic). In order to obtain this the preparation must be cooled slowly introducing the crystal seed from the edge. Under these conditions one of several single crystals will be growing. When the preparation is then melted to the smectic state liquid crystals sections are formed the shape of which exactly resembles the shape of crystal sections. Each of these large homogenious sections may be viewed as a smectic single crystal. In converging light its conoscopic

picture will correspond to the interference figure of a monoaxial crystal plate. All of the known liquid crystals of smectic type are monoaxial and have positive double refraction.

Since the homogenious smectic liquid crystal consists of elongated molecules oriented in one direction, one should expect that rays, the vibration vector E of which coincides with the length of the molecules, will be absorbed stronger than the rays the oscillations of which are normal to the lengths of the molecules. It is quite natural that the absorption will depend on the direction of the propagation of rays in the specimen. Thus, during the investigation of a homogenious smectic liquid crystal of ethyl p-azoxybenzoate in polarized light (with one polarizer) one can easily detect pleochroism. During rotation the preparation changes its coloration from dark yellow to white (dichroism). In disoriented specimens (confocal texture) and without rotation one may note that differently oriented sections of the preparation are colored differently. Pleochroism was also established for other smectic liquid crystals.

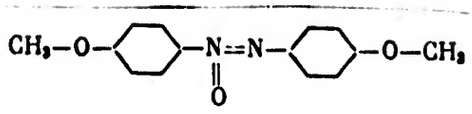
The presently known smectic liquid crystals are incapable of rotating the polarization plane of light. Thus, to summarize, one may say that in optical respects they possess all the properties of monoaxial crystals. According to Shubnikov [14], homogeniously oriented smectic crystal or one single crystal domain can be assigned an assymetry symbol ($m.\infty:m$) of the indicatrix family for monoaxial crystals. This is a limiting symmetry group, having one infinite axis, designated by the symbol $\infty$, one transverse axis, a center of symmetry and an infinite set of longitudinal symmetry planes m and second order axes.

Let us note in conclusion that the optical investigations of smectic liquid crystals give us, as a rule, only qualitative information. Apparently, this results from the complexity of obtaining uniformly oriented smectic media, the necessity of rigorous temperature control and finally mobility of the medium. This also explains the almost total absence of the theory of physical phenomena, observed in smectic liquid crystals. It is quite clear that success in this direction, and, finally, the practical use of smectic liquid crystals can be achieved only by means of quantitative experiments.

## 2. Nematic Liquid Crystals

Let us recall that molecules in the nematic liquid crystal are oriented along a single definite direction. According to Friedel [1] two different variations of the nematic crystals exist: nematic proper and cholesteric. The second variation differs from the former in that the structure of crystals of the cholesteric type is spiral. They shall be considered in a separate paragraph. At this time let us consider nematic liquid crystals proper.

Liquid crystals of nematic type are formed by such compounds as p-azoxyanisole



During the melting of solid crystals of this substance on the stage of a polarizing microscope anisotropic melt droplets are formed (Fig. 20). Liquid crystals of p-azoxyanisole exist in the 115-136° C temperature range. One may frequently find a large number of dark threads in the preparation which are mobile and very well visible in natural light (Fig. 21). These are called disinclinations [15], since they are places of breakage of the optical uniformity of the medium, where the orientation of elongated molecules drastically changes. In the preparation, produced in the form of a thin layer between the slide and a cover glass, disinclinations are frequently located perpendicularly to the glass, and the places where they appear at the surface of the specimen are well visable: they appear as dark spots -- nuclei. When the preparation is viewed with the analyzer current off one may note two types of nuclei: round and rectangular. Between crossed nicol prisms of the polarizing microscope one may note that dark branches emanate from the nuclei. These are those sections of the preparation in which the direction of longitudinal molecular axes coincide with the direction of the oscillation in the polarizer and the analyzer. For this reason in these sections the light is quenched (Fig. 22). When the polarizer is rotated the dark branches near the round nuclei rotate also following the nicol prisms, while in the case of rectangular nuclei their rotation is in the opposite direction to the rotation of the nicol prisms.

The texture of nematic crystals is explained by the nature of the distribution of the molecules about the disinclinations and by deviations of a singular path in these places. The possible types of molecular distribution about these nuclei are shown in Figure 23. These configurations are determined through the theory of elasticity of nematic liquid crystals, developed by Oseen [16] and Frank [15], and are described by parameters $n$ and $\Phi$, which are constant for a given type of nucleus. One can distinguish positive and negative nuclei ($n = +2$ and $n = -2$) and seminuclei ($n = +1$ and $n = -1$). The occurrence of disinclinations is determined by the fact that in the process of growth of liquid crystals the crystallization front may meet obstacles in its path in the form of dust particles of another substance, as a result of which the liquid crystals in this place shall become inhomogenious. When one observes such a preparation between crossed nicol prisms, one may see four dark branches enamating from each nucleus. Seminuclei have only one or two such branches. When the preparation is rotated the branches of positive nuclei and seminuclei remain unchanged, and branches of negative nuclei are rotated in the direction of the rotation of the preparation.

Figure 20. Droplets of a nematic liquid crystal of p-azoxyanisole. The solid crystals are growing in the lower left corner (nicol prisms are crossed; 120 x)

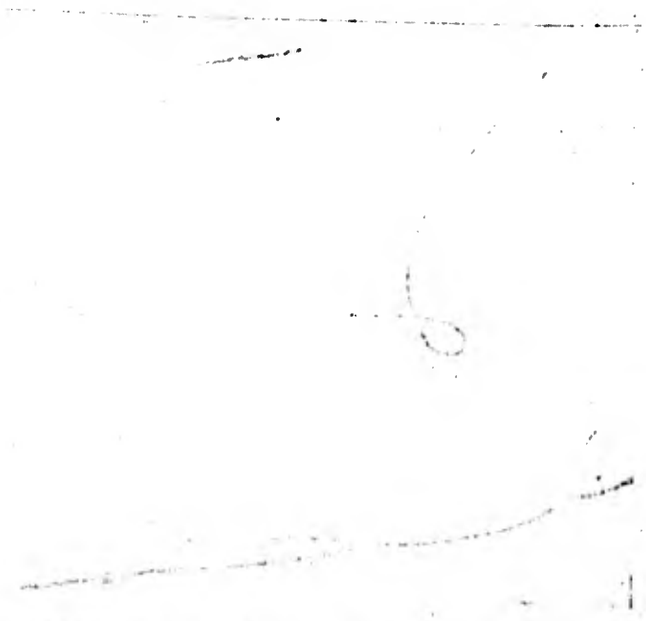


Figure 21. Dark threads are noted in the liquid crystal phase of p-azoxyanisole (natural light; 80 x).

Figure 22. Dark branches emanating from the nuclei are the places where disinclinations appear at the surface of the preparation (120 x).

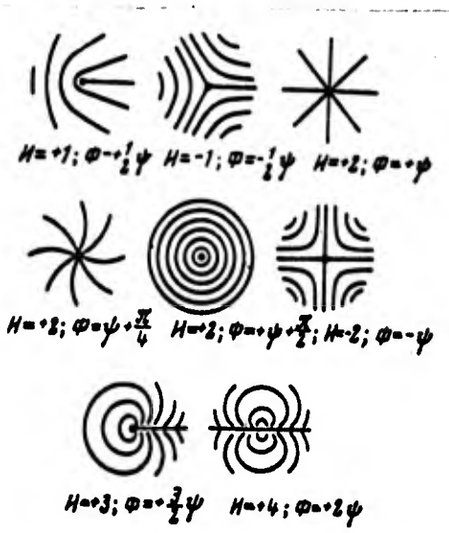



Figure 23. Orientation of longitudinal molecular axes near nuclei; n and C are parameter of the equation which describes the molecular ordering of liquid crystals.

Disinclinations in the form of threads observed in the interior of the preparation may be called "volume disinclinations" in contrast to "surface disinclinations" observed only on the surface of the preparations. The disinclinations of the second type are either dark or light lines depending on the orientation of disinclinations between nicol prisms. Such disinclinations are shown in Figure 24. The uniformly oriented section of nematic preparation is set to extinguish light between crossed nicols. Solid crystals begin to grow in the preparation following which it was again heated. The solid crystals melted, but their contour remained visible, forming surface disinclinations on the slide and the cover glass (more accurately on the surfaces of the specimen which are adjacent to the glass).

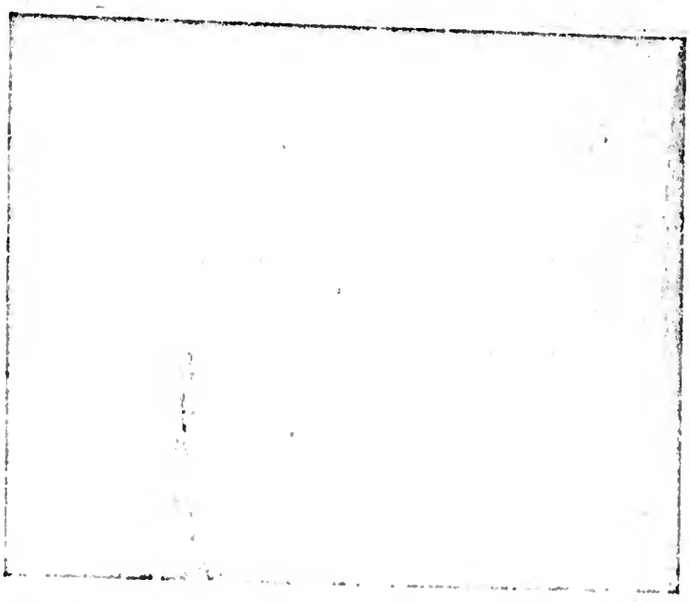


Figure 24. Surface disinclinations which delineate the contours of the melted solid crystals (120 x).

## Nematic Single Crystals

By subjecting glass to special treatment one may achieve the formation of oriented, single-crystal type nematic layers [17-22]. The longitudinally oriented layer of liquid crystals is obtained as follows. The slide and the cover glass are rubbed with a piece of paper or silk cloth in one definite direction. The cover glass is placed on the slide so that the direction of rubbing would coincide. Crystals of substance are then placed on the edge of the cover glass. Due to capillary action during the melting of crystals isotropic melt is drawn between the two glasses and upon cooling forms uniformly oriented liquid crystal layer. The nematic oriented layers possess properties, analogous to the properties of monoaxial crystal platelets, cut parallel to the optical axis.

When the nematic single crystal layers are obtained with optical axis, perpendicular to the surface of the glass, the latter must be thoroughly washed in acids and dried in a thermostat. The following washing sequence is recommended for glass: first in sulfuric acid and distilled water followed by a nitric acid wash and again a water wash. The crystals which are melted between the washed glass form single-crystal nematic layers. The optical properties of these layers are close to the properties of the platelets of a monoaxial crystal, cut perpendicular to the optical axis.

The growth behavior of oriented layers is quite characteristic. Figure 25 shows how longitudinally and normally oriented layers of p-azoxyanisole layers are growing.

The first layer is placed in a position which is close to extinction. The inhomogeneities and disinclination lines are apparent. They appear as flying arrows and are explained as follows. When an obstacle appears in the path of the crystallization front -- dust particles or scratches on the glass -- immediately two volume disinclinations and consequently two nuclei occur on the upper and the lower glass. One of the disinclinations is not elongated, making it appear as though it remained in one place. The second disinclination continues to move along with the crystallization front of the growing crystal. In doing so it leaves behind it a track -- surface disinclination. In the preparation, placed in a position close to extinction, surface disinclinations on the upper and the lower surfaces of the specimen are clearly apparent in the form of flying arrows (Fig. 25a) The occurrence of "arrowheads" in these arrows is explained by the fact that the crystallization of nematic preparations is V-shaped. In the places where arrowheads occur we observe their surfaces, located at an angle with respect to the line of vision. If the moving volume disinclination is not vertical, then the surface disinclinations on the upper and the lower surfaces are located not directly one opposite the other and the tracks, left by the volume disinclination become doubled. When the microscope stage is rotated through an angle of 90° the preparation becomes transparent and the arrows appear dark on the light background.

In well oriented preparations disinclination exists for a short period of time: the nuclei move towards one another and upon contact they disappear. The surface disinclinations are wiped and as a result correctly oriented single-crystal nematic layer is obtained. In nonoriented preparations surface disinclinations, which are the traces of volume disinclinations, do not disappear.

Surface disinclinations may occur also independently of volume disinclinations. They are sometimes formed in places where the V-shaped section of the liquid crystal adjoins the glass (Fig. 26). The cause for their occurrence, just as in the case of volume disinclinations, is defects on the glass or foreign particles. Such disinclinations rapidly disappear regardless of whether the preparation is oriented or not.

Figure 25. Growth of longitudinal (a) and normal (b) oriented nematic layers (120 x).

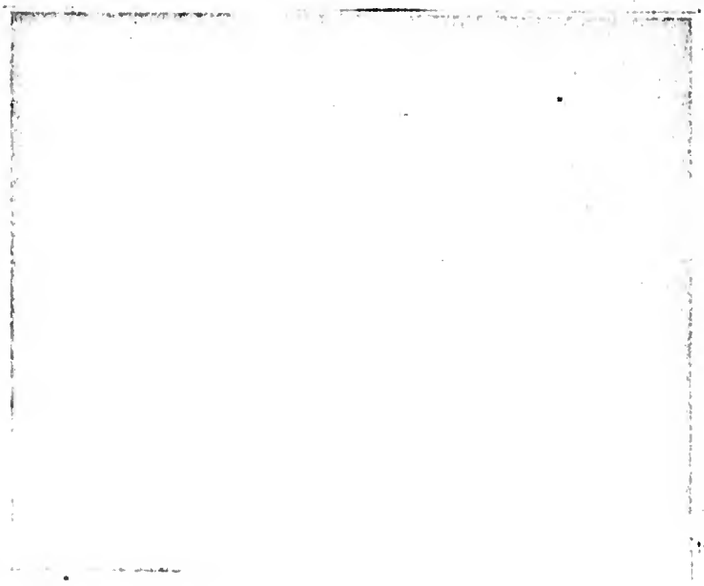


Figure 26. The occurrence of surface disinclinations in the place where the wedge-shaped crystallization front of the liquid crystal adjoins the cover glass.

It is interesting to note that the place of the occurrence of volume disinclinations, just as the place of the occurrence of surface disinclinations, frequently remains the same upon multiple melting and crystallization of the nematic preparation.

The normally oriented nematic layer develops somewhat differently (see Fig. 25 b). Its skewed crystallization front is well visible due to perpendicular orientation of molecules to the surface. Under crossed nicol prisms the normally oriented layer of liquid crystals is always dark.

If the temperature of the preparation is close to the transition point of crystals into isotropic liquid, in the dark field of vision of the microscope one may observe many light blinking points. These are individual microscopic layers of the oriented layer which due to thermal fluctuations change the direction of their optical axis and become visible for a certain period of time. (The optical axis of such regions is other than perpendicular to the interface).

The crystallization of nematic preparations is not always accompanied by the occurrence of disinclinations along the whole crystallization front. In the case of slow growth of the crystal in front of the crystallization front many liquid crystal droplets occur, which merge with the oncoming crystallization front (Fig. 27). Each drop contains volume disinclinations,

and if the latter is perpendicular to the surface of the glass, then the drop has axial cross when the nicol prisms are crossed. The occurrence of spherical nuclei frequently occurs in the same place in the preparation. When the preparation made with a cover glass, i.e., when due to the large temperature gradient turbulent motion of the substance takes place, one may observe how liquid crystal nuclei having reached a certain size tear away from the place of their occurrence and are carried by the stream of the substance into the liquid crystal mass. In the place of the previously ripped off nucleus a new one is formed. In such a manner one makes plain the fact that isotropic phase nuclei inside the liquid phase crystals occur also in the same places in the preparation upon multiple melting and crystallization.

The molecules of nematic liquid crystal are greatly adherent to the glass. If, for example, the cover glass is moved, the boundaries of individual single crystal sections of the preparation double. This indicates that the molecules of the upper layers are adherent to the cover glass, and the molecules of the lower layers are adherent to the slide. Such properties of molecules aid them in preserving the shape of individual sections of the preparation when it is transformed into other phases. The molecules which are adhering to the walls preserve their orientation and in turn have an orienting effect on the bulk molecules. When the crystal is transformed into isotropic liquid, and then cooled again into the nematic state, the shape of the liquid crystal section is almost unchanged. The same occurs during the melting of solid crystals. The orientation of individual liquid crystal sections of the preparation is analogous to the orientation of polycrystalline grains.

Figure 27. Droplets of nematic phase near the crystallization front of liquid crystals. Isotropic liquid is at the top of the figure and the liquid crystal, oriented and extinguished under crossed nicol prisms is at the bottom (80 x).

The foreign particles which accidentally are introduced into the nematic preparation, participate in Brownian motion without the disruption of the optical picture. The molecules of liquid crystal can also be transported from one section of the preparation into another, acquiring the orientation of the latter. This indicates that the position of both molecules is determined by the orientation of molecules which are adhering to the glass, and that in the inner regions of the liquid crystal there exists a high fluidity.

The nematic liquid crystals do not possess optical activity. However, the rotation of the polarization plane of the transmitted light may be produced by artificial rotation of the cover glass. The screwed deformation of substance which occurs upon such rotation indicates strong bonding of the crystal molecules to glass. The "twisted" substance becomes optically active. The angle of rotation of the polarization plane is the same for any wavelength and it is equal to (up to 90°) the angle of rotation of the glass. When the twist angle exceeds 90° the sign of rotation changes erratically. For example, rotation of the cover glass clockwise through an angle of 100° corresponds to the rotation through an angle of 10° counterclockwise (through an angle of 80° clockwise from the initial position).

This phenomenon is observed in convergent light. The oriented sections of the nematic preparations produce an excellent conoscopic figure which does not differ at all from the picture obtained from the ordinary monoaxial crystals. Upon induced vibrations the conoscopic figure vibrates resembling the surface of jelly. In observing the twisting effect of substance a ring made from a cork is placed upon the objective the face of which is glued to the cover glass. By raising and lowering tubus of the microscope one can slightly change the thickness of the liquid crystal layer. Upon rotation of the microscope stage the liquid crystal is twisted and the conoscopic figure rotates in the same direction. As soon as the angle of turn exceeds 90° the conoscopic figure is rotated sharply into a symmetrical position.

The nematic crystals are easily oriented along the cleavage planes of different crystals. The distribution of individual sections of the preparation follows a strict order (Fig. 28).

The investigation of liquid crystals in convergent light showed that they are monoaxial and have positive optical signs. Consequently, the optical symmetry of nematic crystals (single crystal domains) belong to the same symmetry class $m \cdot \infty : m$, as the symmetry of smectic crystals.

## Double Refraction of Nematic Mesophase

The magnitude of double refraction of liquid crystals is generally very great. Thus, for example, for p-azoxyphenetole the difference in the indices of refraction of the ordinary and extraordinary rays $\Delta n \approx (n_e - n_o) =$

=0.37. Let us remember that for such strong double refracting ordinary crystals as calcite and sodium nitrate, $\Delta n$ is equal to 0.17 and 0.25 respectively. The magnitude of double refraction of liquid crystals changes with temperature. For the determination of the indices of refraction of liquid crystals the prism method can be used. The homogenious liquid specimen is prepared between two previously ground glasses, arranged at some angle to each other, so that each crystal would have the shape of three face prisms. By means of a goniometer measurements of the incident angle and the angle of refraction of ordinary and extraordinary rays which leave a liquid crystal prisms it is possible to determine the index of refraction with accuracy to the third significant figure. Figure 29 shows refraction curves for p-azoxyanisole [18, 23]. It is apparent from the figure that with increase of temperature the index of refraction of extraordinary rays decreases, while for the ordinary rays it increases so that the magnitude of double refraction $\Delta n$ lowers and at the transition temperature of the liquid crystal into isotropic liquid (135° C) it becomes equal to zero.

## Dichroism

Many liquid crystals display a strong dichroism, i.e., they absorb rays differently which propagate in different directions, and the vector E of which oscillates in different planes. In viewing disoriented preparations of p-azoxyanisole on the microscope (one polarizer with analyzer turned off), one can easily convince oneself that differently oriented sections of the preparation (optical axes of which coincide with the direction of the oscillations in the polarizer and are perpendicular to those directions) are colored differently ranging from dark yellow to white. When the microscope stage is rotate through an angle of 90° the coloration of each section changes to the opposite coloration. The dichroism phenomenon of liquid crystals, as shall be shown later, is used in technology for the production of polaroids.

## Light Scattering in Nematic Mesophase

The fact that nematic liquid crystals scatter light (become cloudy) is extremely important, not only in the nonoriented form but also in the form of single crystal films [20]. The intensity of light scattering decreases with increase of the angle $\varphi$ between the incident and the scattered rays. It was established that vector E of scattered light oscillates primarily in the direction, perpendicular to the direction of oscillations of the incident light ($H_p$). Thus, for example, if $J_{op}$ are oscillations which lie in the scattering plane YZ, and $J_{ep}$ are oscillations which lie in the plane XZ, then for $\varphi = 9°$ the depolarization coefficient is

$$K = J_{op}/J_{ep} \approx 8$$

Investigation of the scattered light taking into account the dependence of the index of refraction on temperature produces valuable information for the development of the optical theory of liquid crystals. Presumably the accumulation of experimental data will enable further refinement and development of this theory.

Figure 28. Orientation of nematic phase of p-p'-nonoxybenzaltoluidine on the freshly cleaved plane of rock salt (120 x).

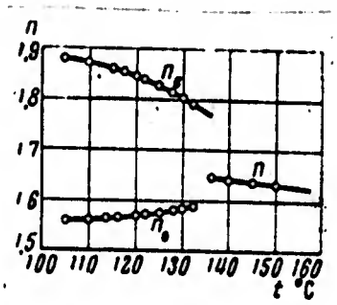


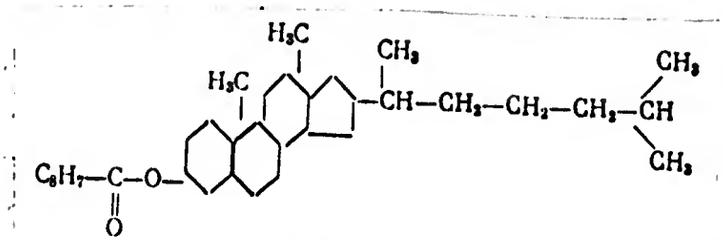

Figure 29. Index of refraction of extraordinary ($n_e$) and of ordinary ($n_o$) rays as a function of temperature. n is the index of refraction of the isotropic melt.

Spectral investigations of liquid crystals also offer promise. Let us note that the visible and the ultraviolet spectra of liquid crystal phase differ slightly from the spectra of the isotropic phase of the given substance. A much more significant difference is found for the Raman spectra of p-azoxyanisole [24]. Here the spectrum of the solid substance and of the nematic phase contains 1247 $cm^{-1}$ line. This line is totally absent in the spectrum of isotropic melt of p-azoxyanisole. This means that the structure of the nematic phase is more similar to the solid crystal phase than to the isotropic phase.

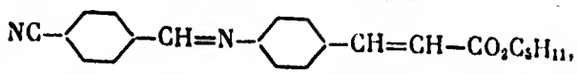
Extremely interesting work has been carried out recently on infrared dichroism of p-azosyanisole by Maier and Englert [25, 26]. They investigated plane polarized light, the oscillation of which in one case coincided with the principal axes of molecules and in another case was perpendicular to the latter. It was found that the obtained data can be used for the evaluation of the degree of orientation of molecules in nematic crystals.

## 3. Cholesteric Liquid Crystals

Generally choleosteric liquid crystals, as the name implies, are formed by the derivatives (esters) of sholesterol Cholesteryl cinnamate



is found in the liquid crystal state at 156-197° C. There are, however, choleosteric liquid crystals which are not cholesterol derivatives. An example of such a compound is amyl-p-(4-cyanobenzylideneamino)-cinnamate



which forms a cholesteric phase at 95-105° C.

During cooling of isotropic melt cholesteric crystals form confocal texture (Fig. 30). Subsequently one may conclude that they are also layered. It would appear that such liquid crystals can be classed as smectic. This, however, is not so. First of all we know of no substance which could (in the appropriate temperature interval) form both cholesteric and nematic phases. At the same time many substances are known which at a temperature which exceeds the corresponding interval, are in the cholesteric

phase, and at lower temperature they are transformed into a typical smectic phase. Such a transition is accompanied by the liberation of latent heat.

Many facts indicate that the cholesteric phase is a variation of the nematic phase, but differs from it in that it has spiral structure [1]. Figure 31 shows schematically the explanation of positioning of the molecules in cholesteric structure. The pace of the spiral p=2s determined its layered structure. Here, XZY is the rectangular system of coordinates, where $\zeta$ and $\eta$ are principal molecular axes. The axes are spiraled along the OZ direction in accordance with the equations

$$\zeta = X\cos\frac{2\pi Z}{p} + Y\sin\frac{2\pi Z}{p};\quad \eta = Y\cos\frac{2\pi Z}{p} - X\sin\frac{2\pi Z}{p}$$

Figure 30. Confocal texture of the cholesteryl cinnamate (crossed nicols; 300 x).

In contrast to the smectic phase, the thickness of layers of which is equal to the molecular length (20-40Å), in the cholesteric phase the thickness of the layers is of the order of 2000Å. Consequently, a possible explanation for the formation of confocal domains in the cholesteric phase is shown on the diagram in the Figure 32a. The spiral formation of molecules which determines the layered structure of the substance is shown only along the cones AC, BC and BD. In contrast to smectic domains the molecules here are arranged in such a manner that their long axis is

perpendicular to the line drawn through the hyperbola and the ellipse. This explains the fact that the domains of the cholesteric phase always have a negative optical sign (in the case of smectic phase they are always positive). Upon a small shift of the cover glass cholesteric confocal texture is destroyed and planar texture is produced which is in fact single crystal cholesteric film. In this case layering also occurs, but not "physical," which presupposes molecular layers capable of slipping along one another, as in the case of smectic stepwise drops, but it results from the spiraling of molecules (Fig. 32b). The thickness of such layers (Grandjean planes) increases with the increase of the temperature of the cholesteric phase.

It is of interest to consider the transitional picture which occurs during the decomposition of the confocal cholesteric structure with the formation of the planar texture. In the beginning confocal domains are layered into long threads, which sometimes consist totally of smaller confocal domains (Fig. 33a). These ribbons later may become very thin. Following this they curl into cylindrical tubes, producing characteristic networks on the background of the single crystal planar structure (Fig. 33b). Such tubes are frequently called oily furrows.

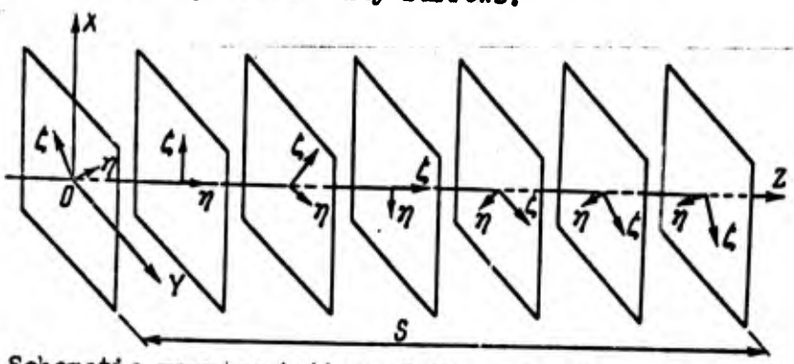



Figure 31. Schematic representation of the spiraling of the cholesteric liquid crystal along the Z axis.

Investigations in converging polarized light show that the optical sign of the cholesteric planar texture is negative. In the case of crossed nicols it appears colored, where the coloring does not change during the rotation of the stage of the microscope. This indicates that the texture is optically active. The specific rotation of the polarization plane may be measured if one places the cholesteric substance between a plain glass and a convex lens. The index of refraction of the glass must not differ greatly from the average index of refraction of the substance. In the monochromatic light between the crossed nicols dark and light rings will be apparent. These are the places where the phase difference reaches 180°. For the first ring $n = 1$, for the following $n = 2$, etc. Knowing the curvature of the lens, the wavelength and the distances between the rings one may determine the optical activity of the crystal.

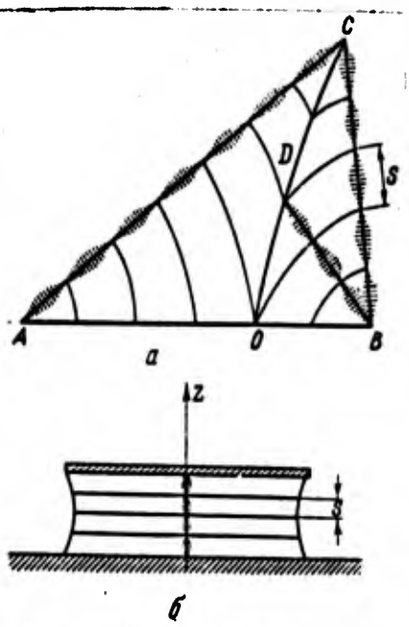



Figure 32. Confocal domains of cholesteric liquid crystals.
a. representation of structure (s -- thickness of the layer or the pitch of the spiral; b. schematic representation of the molecular distribution in the plane monocrystalline layer.

Using a slit diaphragm (Fig. 34) [27] and white light a photograph of the spectrum of amyl-p-(4-cyanobenzylideneamino)-cinnamate an extremely interesting appearance. Figure 35 shows a graph of the specific rotation of the polarization plane which corresponds to this photograph. We can see that an anomaly exists for the dispersatory rotation in the visible region of the spectrum. The specific rotation of the polarization plane is extremely high and reaches 3200 degrees/mm. For certain substances rotation may exceed this value reaching 60000-70000 degrees/mm. This may be one of the most phenomenal properties of liquid crystals. After all the specific rotation of the polarization plane of rodinary organic liquids hardly ever exceeds 300 degrees/mm. The same may be said about the ordinary crystals.

Such strong optical activity cannot be explained by the ordinary rotating ability of molecules. It apparently results from spiraling of the structure of cholesteric liquid crystals, i.e., regular "rotation" of molecules during their mutual packing. The theoretical optical model of cholesteric structure, enabling the explanation of its optical properties, in the first approximation appears as follows. Let us imagine that the plane cholesteric texture consists of doubly refracting platelets with indices of refraction $n_e$ and $n_o$. The platelets are placed upon each other in such a manner that their central line describes the spiral with pitch p. In this case [28], according to the electromagnetic theory of light, the magnitude of the optical activity of cholesteric liquid crystals is

$$\alpha = -4{,}5 \cdot 10^4 \cdot n^2 \cdot \frac{p}{\lambda^2}$$

Figure 33. Transition of the cholesteric confocal texture into planar texture.
a. layering of structure with the formation of ribbons (crossed nicols, 100 x)
b. thin cylindrical tubes on a background of uniformly oriented cholesteric layer (120 x).

Here $\alpha$ is the optical activity in the direction parallel to the axes of the spiral structure, n is the double refraction of the unwound medium and p is the pitch of the screw, equal to 2s (see Fig. 32). This equation produces results which are in good agreement with the experimental data [29, 30].

From the electromagnetic theory it follows further that there exists a definite wavelength $\lambda_0$, at which cholesteric substance selectively and intensely reflects circularly polarized light.

$\lambda_0 = pn$, where $n = \left(\frac{n_e + n_0}{2}\right)$-- average index of refraction. The refraction is great in the region from

$\lambda_0\left(1 - \frac{\alpha}{2}\right)$ to $\lambda_0\left(1 + \frac{\alpha}{2}\right)$, where $\alpha = \left(\frac{n_e - n_0}{n}\right)$ — is the relative double refraction. Beyond this region the refraction greatly increases. In actuality the sign of rotation of cholesteric liquid crystals changes with change of the wavelength, so that the overall curve for the specific rotation of the polarization plane acquires the form shown in Figure 36. The wavelength of inversion $\lambda_0$ is not the same for different substances and it depends on temperature [25]. It can exist not only in the visible, but also in the infrared or in the ultraviolet region of the spectrum. In a narrow spectral band $\Delta\lambda$ (for cholesteryl propionate, for example $\Delta\lambda = 0.02\mu$) in the neighborhood of $\lambda$ the light which passes through the plane cholesteric texture is strongly reflected (scattered), and the wavelength of this band depends not only on the substance and temperature, but also on the angle between the scattered beams and the incident beams. As its angle increases the wavelength of the scattered light decreases. Therefore, in white light even to the naked eye it is apparent that the plain cholesteric texture is brightly colored. The coloration depends on the angle at which the surface is observed [1].

It is very interesting to note the changes of coloration when one observes at a constant angle but varies the temperature of the preparation. Upon cooling in air the temperature gradient is formed. As a result of this in the center of the preparation one may see isotropic melts, along the edges of the cover glass -- solid crystals which begin to grow, and between these two phases -- cholesteric liquid crystals. If the confocal texture is converted into the plane texture (for this it is sufficient to press against the cover glass with a stick), one may observe the newly formed structure glowing with all the colors of the spectrum. In the heated places it shall have blue-violet coloration, in the cooler places adjacent to the solid phase -- red, fixed solid phase -- red color.

A definite relationship exists between the structure of molecules and the sign of the rotation of the polarization plane. We know that each cholesteric liquid crystal depending on the wavelength of the light rotates the polarization plane to the right or to the left. If the compound consists

of molecules with the right structure and if the wavelength of the incident light is less than the wavelength of light which is scattered with maximum intensity, then the polarization plane is rotated to the right. However, when the wavelength of the incident line is gradually increased then upon the passage of the beam through the maximum scattering the rotation becomes less. For levorotatory substances an inverse relationship holds. There is another very interesting fact. The light, scattered by the plane cholesteric structure, is circularly polarized (to the right or to the left) upon illumination of the preparation with light, polarized in such a manner, the following effect is observed. If the dextrorotatory liquid crystal is illuminated with light, circularly polarized to the right, the light would be scattered without the change of sign. This contradicts the normal effect, which occurs upon illumination of nonliquid crystal bodies with polarized light. The circular polarized light to the left passes through the specimen of the dextrorotatory crystals without the change of sign and without any significant scattering. In other words, dextrorotatory choleosteric bodies scatter the right circular components of the incident beam and passes the levorotatory component.

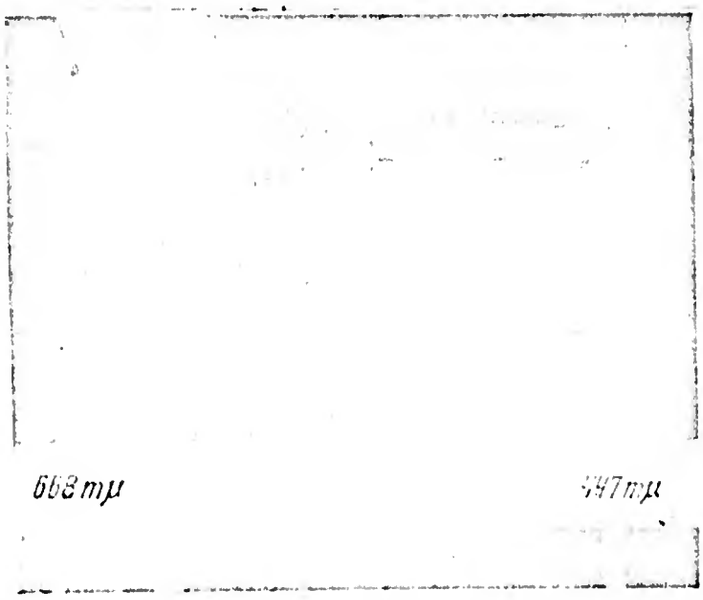



Figure 34. Spectrum of amyl-p-(cyanobenzyladineamino)-cinnamate. The pairs of symmetrical lines correspond to the even rotation of the same sign. The spectrum of helium is shown below for comparison.

Important information about the nature of choleosteric liquid crystals was obtained upon the study of mixtures of substances [31-33]. For example, in a mixture consisting of 2.4 parts of amyl-p-(4-cyanobenzylideneamino)-cinnamate by weight (dextrorotatory liquid crystal) and 2.7

parts by weight of cholesterylbenzoate (levorotatory crystal) it is either levorotatory or dextrorotatory depending on temperature. When a definite temperature $t_0$ is approached the optical activity decreases. At the point $t_0$ it is equal to zero, optical activity becomes positive, and the mixture acquires all characteristics of the nematic liquid crystal. This witnesses to the fact that choleosteric liquid crystals are in actuality a variation of nematic liquid crystals with spiral structure.

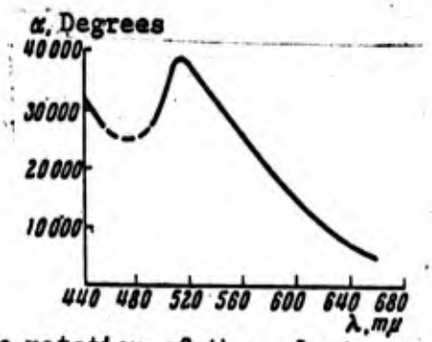



Figure 35. The specific rotation of the polarization plane as a function of wavelength (at 75° C), determined on the basis of the spectrum shown in Figure 34.

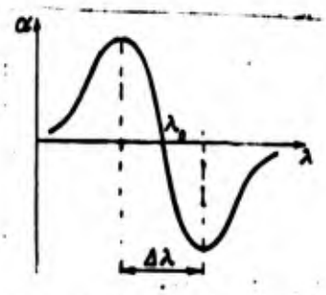



Figure 36. Specific rotation of the polarization plane of liquid crystals as a function of wavelength.

The paradoxical properties are displayed by a mixture of amyl-p-(4-cyanobenzylidenamino)-cinnamate with nematic liquid crystal isoamyl-p-(4-cyanobenzylideneamino)-cinnamate (which does not rotate the polarization plane). When the concentration of the former, optically active component, is increased the optical activity of the mixture decreases. This was also observed for other mixtures of substances, for example, nematic o-azoxyanisole and cholesteric cholesteryl acetate. The optical activity increases as the amount of disymmetrical molecules of cholesteryl acetate decreases and the amount of symmetrical molecules of p-azoxyanisole increases. What does this all indicate? This first of all indicates that the rotation of the polarization plane by the cholesteric liquid crystals depends on the structure of the aggregate of molecules and not on the molecular structure itself. This is very convincingly supported by the fact that nematic liquid crystals can be easily converted into

cholesteric crystals by the introduction of a small amount of optically active component into it, which in itself does not form liquid crystals. An example of such a mixture may be p-azoxyanisole with a small amount of rosin [34]. Liquid crystal droplets, which precipitate from the isotropic melt, have layered structure (Fig. 37), and individual sections of the preparation have periodic structure (Fig. 38). The latter is apparently the result of the spiraling of the structure of the substance.

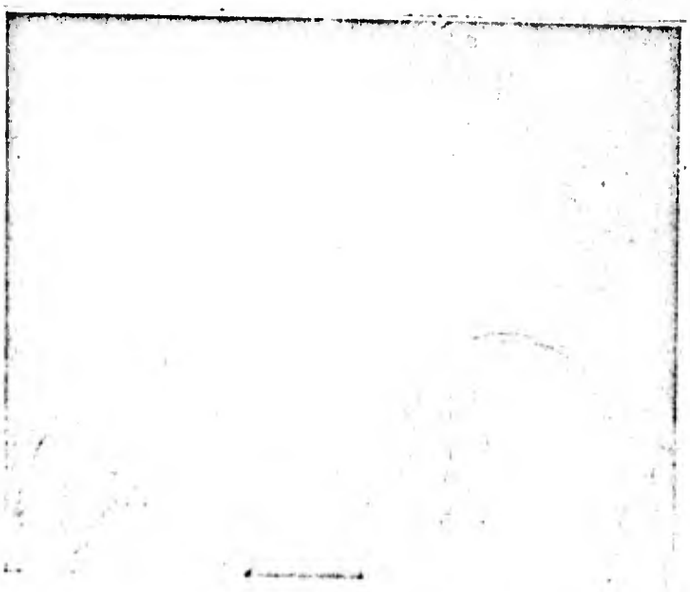


Figure 37. Liquid crystal spherulite of a mixture of p-azoxyanisole with rosin (crossed nicols, 120 x).

The cholesteric liquid crystals just as nematic liquid crystals are oriented on the surface of the solid crystal. In this case the former (just as the spiraled nematic crystals) have lower symmetry of optical properties in comparison with smectic and nematic uncoiled liquid crystals, namely $\infty$ : 2. This symmetry group coincides with the symmetry of rotation of the polarization plane and is subordinate to the group $m \cdot \infty : m$.

## 4. Lyotropic Liquid Crystals

Many colloidal systems produce formations which are similar to nematic, cholesteric or smectic liquid crystals. Such systems are called lyotropic liquid crystals, and they include for example many aqueous systems of soap, tobacco mosaic virus, and certain polypeptides. Lyotropic crystals are formed in the process of dissolution of solid crystalline substances [35]. As the amount of solvent increases the system at first becomes smectic, then nematic and finally isotropic liquid system. Let us

Figure 38. Periodic texture of a mixture of p-azoxyanisole with rosin.
a. at the edge of the preparation,
b. in the center of the preparation (crossed nicols, 75 x).

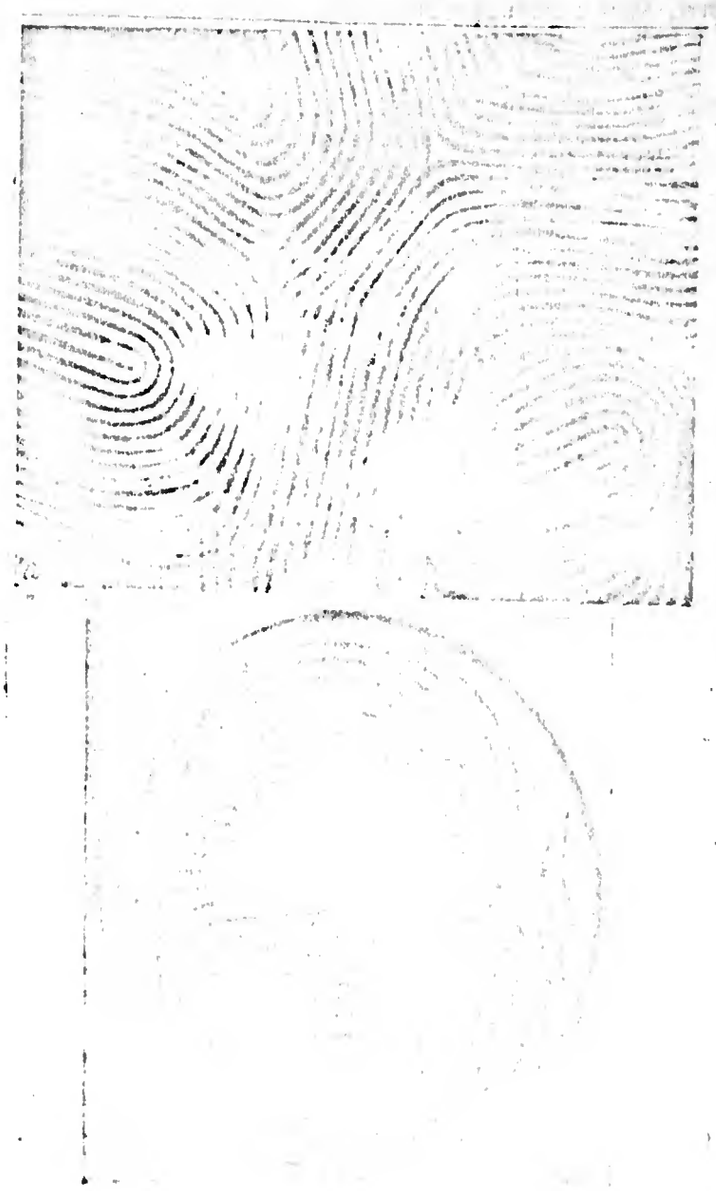


Figure 39. Periodic texture (a) and liquid crystal spherulite (b) of poly-$\gamma$-benzyl-L-glutamate (photograph of Robinson) [29].

note that many substances form liquid crystals of only one type. For example, poly-$\gamma$-benzyl-L-glutamate in mixture with a definite quantity of dioxane it is capable of forming only cholesteric phase [29, 30] with periodic texture, which results from the spiral structure of the substance (Fig. 39).

An extremely convenient substance for investigation of the texture of lyotropic liquid crystals is potassium oleate [36]. Water-alcohol solutions of potassium oleate are available under the name "liquid potassium soap." If a drop of such a solution is placed between the slide and a cover glass then after several hours along the edges of the cover glass smectic lyotropic liquid crystals begin to grow (Fig. 40a). Closer to the center of the preparation a texture is formed, the domains of which are similar to spherocrystals (Fig. 40b). It is noticeable that domains begin in pairs from two points, located next to each other. Sometimes the points may exist at a significant distance from each other. When the growth of such a domain is not impaired by the neighboring domains it acquires the shape of the body of revolution (Fig. 41). As the dimensions of the domain increase it comes in contact with the glass, its smectic layers, perpendicular to the axes of the domain, begin to curl into Dupin cyclides, and as a result a more complex structure is formed (Fig. 42). The domains of the described texture are not stable: in the course of 1-2 days upon evaporation of the solvent they begin to stratify (Fig. 43). At first ribbons are formed which frequently consist of a chain of small confocal domains. By slightly moving the cover glass one may achieve the disappearance of the ribbons: smectic layers will arrange themselves parallel to the glass and the separation will darken between the crossed nicol prisms of the microscope. In such a manner a single crystal layer of lyotropic smectic liquid crystal is formed.

Potassium oleate forms lyotropic liquid crystals not only in a water-alcohol medium. For example, in chloroform potassium oleate is rapidly swollen, forms liquid crystalline spherulites, which tear away from the principal mass and flow to the top. Thus, rapidly two phases are formed -- liquid crystal and isotropic at the bottom. In xylene potassium oleate is dissolved better, isotropic phase contains more of the oleate than in the case of chloroform. Here the isotropic liquid phase remains at the top and the liquid crystalline phase remains at the bottom. In the case of crossed nicols one may observe the formation of liquid crystal spherulites in the xylene solution. Sometimes in the freshly formed preparation one may observe an intense microturbulent motion of the substance: dust particles, inside the spherulite, are rapidly rotating in the circle up and down. The surface of the spherulite in this case remains motionless, just as the spherulite cross. Such a mobility of substance inside the spherulite indicates the nematic nature of the structure of the spherulite. After several minutes of motion it ceases, spherulites increase in size, merge with each other, forming a typical smectic texture.

Figure 40. Texture of lyotropic liquid crystals of potassium oleate near the edges of the cover glass (a) and in the center (b) (crossed nicols, 288 x).

Figure 41. A single domain of the lyotropic liquid crystal texture, having the shape of a body of revolution (natural light, 1880 x).

Figure 42. A fragment of the domain texture, in contact with glass. The lower part of the domain has the shape of a body of revolution (crossed nicols, 300 x).

Figure 43. Stratification of the smectic texture of potassium oleate (80 x).

The aqueous solutions of thyazine dyes in particular neomethylene blue also produce lyotropic crystals [37]. In the case of high concentration of solvent on the slide (without the cover glass) they appear in the form of anisotropic droplets, floating in the isotropic solution. Upon contact droplets merge and can form a solid (or lattice) film, which displays fibrous extinction. Sometimes quite large uniform sections of the film appear all at once. In the case of crossed nicols it is apparent how individual sections of the film suddenly darken or become lighter. This occurs due to the sudden change in the orientation of molecules in a given section which results from the flow of the film. The properties of such lyotropic liquid crystals are analogous to the properties of the ordinary nematic phase. Upon gradual drying of the preparation the nematic phase, apparently is transformed into smectic phase, which is accompanied by the appearance of a new fibrous texture.

Even with little experience in work with the microscope one can still observe the changes which occur in lyotropic liquid crystals. Moreso, they are always handy. They are ordinary inks, which are unsaturated solutions of dye, from which upon evaporation of water liquid crystals precipitate.

The solvent -- smectic liquid crystal system frequently gives rise to a characteristic texture in the so-called myelin (Fig. 44). The occurrence of these forms is best observed in the cholesterin-glycerine system. Upon heating to a definite temperature $t_1$ cholesterin combines with glycerine and produces smectic type liquid crystals. Upon further

heating to temperature $t_2$ liquid crystals are melted, dissociated into initial components -- cholesterin and glycerine. This phenomenon, discovered by Mlodzeyevskiy [39], is called dissociation of liquid crystals, since the latter are stable only in a definite temperature interval $t_2 - t_1$. If such crystals are heated between the slide and the cover glass smectic phase absorbs the excess glycerine and the growth of myelinic form increases. Here glycerine plays the role of solvent for liquid crystals, and therefore the texture in the form of myelinic form is classified as liquid crystalline formation of lyotropic character. In the process of the growth of the myelinic forms they move interweaving with each other similar to a clump of snakes. Under the crossed nicol prisms the center of myelinic tubes always appears extinct, while the edges display strong double refraction. The sign of the elongation of tubes is positive. Myelinic tubes 0.01 - 0.02 mm in diameter have bright interfering coloration.

Figure 44. Myelinic forms of the texture of cholesterin-glycerine systems (crossed nicols, 600 x).

Lyotropic liquid crystals may be formed in three component systems [39-44]. It is known that certain organic substances, insoluble in water, become soluble in soap-water solutions (solubilization). Such three component systems, soap-water-insoluble in water substance in a definite region of the phase diagram exist in liquid crystalline state. Thus, for example, cholesterin having a melting point of 148.5° C exists at room temperature in a stable liquid crystalline state in soap-water solution at 1 mole cholesterin per 1 mole of soap concentration. In the course of dissolution of solid substance liquid crystalline spherulites are formed as well as myelinic forms. The scheme for the structure of myelinic forms for this case was proposed by Lawrence [41] and is shown in Figure 45.

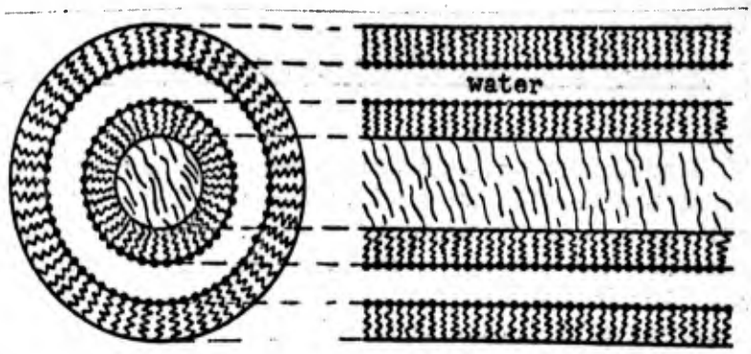



Figure 45. Structure of myelinic tubes, formed during solubilization. Myelinic shells consist of two cylinders, formed by the molecules of soap. Inside is the substance, dissolved in the soap-water solution.

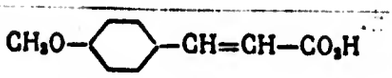
## Chapter 2

## STRUCTURE OF LIQUID CRYSTALS

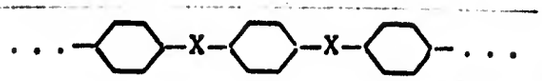
### 1. Structure of Molecules Which Form Liquid Crystals

Over 3000 organic compounds are known which are capable of existing in liquid crystal state. The work of Vorlander [7], Weygand [45], Gray [47] and others have shown that liquid crystals are formed principally from these compounds the molecules of which have elongated lath shape or platelet shape. The presence of branch molecules with side chains greatly hinders the occurrence of liquid crystals.

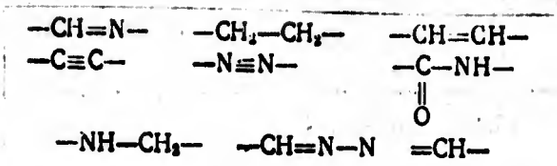
Many substances which produce liquid crystals are found among the aromatic compounds. It is noted that the majority of them have para-substituted benzene rings. If the substituent is in the ortho or in the meta position, the compounds become incapable of forming liquid crystals. An example of a liquid crystal with one benzene ring may be trans-p-metoxycinnamic acid.



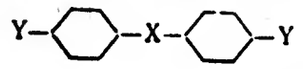
The tendency to the formation of liquid crystals increases with the increase of the number of interconnected benzene rings. The grouping of atoms X plays an extremely important role in connecting benzene rings into a chain



The liquid crystal state is most frequently found in compounds with the following X-groups of atoms



There is evidence [46] regarding the similar effect of the end group Y in the aromatic type compound



A list of such end groups is given below.

| | | |
|---|---|---|
| $CH_3(CH_2)_n$ | — | n- alkyl |
| $(CH_3)_2CH(CH_2)_n$ | — | alkyl |
| $CH_3(CH_2)_n O$ | — | alkoxy |
| Cl, Br, J | — | halogens |

There also exist liquid-crystal compounds containing naphthalene rings. One must remember, however, the tendency to formation of liquid crystals in these compounds in lesser than in the compounds with benzene rings. An important group of substances is formed by compounds which contain cyclopentanonperhydrophenanthren group and a long side chain (cholesterin esters). Liquid crystals are much less frequently found among the aliphatic compounds. This is apparently explained by the relative instability of the long aliphatic chains: during the transition from the solid crystal state into liquid crystal state it is difficult for these molecules to preserve their linear form. Nonetheless the study of this group of compounds is of interest since they have great practical importance (soaps, polymers).

We have presented the most widely known information regarding the structure of molecules which form liquid crystals. In conclusion let us note that on the average for every 200 newly synthesized organic compounds one such substance is found which forms liquid crystals.

The structural formulae of liquid crystal substances may be most diversified. This is apparent from the Table 1 given here. It was borrowed by us from the work of Gray [47].

TABLE 1

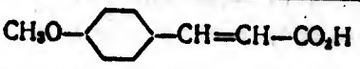
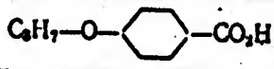
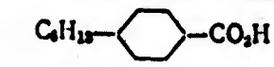
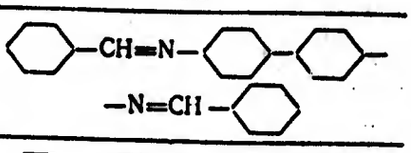
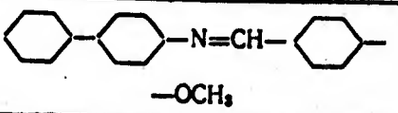
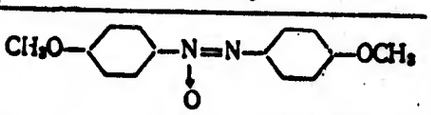
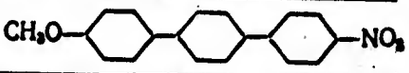
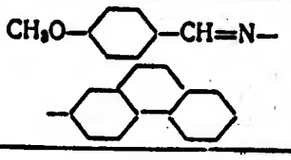
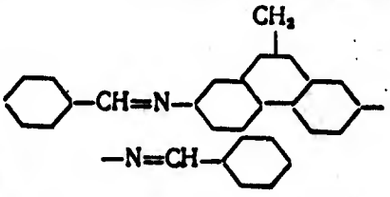
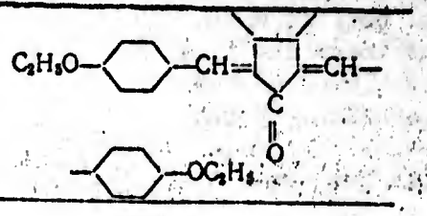
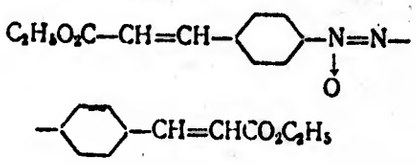
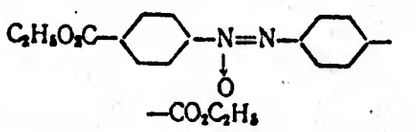
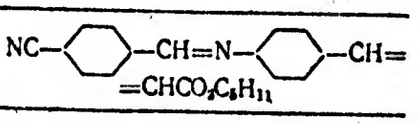
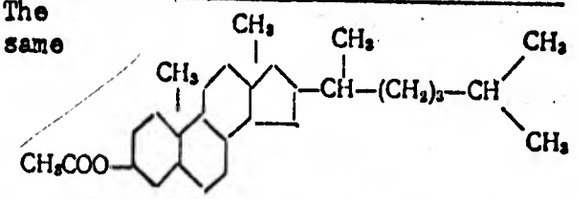
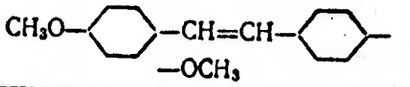
| Compound | Type of liquid crystal | Structural Formula |
|---|---|---|
| 6-methoxy-2-napthoic acid | Nematic |  |
| Trans-p-methoxycinnamic acid | The same |  |
| p-n-propoxybenzoic acid | " |  |
| p-n-hexylbenzoic acid | " |  |
| 4,4'-di-(benzylidenamino) diphenyl | " |  |
| 4-p-methoxybenzylidenimino-diphenyl | " |  |
| p-azoxyanisole | " |  |
| 4-methoxy-4"-nitro-p-terphenyl | " |  |
| 2-p-methoxybenzyliden-eaminophenonthrene | " |  |
| 2,7-di-(benzylidene-amino)fluorene; | " |  |

Table 1 (continued)

| Compound | Type of liquid crystal | Structural Formula |
|---|---|---|
| 2.5-di-(p-ethoxybenzylidene)cyclopentanone | Nematic |  |
| ethyl-p-azoxycinnamate | Smectic |  |
| ethyl-p-azoxybenzoate | The same |  |
| amyl-p-(4-cyanobenzylideneamino)cinnamate | Cholesteric |  |
| cholesteryl acetate | The same |  |
| 4,4'-dimethozystilbene | Nematic |  |
| potassium oleate | Smectic | $CH_3(CH_2)_7CH=CH(CH_2)_7CO_2K$ |
| ammonium oleate | The same | $CH_3(CH_2)_7CH=CH(CH_2)_7CO_2NH_4$ |
| nona-2,4-dienoic acid | Nematic | $CH_3(CH_2)_3CH=CH-CH=CHCO_2H$ |
| undeca-2,4-dienoic acid | The same | $CH_3(CH_2)_5CH=CH-CH=CHCO_2H$ |

## 2. Symmetry of Liquid Crystals

The general principles of symmetry of liquid crystals have been established by academician Shubnikov [48]. For the description of smectic liquid crystals spacial semicontinuum symmetry of the first kind is applicable. The concept of semicontinuum is introduced for the description of objects which have periodic structure not along three directions, as in ordinary crystals, but in two directions or in one direction. The semicontinuum of the first kind has layered structure, determined by one parallel transition at the end along the C axis and infinitesimally small shifts along all perpendicular directions to the C axis along the layer A (in the plane of the paper). The symbol for such summetry is C:A.

For the nematic liquid crystals spacial spacial semicontinuum symmetry of the second kind is proposed, formed by the infinitely small shifts along C and finite shifts along the perpendicular direction B. The symbol for symmetry is C':B (C' is the axis of infinitesimally small shift and B is the symbol of symmetry for the lattice arrangement).

Recently it became clear that the symmetry of real liquid crystals may be described through the use of the statistical idea and introducing the element of statistics into the symmetry operation. In particular, symmetry was considered for the aggregates of chain molecules by B. A. Vaynshteyn [9].

It is known, that molecular order, analogous to liquid crystal order is observed in many high molecular compounds (for example in lyotropic liquids polypeptides and virus crystals). The molecules of plastic or liquid crystals are not truely chain molecules, but they are significantly elongated. This enabled us to expand systematization which referred to chain molecules.

In the theory of symmetry of chain molecules and their aggregates, developed by Shubnikov, it is significant that in contrast to the earlier theories, it considers the symmetry of individual molecules and investigates the relationship between their structure and the symmetry of the aggregates which are formed by them. On the basis of this theory, using the well known values of covalent and intermolecular radii, it is possible to construct molecular models (Fig. 46), where their structure is represented as some geometrical body of a definite shape.

A multitude of investigations has shown that substances which form liquid crystals are constructed, as a rule, from sharply anisometric molecules with very low symmetry. The general characteristics for nematic and smectic liquid crystals are that their molecules are located parallel to each other. This produces more dense packing of molecules than in the case of chaotic orientation. This very geometric factor presupposes that for liquid crystals a certain minimum energy of packing is characteristic, intermediate between the values of energy of true crystals and the true liquid.

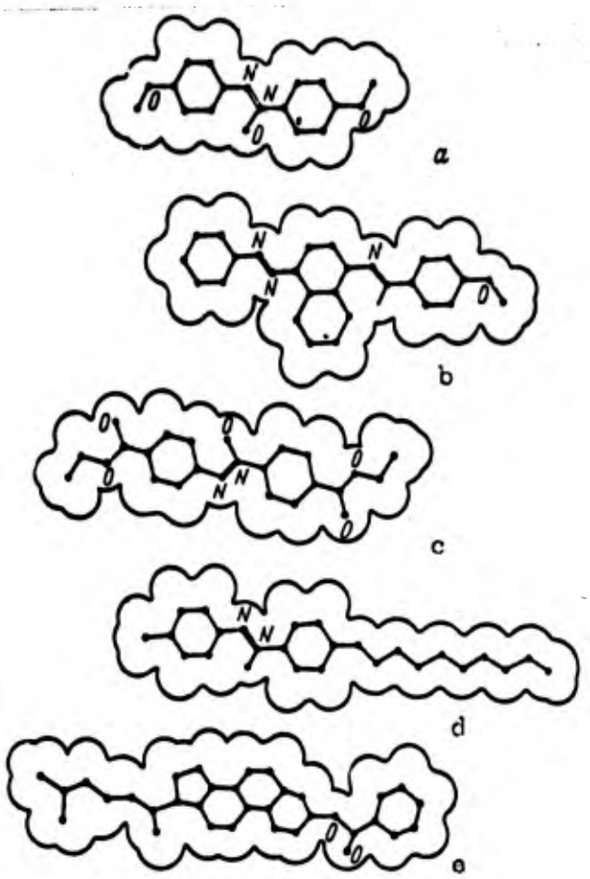



Figure 46. Shapes of liquid crystal molecules.
a. p-azoxyanisole; b. $\alpha$-benzazo-(anisole-$\alpha'$-naphthalanine);
c. ethyl p-azoxybenzoate; 2-n,n'-nonoxybenzaltoluidine;
d. cholesteryl benzoate.

In considering the theory regarding the disruption of symmetry, which always takes place in the real molecular aggregate, statistical ideas are widely used.

Let us consider the principal ideas of this theory.

In an ideal crystal the axes of long molecules are generally parallel to each other, the positioning of molecules is periodic and along these axes as well as in two other directions. In the case of such three dimensional periodic scheme of molecular packing the following disruptions may occur: a) the sphere of molecules in the direction of the longitudinal axes in the parallel position; b) rotation around the principal axis and c) disruption of the two dimensional periodicity in the projection along the principal axes ("disruption of lattice"). All these forms of disruptions

are generally associated with each other, but in order to have the possibility of investigating the effect of disruption on the diffraction of x-rays, they can be more easily viewed as separate entities, and then one could take into account the existing interrelationship. Let us consider the effect of individual forms of dislocation on the nature of aggregation of molecules.

Shear. Let us mentally place all of the molecules of the given aggregate on one axes Z without displacement in the direction parallel to the position of molecules. If the structure were that of an ideal three dimensional crystal all of the molecules would coincide precisely. The point, taken in molecules at the beginning of coordinates, (for example the center of gravity of the molecule) would fall in this case in the manner shown in the graph in Figure 47a. However, if there are shifts in the aggregates, the shear of function $\tau$ (z) describing the statistical distribution of molecules would have another form (Fig. 47b). In the case of completely random and equally probable shears the magnitude of the shear function would become constant and the graph will be linear (Fig. 47c). Such distribution may be characterized by the operation of infinitesimally small transport $\tau_\infty$.

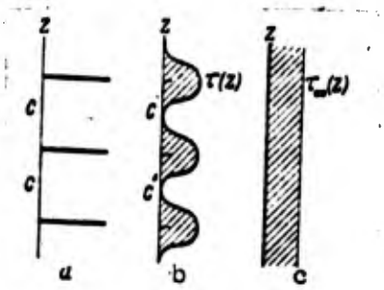



Figure 47. Shear function $\tau$(z) in the case of different arrangement of molecules.

Rotation. Rotation is statistical scattering of the molecular orientations about some equilibrium position (Fig. 48a). It may be characterized by the function $f(\Psi)$, which defines the probability of finding a molecule at some angle $\Psi$ (Fig. 48b). The circular cross section of molecules favors the angular scattering of molecules being transformed into a complete spectrum of all possible orientations. In this case it is possible to speak of "rotation" of molecules. The function $f(\Psi)$ becomes constant (Fig. 48c). The term "rotation" should be thought of as statistical, i.e., that all molecules are oriented differently. However, cases are known when thermal oscillations of molecules about the principal axes are so great that one may speak of real rotation.

Lattice defect. The projection of molecular axes on some plane forms a lattice, which is characterized by translations a and b. Depending on the magnitude of translation and the angle between them the lattice may

be classified into five different types: square, hexagonal, thombic, rectangular and oblique parallelogram. The occurrence of different types of lattices is determined primarily by the shape of molecular cross sections. During packing in the general case sixfold coordination is maintained (each molecule is surrounded by six neighbors). If the molecules have a cross section which is close to circular the mosr symmetrical hexagonal lattice is produced.

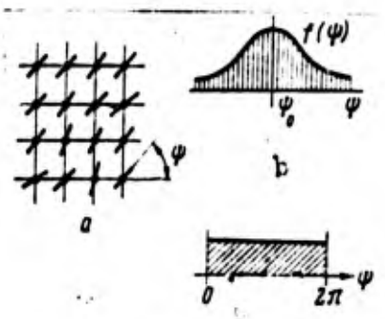



Figure 48. Rotation function. a. molecular rotation; b. function $f(\psi)$; c. $f(\psi)$=const.

The lattice defects are determined by the fact that in each unit cell there are translation parameters a and b. Such a system, however, can remain static on the average. For all crystals lattice defects of the second type are characteristic (Fig. 49a) when a and b determine the probable position for only the neighboring molecules with respect to each other. This close order in the arrangement of molecules may be characterized by the distribution function of the second kind w(xy). The following approach is taken in construction of this function. The position of the center of gravity of molecules, surrounding some one molecule, then the second, then the third, etc. is plotted around the origin of the coordinate while maintaining the orientation of translations a and b. This in essence constitutes the superposition of the molecular distribution schemes, shown in Figure 49a, with stepwise shift of the center of each molecule to the origin of the coordinates. As a result the distribution function w(xy) is determined for the neighbors in the given molecular aggregate (Fig. 49b). This function clearly expresses the distribution of the nearest molecules, i.e., the closest order is determined, which depends on the minimum distance in the aggregate beyond which the molecules cannot approach each other. However, there can also be no large vacancies between them. It is clear that in the case of such an arrangement the distance to the second nearest neighbor varies within broad limits, since deviations in translations a and b are accumulated not only from the given molecule to the first neighbor, but also from it to the second neighbor. The further is the neighbor the more "smeared" is the distribution function. At some distance away it becomes constant. The probability of finding molecules becomes the same everywhere. It is possible to say, that translations a and b

become gradually degenerate into continuous shifts $\tau_{\sim}^{a}$ and $\tau_{\sim}^{b}$. The graphical representation of the distribution at w(x) for one direction of OX shows that its peaks become less and less pronounced as the distance from the origin increases and at some distance from O they disappear and the curve becomes smooth.

In the liquid crystals in plane XY molecules possess close order (it is assumed that longitudinal axes of molecules of the domain are perpendicular to the plane XY and are directed along the Z axis). The close order is characterized by the two dimensional distribution function w(xy) or the function x(r), which gives the probability of the occurrence of vector r (the distance between molecular axes). The function w(r) is periodic, but it has attenuating maxima (just as function w(x)). If the cross section of the molecule varies greatly along its length, then the static periodicity, described by the function w(r), becomes impossible. In this case the neutral distribution of molecular axes may be described by the cylindrically symmetrical function Z(r), in the case of which r is the probable distance between molecular axes. In the case of averaging of the function Z(r) the cylindrical distribution function of molecular axes is projected on the plane XY-$2\pi rZ(r)$.

Thus, the disruption of the periodic distribution of molecules may always be characterized by definite functions: shears -- shear functions $\tau(z)$, rotations by the function $f(\psi)$ and lattice defects by the distribution function w(xy) or w(r).

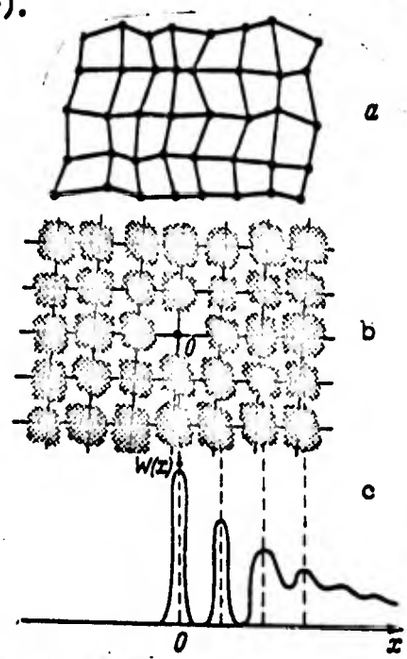



Figure 49. Lattice defects of the second kind.
a. defect scheme;
b. distribution function;
c. a plot of the distribution function.

We have said previously that all of the above considered lattice defects are mutually related. Thus, if we have shears, this will invariably produce defects (due to nonuniform molecular cross section). The presence of rotation also always leads to lattice defects, which may be accompanied by the increase of the statistical symmetry of the lattice to hexagonal: $w(xy) \rightarrow w(H)$, where H is hexagonal order. The mutual effect of shears and rotations produce the same result: the tendency appears for the formation of hexagonal close order.

Applying these functions to the liquid crystal aggregate one may assign to the smectic liquid crystals symmetry $C\tau(z)\, w(xy)$, where $\tau(z)$ is the shear function, w(xy) is the distribution function and C is the period of the layer as a whole. From the x-ray data it is clear that it is possible to have smectic liquid crystals of the $C\tau(z)w(H)$ type, where H designates hexagonal ordering of molecules in the layer. Investigation of structure by means of x-ray diffraction enables us to write general symmetry formulas for liquid crystals in greater detail and to write them in a more resolved form. Thus, for example, smectic liquid crystals of cerebron, cholesteryl caprinate, p,p-nonoxybenzaltoluidine have lamellar structure with antiparallel packing of molecules in the layers. Their symbol of symmetry $C\tau(z)w(xy)$: 2 also include statistical axes of the second order, which assign antiparallel characteristic of molecules in the layer and lying in the planes of the layers.

The nematic liquid crystals have $\tau\, x(xy)$ or $\tau_\infty w(H)$ type symmetry. As it was earlier noted they are optically inactive, but if the layers of substance are subjected to spiralling, then the liquid crystal becomes optically active, which results from the congruent spiralling of the molecular aggregate. This case should be referred to the $\tau_\infty w(xy)$ or $\sigma_\infty w(H)$, where $\sigma_\infty$ designates the screw axes and the corresponding continuous screw type of translation. Apparently this type of symmetry also includes cholesteric liquid crystals.

Thus, we can see that for a higher degree of ordering of the molecules in a liquid crystal a more detailed description is required than in the case of ordinary liquids. In order to characterize close order in the liquid one radial function is used for the distribution of atoms w(r) (or for the averaged form the function $4\tau r^2 \rho(r)$, which determines the number of molecules in the spherical layer with radius from r to r+dr).

## 3. X-ray Structural Analysis of Liquid Crystals

The first attempts to investigate liquid crystals by means of x-ray structural analysis were made immediately after the discovery of the diffraction phenomenon of x-rays [49-51]. However, originally it was not possible to uncover the difference between the diffraction of liquid and of ordinary liquids. Both of them produce instead of the sharp narrow rings, characteristic of powder diffraction patterns, broad diffused rings.

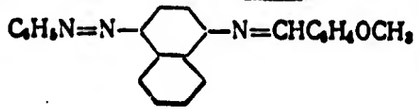
Later on it was still found that the maxima of rings from liquid crystal substances are somewhat shifted with respect to the maxima of its isotropic melt. The sharpness and the intensity of peaks are also different. The significant difference between the x-ray diffraction patterns of liquid crystals and of ordinary liquids was discovered during the study of scattering of x-rays by the textured specimens [52, 53], which were obtained by the action of the magnetic or the electric fields. The diffused rings for such specimens of liquid crystals dissociate into half moons, which indicate the orientation of the crystal in the external field. The x-ray pattern of ordinary liquids in the electric field preserve the shape of diffused rings.

In the low frequency alternating electric fields, parallel to the beam of x-rays the diffused ring of liquid crystal p-azoxyanisole dissociates into two half moons, where the axis of the half moon figure is directed along the field, which indicates that the molecules are oriented parallel to the field. When the frequency is increased to 300,000 Hg the half moon figure is replaced by diffused rings. With further increase of the frequency of the field the half moon figure again reappears but its axes are located now perpendicular to the original direction. Kast [54], who observed this phenomenon explained it on the basis of the existence of dispersion of friction. The period of oscillations of the field becomes smaller than the relaxation time, and molecules (or their clusters) do not have the time to align themselves along the field.

As the x-ray analysis methods were improved new details of the structure of liquid crystals were discovered. Thus, Falgueirettes [55] established that the diffraction pattern of the oriented specimen of p-azoxyanisole has the shape of two equatorial diffused arcs and three pairs of weaker meridial arcs. Assuming that the distribution of molecules results from their rotation about optical axes Falgueirettes associated the changes of the intensity along the principal maximum (equatorial arcs) with the variation of the number of molecules, which the angle $\alpha$ with respect to the axis. The position of the principal equatorial maximum was explained by him by the intermolecular interference, and the position of the three weaker meridial maxima he calculated on the basis of the assumption that they are associated with intramolecular interference.

Recently Vaynshteyn and the author [56-59] showed that the structure of liquid crystals may be determined by the Fourier method, i.e. by finding the distribution function which characterizes the structure of liquid crystals directly from x-ray diffraction patterns.

Let us consider the following example. The crystalline $\alpha$-benzeneazo-(anisole-$\alpha'$-naphtylamine) or BAN



melts to form isotropic liquids at 151° C. Upon cooling nematic liquid crystals are obtained in the form of resin, which at 35.5° C has viscosity of 15000 poise. Upon further cooling the resin solidifies. The specimens of BAN for x-ray diffraction analysis were prepared as follows. Isotropic melt was drawn up into a thin capillary tube (wall thickness 0.001 mm, diameter 0.4 mm), which immediately after the appearance of liquid crystals was immersed into cold water for supercooling. The liquid crystals were thus vitrefied.

In order to obtain oriented crystals BAN melt was poured into cold water, where it was converted into a thick liquid crystal resin. From the resins by means of drawing rods 0.3 - 0.5 mm in diameter were manufactured. In the course of drawing oriented texture was obtained. The longitudinal axes of molecules acquired predominantly the orientation along the axes of the cylindrical rod. The specimens were placed in the path of a narrow monochromatic x-ray beam and a flat photographic plate was placed behind the specimen (Fig. 50). On the x-ray pattern of the oriented specimens obtained in such a manner equatorial and meridial maxima were clearly visible. Study of the intensity of x-ray scattering by the solid crystal powders and vitrified liquid crystal BAN showed that the shapes of intensity curves are in general similar (Fig. 51). One will note, however, that the sharp peak on the curve of the first specimen becomes somewhat washed out and merged together forming a diffused maximum.

On the basis of the Fourier transformation method one may construct a curve for the radial distribution of atoms. The BAN molecule contains 24 carbon atoms and only 3 atoms of nitrogen and 1 atom of oxygen (the atoms of hydrogen which have very low scattering efficiency may be neglected). Therefore, for the first approximation BAN may be assumed to consist of only carbon atoms and in order to find the radial distribution function one may use spherical Fourier's integral.

$$4\pi r^2\rho(r) = 4\pi r^2\rho_0 + \frac{2r^2}{\pi}\int_0^{s_{max}} s^2 i(s)\,\frac{\sin sr}{sr}\,ds$$

Here $4\pi r^2\rho(r)$ is the radial distribution which determines the number of atoms in the spherical layer of thickness dr at a distance r from the initial atoms, $\rho_0$ is the average atomic density of substance, or the number of atoms per cubic angstrom, i(s) is the function which may be found from the normalized and smoothed out experimental intensity curve for scattered x-rays and $s = \frac{\pi \sin\theta}{}$ is a function of the scattering angle $\theta$.

The normalized and smoothed out curves of the intensity of scattered x-rays by an unoriented specimen are shown in Figure 52A. The smooth broken line represents the atomic scattering factor $f^2$. The conversion of this intensity curve by means of Fourier's integral enables the construction of radial atomic distribution function in the object (Fig. 52B). The peaks

on this curve correspond to the accumulation at a corresponding distance from the initial atom (chosen to serve as the origin of coordinates), i.e., the frequently found interatomic distances. The valleys on the curve are those places where the number of atoms is smaller. The study of the radial distribution curve leads one to the conclusion that scattering centers (atoms) are periodically distributed in the substance. One must, however, remember that the obtained radial distribution function of atoms is insensitive to whether the atoms belong to one molecule or to different molecules. For this reason in order to determine whether the peaks are "intramolecular" or "intermolecular" should be solved on the basis of other data.

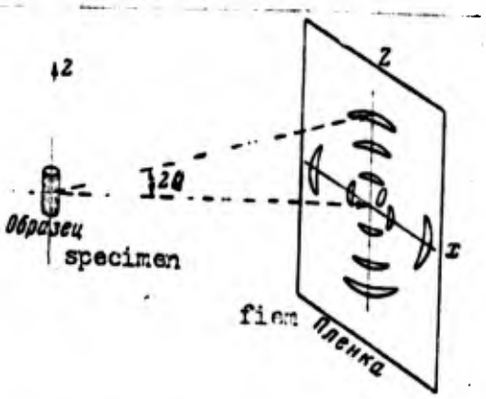



Figure 50. Placement of specimen, oriented along the principal axis Z. Broken lines indicate the primary beam of x-rays and one of their diffraction beams. The film shows reflections in equatorial OX and in the meridial OZ directions.

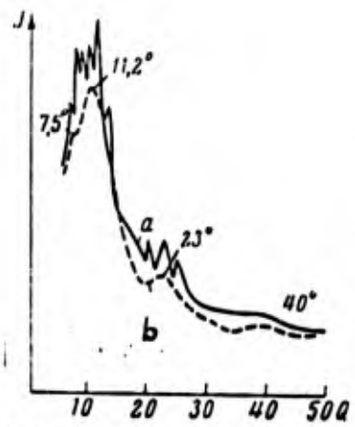



Figure 51. Intensity of scattering of x-rays by a liquid crystal (a) and a solid (b) specimen of BAN.

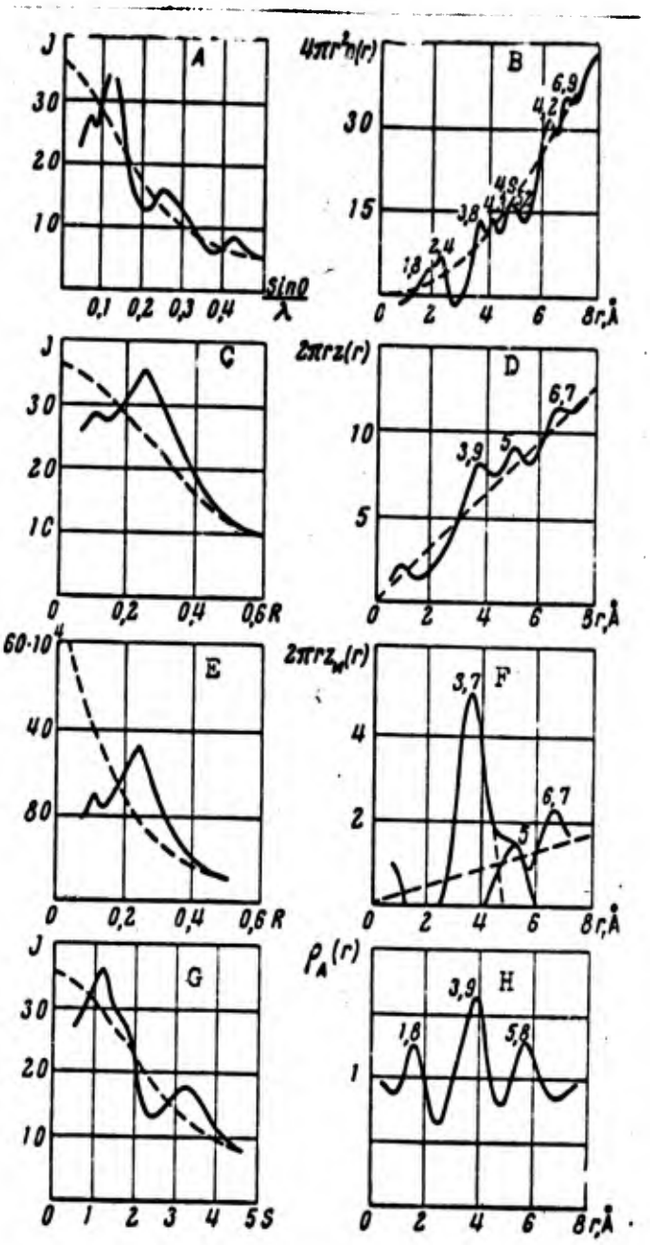



Figure 52. Intensity curves (left) and the corresponding distribution functions (right).

In considering certain most frequently found interatomic distances in BAN molecules with the position of peaks on a radial distribution curve it was established that many distances are close to the values of peaks. The interatomic distances, found in the experiments with BAN molecule models are also close to the values of peaks.

Such a comparison of the values of distances and peaks enables us to make preliminary conclusions about the nature of the mutual orientation of molecules in the specimen.

More definite conclusions regarding the structure of liquid crystals are obtained from the study of the intensity distribution on x-ray diffraction patterns of the oriented specimens. In this case (Fig. 52C) intensity distribution along the equator of the photograph enables one to construct the so-called cylindrical distribution function of atoms in the projection on the base plane of the specimen (perpendicular axis of the cylindrical specimen), by calculating it by means of Fourier-Bessel integral

$$2\pi r Z(r) = 2\pi r Z_0 + 4\pi^2 r \int_0^{R_{max}} i(R)\, J_0(2\pi r R)\, R dR$$

$$R = \frac{2 \sin \vartheta_{\text{экв}}^{\text{equiv}}}{\lambda};\quad J_0(2\pi r R) - \text{zero order Bessel function}$$

The cylindrical distribution $2\pi rZ(r)$ indicates the number of atoms, included into the circular belt (radius r, thickness dr) of the plane, perpendicular to the axis of the specimen. The shape of this function is shown in Figure 52D. The peaks of this curve indicate intermolecular distances in the specimen despite the fact that $2\pi rZ(r)$ function refers to the distribution of atoms. This results from the fact that the greatest number of atoms.in the projection falls on the atoms which are located along the molecuarl axis. Consequently, the principal contributions of the peaks of the $2\pi rZ(r)$ curve are made by these "axial" atoms.

This is also verified by other methods of correlation of experimental values of the intensities along the equator. The curve may be calculated on the basis of scattering not per atom, but per molecule (Fig. 52E). In this case from the Fourier-Bessel integral a cylindrical distribution function is constructed for the projections of the molecular axes on the base plane. The peaks of the functions (Fig. 52F) indicate the intermolecular distances in the specimen. It can be seen that they are in good agreement with intermolecular distances found on the bases of model representations (3.6; 5; and 6.7Å). The area under the peaks indicates the number of molecules which are found at the corresponding distance from the origin of the molecules. Thus, calculation of the area under the 3.7 and 5Å peaks indicates that the number of the closest neighbors, surrounding the given molecule is approximately 6.

Finally, studying the distribution of the intensities along the meridian of the photograph (Fig. 52G), one may construct linear distribution function for atoms along the texture, using for this one dimensional Fourier's integral.

$$\rho_x(r) = \rho_{ox} + \frac{1}{\pi}\int_0^{s_{max}} I(s)\cos srds$$

This function is shown in Figure 52H. The peaks indicate intramolecular distances.

Comparison of the distribution curves enables us to construct the most probable model for the structure of the liquid crystal of BAN specimen (Fig. 53). The symmetry symbol for such structure will be: $\infty\infty w(xy)$, which corresponds to the theoretical data presented earlier. A number of liquid crystals of nematic, cholesteric and smectic type were investigated by this method.

The x-ray photographing of substances, which cannot be obtained in the supercooled state, should be conducted in a special high temperature chamber. One of the designs of such a chamber is shown in Figure 54. The housing of the camera 1 is covered inside with a double layer of thermal insulation (texolite-asbestos). The removable cover 2 has two openings for the mercury thermoregulator 7 and the control thermometer (not shown). The x-ray beam passes through the collimator 6, falls on the specimen, mounted in a special holder 3. The inner part of the holder is made from brass, and the outside part from bakelite. It may be rotated along with the specimen through an angle of 30° with respect to the vertical plane. Heating block 4 is used for heating of the specimen, located in the lower part of the holder, and when the whole chamber is thermostated the heating element 5 is sued. Mercury thermoregulator 7 is connected to the electromagnetic relay. The temperature is regulated (with accuracy to $\pm$ 0.2° C) by means of copper-constantan thermocouple. In addition a control thermometer with 0.1° C calibrations is available. The phase transitions of crystals are observed through a mica window 8, which serves for the measurement of the diffracted rays. The thickness of the investigated specimens is generally 0.5 mm. During the preparation the substance is suspended in a circular loop of platinum wire. The diameter of the loop is 0.5 mm.

The x-ray diffraction patterns of cholesteric and smectic specimens are interpreted in the same manner as the x-ray patterns of nematic crystals. Let us only note that the x-ray diffraction patterns of smectic specimens at low angles always contain d reflection, for which the interplanar distance calculated from the Bregg-Wolf equation $2d \sin\theta = n\lambda$, is approximately equal to the molecular length. This is the proof of the existence of crystal layers in the smectic crystal, formed by the molecules, the longitudinal axes of which are approximately perpendicular to the plane of the layer.

For tight packing of the molecules in smectic layers the most convenient is antiparallel distribution of molecules. This means that the symmetry symbol of smectic specimens may be written as $C_{\tau}(z)w(xy):2$. Let us remember that here C is the period of the layer as a whole, equal for example in p-p'nonoxybenzaltoluidine to 25.2Å; $\tau(z)$ -- shear function; w(xy) -- distribution function, and 2 are the statistical axes of the second order, lying in the plane of the layer and describing the "inter-parallel" packing of molecules [58].

A number of lyotropic liquid crystals have been investigated by means of the x-ray analysis method, primarily the crystals of different soaps. The typical phase diagram for soap-water is shown in Figure 55. The area included between $T_1$ and $T_2$ corresponds to the lyotropic liquid crystals. Luzzati and coworkers [60] established that phase A is formed as smectic double layer, formed by the soap molecules. On the surface of the layers the polar ends of the molecules appear, and "liquid" hydrocarbon chains are directed inward. As the concentration of the soap increases the thickness of the soap layers increases and the layers of water between them become thinner and thinner. The phase is formed in the shape of long cylinders, ordered hexagonally. The diameter of the cylinders is independent of the concentration within the bounds of the region B at constant temperatures. In addition to these two phases, in the region C of the phase diagram three intermediate phases were discovered: complex hexagonal, deformed phase B (with orthorhombic lattice) and cubic lattice (isotropic), in which the hydrocarbon chains are ordered into spheres, separated by water. In fact the phase B and two intermediate phases are the new structural types of liquid crystals.

The lyotropic liquid crystals of the tobacco mosaic virus were also investigated [61]. Their x-ray patterns have four sharp equatorial reflections, which enables us to speak of the distribution of particles in the form of a two dimensional hexagonal lattice (Fig. 56). The cholesteric lyotropic liquid crystals of certain polypeptides (for example, poly-$\gamma$-benzyl-L-glutamate) have a structure analogous to that shown in Figure 56, but spiraled in addition to that along the Z axis [30].

In conclusion of this section one must note that x-ray diffraction study of liquid crystals, especially specimens subjected to the action of electric or magnetic fields is at present the most promising method for further investigation of the structure and the nature of substances in the liquid crystal state.


Figure 53. Model of the structure of BAN.

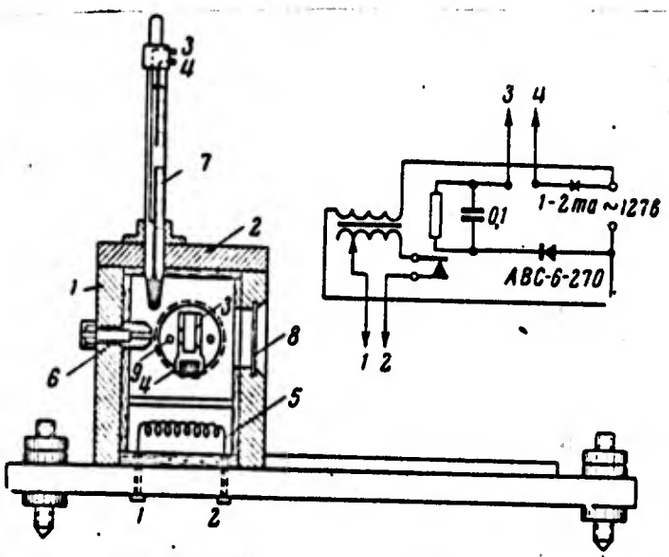



Figure 54. Heated x-ray camera for the investigation of liquid crystals.

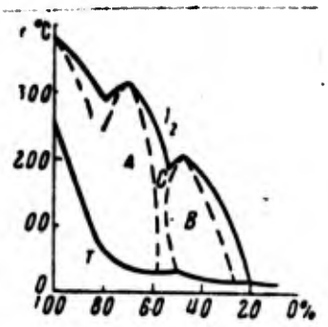



Figure 55. Diagram for the potassium palmitate-water system. The liquid crystal phase exists in the region between $P_1$ - $P_2$.

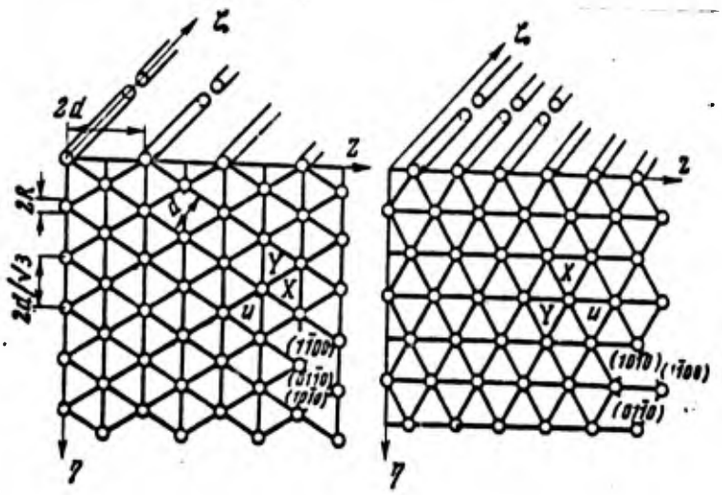



Figure 56. The structure of tobacco mosaic virus in solution. XVZU -- crystalographic axis; $\xi$ , $\eta$-- molecular axis.

## 4. The Theories of the Liquid Crystal State of Substance

A number of such theories exist. Each of these theories explains in some manner the properties of liquid crystals and at the same time each of the theories is in some manner limited, since it refers to only one of the types of liquid crystals or interprets some individual characteristics of the liquid crystal state, leaving other characteristics without any explanation. Nonetheless one may constitute that at present there is definite progress in this direction and apparently unification of these theories and their advancement is something which will take place in the near future.

At present there are two principal directions in the development of the theory of the liquid crystal state -- the molecular-statistical theory and the theory of elasticity of liquid crystals. Let us consider these theories in general terms.

The first attempt to construct the molecular-statistical theory of liquid crystals was made by Born [62]. The starting moment of this theory was the assumption about the existence of a constant dipole moment in liquid crystal molecules. The internal electric field E, affecting the dipole molecules in this case will be of the following magnitude

$$E = \frac{4}{3}\pi P,$$

where P is the electrical polarization vector.

The existence of the internal electric field, is, according to Born, the cause of spontaneous orientation of molecules in the liquid crystal. Applying the laws of Boltzman statistics enables the derivation of the following relationship

$$p = \sqrt{\frac{9kTM}{4\pi\rho N}},$$

where p is the dipole moment of molecules, M is the molecular weight of the substance, $\rho$ is the density, N is Avogadro's number, P is the temperature (at the loop) of the transition of the liquid crystal into isotropic liquid. The use of this formula for the case of p-azoxyanisole gives $p=3.6\cdot10^{-18}$ cgs units. However, the experimentally found values for the molecular dipole moment of p-azoxyanisole is one and a half times smaller, than the value on the basis of theoretical calculations. Thus, the theory does not give results which are in satisfactory agreement with the experimental data. Moreso, such liquid crystal substances are known, the molecules of which do not have permanent dipole moments. For such substances the theory is altogether inapplicable.

Not very long ago Maier and Saupe [63-65] again made attempts to construct the molecular-statistical theory of nematic liquid crystals. In contrast to the previous theory the cause for the nematic ordering of particles is the presence of intermolecular dispersion forces. The energy of interaction of molecules in the liquid crystal phase, according to this theory is expressed by

$$\vartheta = \frac{A}{V^2} S\left(1 - \frac{3}{2}\sin^2\theta\right),$$

where $\theta$ is the angle between the longitudinal axes the optical axis of the domain, A is constant, V is the molecular volume, S is the degree of ordering of molecules in the liquid crystal. It follows from this theory that the relationship

$$\frac{k_{ik} V^{\frac{7}{3}}}{S^2}$$

is independent of temperature. Here $K_{ik}$ is the deformation constant of the liquid crystal. The values of $k_{ik}$, calculated theoretically and found experimentally for p-azoxyanisole give quite satisfactory agreement. Let us note, that certain principal formulae of this theory were found emperically by the Tsvetkov [66] method long before the rigorous development of the theory. It appears that this theory is in agreement with the experiment. It should be noted that for verification of the universality of this theory experiments must be conducted with a larger number of substances than have been done thus far. Let us also note that it only refers to the nematic liquid crystals.

The theory takes into account the fact that the liquid crystal consists of clusters. From this standpoint, proposed bu Bose [67] and developed by Ornstein [68-70] and other scientists, nematic liquid crystals in a large volume (several cubic millimeters) consist of multiple molecular groups -- clusters. In each cluster the molecules are oriented in a definite direction. The clusters themselves are distributed randomly, as a result of which the liquid crystal in a large volume appears cloudy. The clusters possess double refraction, and are dielectrically and diomagnetically anisotropic. Each cluster contains $10^4$ - $10^6$ molecules. The thermal motion is manifested in that the clusters experience vibrations and are destroyed, but in accordance with the principal properties of the nematic state they are immediately reformed, acquiring new orientation. Let us note that the cluster concept is not equivalent to the domain. The uniformly oriented single crystal layers of nematic liquid crystals may be viewed as an individual large domain. When the optical axes of such a domain are perpendicular to the glass, it always appears extinct between crossed nicols of the polarizing microscope. However, in a dark field twinkling light points appear. According to the theory these points are clusters the optical axes of which for an instant deviate as a result of thermal motion from the direction of the optical axis of the whole domain and becomes visible between crossed nicols.

This theory may be verified by studying the behavior of liquid crystals in the external lds and comparing the theoretical conclusions to the experimental data by the interaction of the magnetic field, for example, on the liquid crystal it is possible to determine the magnitude of the magnetic moment of the liquid crystal particle. It was found to be $10^4$ times larger than it would be expected on the basis of the interaction of the field with a single molecule. On the basis of this fact conclusions were made that liquid crystals consist of clusters each of which contain at least $10^4$ molecules. However, subsequently it was established that liquid crystals (p-azosyanisole, p-azoxyphenetol) possess diamagnetic anisotropy. Consequently, the orientation of the liquid crystal occurs not as a result of the fact that molecules or clusters of molecules possess permanent dipole moment, but as a result of diamagnetic anisoptropy. The rotating moment of the magnetic field, operating on the diamagnetic particle is

$$M = vH^2(\chi_1 - \chi_2)\sin\varphi\cos\varphi,$$

where v is the volume of the particle, $\chi_1$ and $\chi_2$ -- the magnetic stability and the susceptibility in the direction parallel and perpendicular to the optical axes respectively, H -- magnetic field intensity and $\varphi$ is the angle between the direction of the magnetic field and the optical axis.

If one assumes that in addition to the rotating moment produced by the magnetic field the particle of liquid crystal experiences orienting interaction of the container walls, in which it is placed, the moment of the pair of these forces may be expressed as

$$D = A\frac{d^2\varphi}{dx^2},$$

where A is constant (modulus of elasticity of the substance), having dimensions of force, $\varphi$ -- the angle between the axis of the particle and the direction of the magnetic field, x is the distance between the particle and the orienting surface of the solid (container walls). In the case of the stationary state the orienting effect of the walls of the container must be in equilibrium with the rotating moment of the magnetic field, consequently D = M.

$$A\frac{d^2\varphi}{dx^2} = vH^2(\chi_1 - \chi_2)\sin\varphi\cos\varphi$$

This equation was derived on the assumption that the clusters of volume v possess diamagnetic anisotropy $\chi_1 - \chi_2$. However, as was noted by Tsvetkov, experimental verification of the correctness of this equation is still not proof of the existence of molecular clusters in liquid crystals. First of all, not one of the experiments enables the evaluation of the

volume v, secondly this equation written without v, will not lose its validity and will refer only to the equilibrium unit of volume of the substance.

In any case, as was convincingly noted Tsvetkov [71], the theory of clusters requires further development. In particular one can hardly say that clusters possess the same independence and rigidity as ascribed to them by the theory and undoubtedly the liquid crystal medium is more continuous than the cluster theory proposals. This certainly does not mean that the theory is absolutely incorrect. In any case it explains satisfactorily a number of characteristics which appear in liquid crystals: the scattering of light, the rotation of liquid crystals in a rotating magnetic field, etc. One may always say that the theory becomes less convincing when one views the liquid crystal not in a large volume, but in thin specimens, included between solid surfaces. Here the explanation of the properties of liquid crystals, apparently, may be made only on the basis of the theory of elasticity.

In contrast to the cluster theory, Xocher [72-74] proposed that the direction of the orientation of molecules of liquid crystals varies continuously from point to point and near disinclinations (threads) sharp changes of this orientation take place. Let us note that the equations for the effect of diamagnetic field on liquid crystals have in this case exactly the same form as in the theory of clusters, only the physical interpretation of coefficients is different.

Oseen [16], taking into account the potential energy of two interacting molecules, constructed a theory developed and augmented recently by Frank [15]. According to this theory the molecules may be oriented along the directions of different curvatures. The curvature may occur also in the case when the effect of the magnetic field, orienting the molecules parallel to the glass, does not correspond to the orienting effect of the container walls, which attempt to orient molecules perpendicular to the walls. If L is a unit vector, determined in the direction of molecular orientation (Fig. 57), then the curvature of the liquid crystal specimen may be characterized by six components.

$$b_1 = \frac{\partial L_x}{\partial z};\ b_2 = \frac{\partial L_y}{\partial z};\ s_1 = \frac{\partial L_x}{\partial x};$$
$$s_2 = \frac{\partial L_y}{\partial y};\ t_1 = -\frac{\partial L_y}{\partial x};\ t_2 = \frac{\partial L_x}{\partial y}$$

Components $b_1$ and $b_2$ characterize the longitudinal curvature; $s_1$ and $s_2$ -- transverse curvatures; $t_1$ and $t_2$ -- torsion (Fig. 58). The free energy density of the liquid crystal specimen in this case may be written as

$$g' = \frac{1}{2} k_{11} (s_1 + s_2 - s_0)^2 + \frac{1}{2} k_{22} (t_1 + t_2 - t_0)^2 +$$

$$+ \frac{1}{2} k_{33} (b_1^2 + b_2^2) + k_n (s_1 - s_2)(t_1 + t_2) -$$

$$- (k_{22} + k_{24})(s_1 s_2 + t_1 t_2)$$

$$s_0 = -\frac{k_1}{k_{11}}; \quad t_0 = -\frac{k_2}{k_{22}}$$

In accordance with the values of $k_{ik}$ (deformation moduli) we deal with different types of liquid crystals. In the case of smectic liquid crystals the free energy is minimum:

$$L\nabla \times L = 0; \quad (L\nabla) L = 0$$

Coefficients $k_{ik}$ are extremely small in comparison with the deformation moduli of torsion $k_{22}$ and longitudinal banding $k_{33}$, which principally characterizes the smectic specimen.

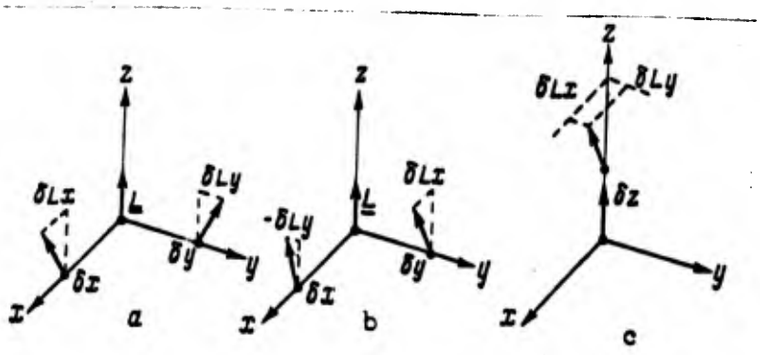



Figure 57. Vector components of the molecular orientation L in the case of different deformations.
a. transverse bending deformation
b. torsion
c. longitudinal flexure deformation.

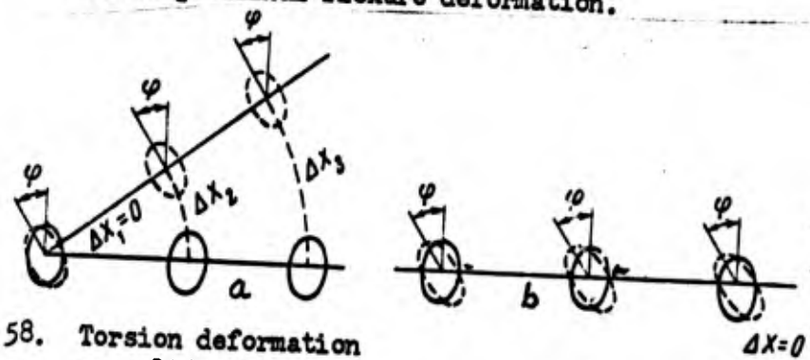



Figure 58. Torsion deformation
a. solid cylinder; b. liquid crystal; Δx-displacement.

For nematic liquid crystals $s_0=t_0=k_{12}=0$, and only four moduli $k_{11}$, $k_{22}$, $k_{33}$ and $k_{24}$ differ from zero. If the liquid forms planar texture, these moduli are equal to zero. In the case of cholesteric liquid crystals

$$k_{22} \neq 0, \quad k_2 \neq 0 \quad \text{and} \quad t_0 = \frac{k_2}{k_{22}} \neq 0$$

In the case of uniform orientation of specimens only the torsion exists which is characterized by $k_{22}$. The pitch of rotation is equal to $\pi/t_0$. If $k_1 \neq 0$ and $k_1 = k_1/k_{11} \neq 0$, then uniform transverse flexure takes place in a three dimensional space region. In practice this space is proven by the existence of texture in the form of cylindrical tubes (see Fig. 33).

The theory explains also the occurrence of disinclinations in the nematic specimens. The molecular configureation near the disinclination is calculated for the case $k_{11}=k_{33}$ and $k_{12}=0$. If vector L is parallel to the plane, the free energy is at a minimum in the absence of the moment of rotation when

$$\frac{d^2\Phi}{dx^2} + \frac{d^2\Phi}{dy^2} = 0,$$

where $\Phi$ is the azimuth of the vector L in the plane.

The solution of this equation expresses different types of disinclinations

$$\Phi = \frac{1}{2} n\psi + \Phi_0; \quad \operatorname{tg}\psi = \frac{x_2}{x_1},$$

where n = 1, 2, 3... (see Fig. 23).

Thus, the considered theory encompasses the characteristics of different types of liquid crystals. It is significant that it contains deformation coefficients, which may be measured experimentally. Extremely important work in this direction was carried out by Frederiks, Tsvetkov and Zolina [23, 75-77]. They established that the measurement of the moduli of deformation $k_{ik}$ may be realized by the interaction of the magnetic field on the specimen. In the case of liquid crystals it should be noted that the deformation differs significantly from the deformation of the rigid solid body. For example, if a magnetic field is applied to the layer of liquid crystals parallel to the glass (initially longitudinal axes of molecules are parallel to the glass, but perpendicular to the magnetic field), then it will rotate molecules in the plane of the preparation. This is opposed by the forces of the elasticity of the

liquid crystals, the surface of which is "mounted" on the glass. Deformation takes place, analogous to the torsion of a solid cylinder mounted at its base. Here there is a difference, since in the solid cylinder each element experiences in addition to the pure rotation gradual shift, the magnitude of which for different elements of the same layer perpendicular to the axis to the cylinder is different and it changes from zero at the axis to a maximum at the periphery. In the liquid crystal only rotation takes place, and the gradual shift does not exist (Fig. 58b). Analogous to this in longitudinal and transverse flexures in the liquid crystal cracking does not take place and the compression of layers does not take place, as it does during the flexure of solid specimens.

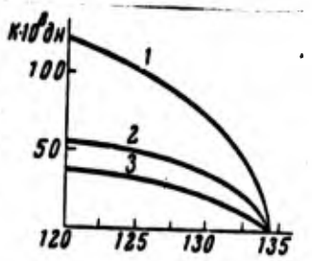



Figure 59. The values of moduli of deformation for p-azoxyanisole.
1. deformation of longitudinal flexure $k_{33}$
2. deformation due to transverse flexure $k_{11}$
3. torsional deformation $k_{22}$

The data on the measurements of deformation moduli by means of the interaction of the magnetic field [8, 78] are given in Figure 59. It is apparent that moduli $k_{11}$, $k_{22}$ and $k_{33}$ are strongly dependent on temperature and become equal to zero at the point of the transition of the liquid crystal to isotropic liquid.

In conclusion let us note that the theory of clusters and the theory of elasticity a re apparently not contradictory. The theory of clusters is in approximate agreement with the statistical-mechanics hypothesis, the interpretation of which in the limit may be given in terms of the theory of elasticity.

## Chapter 3

## CERTAIN PROPERTIES OF LIQUID CRYSTALS

### 1. Thermodynamic Properties

Let us now consider the thermal properties of liquid crystals. Let us remember, the substance may exist in the liquid crystal phase only within definite temperature boundaries $t_2 - t_1$. This temperature interval is called the region of the existence of liquid crystals. For some substances this region may be quite broad. Thus, for p-propyl-p-azoxycinnamate the liquid crystal region lies within the 123-243° C range. Other substances are known for which the region of the existence of the liquid crystal does not exceed several degrees. For example, for methylbenzal-p-aminobenzene-p-hydroxybenzoate it is equal to 3° C (174-177° C).

The study of phase transformations in liquid crystals is most conveniently conducted by means of thermal analysis [79-82]. For this purpose one may use a photographically recording Kurnakov pyrometer. One of the junctions of the thermocouple is placed into a Stepanov vessel with the investigated substance, the other -- into a container with reference material (aluminum oxide). In the reference substance phase transformations do not take place in the investigated temperature interval. The pyrometer indications record the heating curve for the investigated substance and the temperature-time coordinates, and also a differential heating curve, which shows the temperature difference between the reference and the investigated substance. It is clear that in the case of exothermic or endothermic reactions in the investigated specimen the differential curve will have a maximum or a minimum, indicating the existence of such processes. As an example let us cite the thermal analysis of p-azoxyanisole (Fig. 60). The differential heating curve displays two sharp peaks, corresponding to the transition temperature of the solid crystal to a liquid (116° C) and liquid crystals to isotropic liquid (136° C). The peaks at 119 and 138° C correspond to the maximum thermal effects of the indicated transitions. In addition poorly pronounced endothermic effect with minimum at 132° C is

apparent, which probably results from the thermal decomposition of the substance or due to pretransitional thermal effects. The phase transitions may be recorded by the measurement of the transparency of the specimen [83]. This method also records the changes in the texture of the investigated substance (enlargement of domains, rearrangement of the confocal texture to a single crystal layer, etc.). Thermal analysis and investigations of the transparency in combination with polarizing microscope analysis enable us to interpret completely the nature of transitions in the specimen upon changes in temperature.

The transition of liquid crystals to isotropic liquid, just as the transition of a solid crystal to a liquid crystal is accompanied by latent heat of transition [84-86]. For example, for p-azoxyanisole the specific heat of fusion of solid crystals to a nematic liquid crystal is equal to 28.2 cal/g, and the specific heat of fusion of the nematic liquid crystal to isotropic liquid is 0.69 kal/g. It is apparent that the latter quantity is quite small. One must note that different investigators find somewhat different values for the heat of transition to isotropic liquid. This, is apparently associated with errors in the measurement of such a small thermal effect. Let us also note that such measurements are very scarce (measurements were made for 2-3 substances). Broader, more precise measurements of the heat of transition of liquid crystal substances could give valuable information regarding the nature of phase transformations of substances of this class. There is even less information in literature on the changes of the specific volume of liquid crystals during changes of temperature [87]. This relationship has been most accurately investigated for p-azoxyanisole. It was established that the specific volume during the liquid crystal-isotropic liquid transition changes discontinuously. Thus, during this transition we deal with phase transitions of the first kind, i.e. the transition is accompanied by the absorption of latent heat and changes of the specific volume. In order to verify the general applicability of this proposal a large number of experimental data is needed.

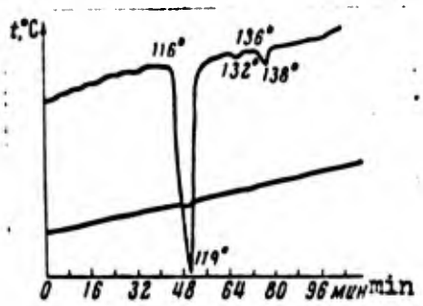



Figure 60. Thermal analysis of p-azoxyanisole.

It was noted before that liquid crystals are characterized by close order in the distribution of the centers of gravity of molecules and the parallel arrangement of their longitudinal axes. The transition of solids

to liquid crystals corresponds to liquidation of the long range order in the distribution of the centers of gravity of the molecules yet they preserve the long range order in the distribution of the centers of gravity of molecules, and they preserve long range order in their orientation. The transition of liquid crystals to isotropic liquid is accompanied by the liquidation of the long range order also by the liquidation of the long range order in the orientation of molecules. The latter transition is called by Frankel "orientational melting" [88]. According to Frankel's theory near the transition point of one stage into another the formation of nuclei of the new phase occurs prior to the time when the transition point is reached, in the old phase local and temporary fluctuations of the curve which are called heterophases. Tsvetkov [66] expanded the theory of the heterophase fluctuations for the transitions of the liquid crystal-isotropic liquid type. According to his opinion in the isotropic phase near the transition point formation of liquid crystal nuclei takes place (clusters). This fact is supported by the anomalous changes in a number of physical properties (double refraction in a stream, the velocity and absorption of ultrasound, etc.) near the transition point of the isotropic liquid to a liquid crystal. For example, the magnitude of double refraction in a stream of isotropic liquid p-azoxyanisole begins to increase several degrees prior to this temperature (134° C) [89].

When we speak of phase transformations of substances for these liquid crystals we must note that not all liquid crystals are stable in a definite temperature region. If they occur both during heating and cooling of the substance than the liquid crystal phase is called enantiotropic. The scheme for phase transformations in this case may be written as:

$$SC \leftrightarrows LC \leftrightarrows IL.$$

Here SC designates solid crystalline phase, LC -- the liquid crystal phase and IL -- the isotropic liquid phase. An example of such substances may be p-azoxyanisole, p-azoxyphenetol, anisaldazine, ethyl-p-azoxybenzoate and many others.

Along with enantiotropic substances there are also such substances which form liquid crystals only upon supercooling. In this case the liquid crystal phase is called monotropic with respect to the solid state. A scheme for the phase transformation may be written as follows

$$\begin{array}{ccc} SC & \rightleftarrows & IL \\ & \nwarrow\ LC\ \nearrow & \end{array}$$

Cholesteryl acetate is one such substance. Its solid crystals melt directly to isotropic liquid at 114° C. If the isotropic melt is cooled very slowly, then liquid crystals may not occur at all, but solid crystals will begin to grow immediately. Upon rapid cooling ~90° C the preparation is transformed

into the liquid crystal phase. At 114° C liquid crystals again begin to melt to isotropic liquid. Let us note that the solid crystals have two solid crystal modifications -- stable and unstable. The latter is formed only from the liquid crystal phase and at room temperature it is very slowly transformed (in the course of days or even months) to a stable solid crystal phase. The unstable solid crystal modification grows ordinarily in the form of spherocrystals, which frequently have extremely bright and beautiful interference coloration in polarized light.

Certain substances possess different liquid crystalline phases. Thus, p,p'-nonoxybenzaltoluidine in a 70-73° C region forms smectic liquid crystals and in the 73-76° C region it forms nematic liquid crystals. The scheme for phase transformations for such substances may be written as: $SC \rightleftarrows SLC \rightleftarrows NLC \rightleftarrows IL$, where SLC designates smectic liquid crystals and NLC -- nematic liquid crystals.

There are substances for which one of the liquid crystal phases may be monotropic. For example, solid cholesteryl caprinate crystals upon heating to 82.2° C are melted to cholesteric liquid crystals. The latter form isotropic liquid at 90.6° C. Upon cooling to 90.6° C the liquid crystals of the cholesteric type appear again and they may be supercooled down to 78° C. At this point the appearance of smectic liquid crystals occurs, which exist down to 53° C, and then solid crystals begin to occur. Thus, the scheme of phase transformations for such substances may be written as

$$SC \rightarrow CLC \rightleftarrows IL$$
$$\nwarrow_{SLC} \updownarrow$$

There are indications that there exists polymorphism in liquid crystal phases (smectic type). These data, however, are based primarily on the polarizing microscope investigations and require verification since changes of the liquid crystal texture, having nothing in common with phase transformations, may be easily mistaken for the latter. In general, however, the fact that polymorphism exists in liquid crystals is quite probable. Shubnikov noted that the number of transformation schemes and modifications of liquid crystals increases with increase of the thermodynamic variables (pressure, concentration) and may be thus indefinitely large.

## 2. Magnetic Properties

Liquid crystals posses anisotropy [90,91]. The graph representing specific diamagnetic permeability as a function of temperature for p-azoxyanisole is shown in Figure 61. For the liquid crystal p-azoxyanisole (as for all nematic liquid crystals) diamagnetic anisotropy is generally

positive. This means that the specific diamagnetic permeability of nematic single crystals, measured in the direction of the optical axis, is always smaller than the permeability in the direction perpendicular to the axis. The diamagnetic anisotropy results primarily from the presence of benzene rings in the molecule and is proportional to their number.

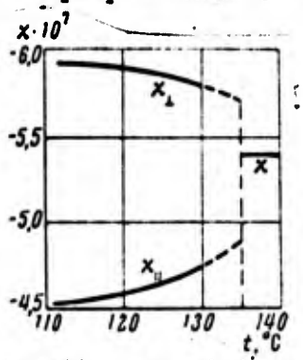



Figure 61. Specific diamagnetic permeability of p-azoxyanisole as a function of temperature.
$\chi_{11}$ - diamagnetic permeability in the direction of longitudinal molecular axes; $\chi_{\perp}$ - in the direction perpendicular to the longitudinal axes.

In a sufficiently strong magnetic field the longitudinal molecular axes of nematic liquid crystals are oriented parallel to the lines of force, and the preparation is thus monocrystalline. The orienting effect of the field on the layers of substance, adjacent to the walls of the container, are opposed by the cohesion forces of molecules in these layers with the walls. For p-azoxyanisole, for example, the thickness of layers, these molecules do not arrange themselves parallel to the field (when the overall thickness of the preparation layer is up to 2 mm), comprises: for the 1260 gauss field -- 0.01 mm and for the 10,000 gauss field -- 0.002 mm.

Smectic liquid crystals due to high viscosity are oriented by the magnetic field up to 30,000 gauss. However, it is possible to orient smectic crystals by cooling the isotropic melt in a magnetic field. The optical axes of the liquid single crystal are directed parallel to the field, i.e. just as in the case of nematic substance. When the field is turned off the orientation of the preparation is preserved which does not take place in nematic preparations.

If the nematic liquid crystals are placed between the slide and a watchglass, then for each value of the magnetic field intensity H there exists a certain limiting layer thickness $Z_k$ [78, 92]. Up to this thickness the optical axes maintain their initial direction (due to the effect of the glass). A relationship exists between H and $Z_k$: $Z_k H=K$, where K is a constant. It should be noted, that the limiting thickness of the layer $Z_k$ is independent of the types of glasses and whether they are or are not coated with a thin layer of metal.

When the magnetic field is turned on perpendicular to the plane glasses, between which the liquid crystal is placed, an increase of the temperature of the liquid crystal is observed. Thus, in the case of p-azoxyanisole the temperature of the specimen increases 1° C when the field intensity is increased by 2300 gauss. The study of this thermomagnetic effect as a function of the magnetic field intensity H and temperature may produce interesting information regarding the spontaneous orientation and the orientation of liquid crystals by the magnetic fields.

An extremely interesting phenomenon was discovered by Tsvetkov [9]. When the liquid crystal specimen was placed into a rotating magnetic field: the liquid crystal matter begins to rotate in the direction of the rotation of the field. Tsvetkov explained the presence of the rotating moment, affecting the liquid crystal particles, by the phase shift between the field intensity vector and the magnetization vector of the substance. The principal equation for the motion of liquid crystal particles (clusters) in this case is written as

$$6B\eta \frac{d\varphi}{dt} = \frac{1}{2} H^2 \Delta\chi \sin 2\alpha,$$

where $\varphi$ is the angle between the magnetic axis of the cluster and the axis of the immobile system of coordinates, $\alpha$ is the angle between the field intensity vector and the magnetization, $\Delta\chi$ is the diamagnetic anisotropy of the cluster, B is the coefficient which is a function of the shape of the cluster and $\eta$ is the viscosity coefficient.

From this equation it follows that the stationary state of the system is possible only when $\alpha < \pi/4$. In this case all particles are uniformly rotated with angular velocity $\omega$. When H and $\omega$ are increased the phase shifts become equal to $\pi/4$, and the substance begins to move turbulently as a result of the disruption of equilibrium between the rotating moment and the frictional moment. An analogous phenomenon was discovered in a rotating electric field.

The determination of the moment in a rotating magnetic field enabled determination of the magnitude of diamagentic anisotropy of liquid crystals.

## 3. Electrical Properties

The dielectric anisotropy of substance, capable of existing in the liquid crystal state may be both positive and negative [94-100]. This depends on the magnitude and the direction of the dipole moment of the molecules. It is apparent from Figure 62 that the magnitude of dielectric anisotropy of p-azoxyanisole decreases with increase of the temperature of the nematic phase, which is associated in turn with decrease of the degree of ordering of the molecules.

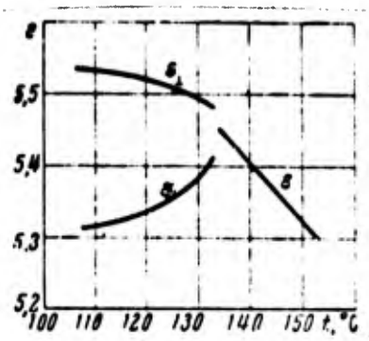



Figure 62. Dielectric permeability of p-azoxyanisole as a function of temperature.
$\varepsilon_{11}$ coincides with the direction of longitudinal molecular axes, $\varepsilon_{\perp}$ is perpendicular to the optical axes.

Many contradictory viewpoints exist in regard to the orientation of liquid crystals in the electric field. Some scientists came to the conclusion that liquid crystals possessing symmetrical molecules and negative electrical anisotropy, are oriented with the optical axes in the direction perpendicular to the field. On the other hand the substances with assymetrical molecules possess positive electrical anisotropy and arrange themselves with the optical axes parallel to the field [94, 95]. However, the study of the changes of dielectric constants of p-azoxyanisole and p-azoxyphenatol (substances with negative electrical anisotropy) in an electric field show that when the field is turned on perpendicular to the capacitor plate, in which the substance is placed the capacity and consequently the dielectric constant decreases [101]. This means that the optical axes of molecules are arranged parallel to the field. Analogous conclusions were made in the experiments with simultaneous interaction of the electric and the magnetic field on liquid crystals.

The indicated contradiction is explained by the fact that the electric field, while orienting liquid crystal molecules, produces at the same time a flow of liquid crystal substance. Tsvetkov [71] along with his students established that liquid crystal substances, the molecular dipole moment of which forms a large angle $\alpha$ with the optical molecular axis, possess negative electrical anisotropy and their optical axes are oriented perpendicular to the field. The molecules with small angle $\alpha$ are oriented in the direction of the field. Table 2 shows the data of Tsvetkov.

During the study of the texture which occurred under the influence of the electric field the liquid crystal is placed on a cover glass. Foil electrodes are attached to the glass, to which a current power supply is connected. In the case of small field intensity the vortex motion in the layers of substance, adjacent to the electrodes, is observed. With increase of the field intensity the motion is propagated throughout the whole specimen. Then, in the field of vision one may see many parallel threads, extending from one electrode to the other. When the field is removed the

threads disappear. For the investigation of texture in the field, perpendicular to the layer of substance, the preparation is placed between the glass peices, coated with transparent current conducting layers of tin oxide.

In a constant and an alternating field domain texture is formed in the liquid crystal preparation. The long and narrow domains are arranged parallel to each other [102]. The domains occur 2 msec after the application of the field and disappear 20 msec after the field is turned off. The width of the domains increases with the increase of the thickness of the specimens. Thus, when the thickness of the specimen is 50$\mu$ the width of each domain is equal to $\sim 20\mu$, and when the thickness is 150$\mu$ it increases to 90-100$\mu$. In the neighboring domains the vectors of molecular orientation have the opposite direction. Since the liquid crystal possesses anisotropy of the index of refraction, the domain structure is visible in natural light due to different molecular orientation inside the domains and at their boundaries.

The liquid crystals possess anisotropy of the electrical conductivity. When a magnetic field is applied in the direction parallel to the electric field, through the liquid-crystal p-azoxyanisole, its conductivity increases. This means that the substance possesses anisotropy of the electrical conductivity, and its value is maximum around the longitudinal axis of the molecule. In the case of 50 Hz alternating current the application of the magnetic field (1000 gauss) perpendicular to the capacitor plates, to which the electric field is applied the field of 50 v/cm causes the increase of the conductivity by 15% after 30 sec following the application of the field. The same magnetic field, but with the electric field intensity of 100 v/cm, increases the conductivity by only 10%, but after only 4 sec. Consequently, in the case of strong current the increase of conductivity, and consequently molecular orientation is lesser than in the case of weak current. This is explained by the fact that in the case of strong current large flows of substance take place in the liquid crystal, which deorient the particles. The mutual attraction forces between particles are thus decreased which leads to a more rapid but less complete orientation of molecules than in the case of weak current. It should be noted here that study of the liquid crystal state in the electric and in the magnetic fields is extremely promising with respect to the use of the crystals in electric and magneto-optical devices.

Table 2

| Substance | $(n_e-n_o)\cdot 10^{25}$ | Dipole Moment, $\mu\cdot 10^{18}$ | $\alpha$ | Optical axis orientation of the liquid crystal |
|---|---|---|---|---|
| p-azoxyanisole | 180 | 2.48 | 57°30' | Perpendicular to the field |
| p-azoxyphenatol | 200 | 2.55 | 58°20' | the same |
| anisaldazine | 200 | 1.84 | 62°45' | " " |
| p-acetoxybenzaldazine | 230 | 2.3 | 60°45' | " " |
| ethyl-p-azoxybenzoate | 240 | 3.11 | 56°30' | " " |
| anisal-p-aminobenzene | 250 | 2.58 | 32°25' | Parallel to the field |
| dibenzalbenzidine | 280 | 1.4 | 0° | the same |

## 4. The Effects of Ultrasound

The behavior of liquid crystals in ultrasonic fields had been studied by a number of scientists [103-105]. The simultaneous action of ultrasound and electric field on liquid crystal specimens has also been investigated.

The ultrasonic irradiation (f=1.8 MHz) changes significantly the texture of the nematic liquid crystal. The nematic threads are put into motion. Some of them hook to each other, while others are broken thus producing a very characteristic texture. In a thin layer of liquid crystal of p-azoxyphenetol during the interaction of high intensity of ultrasound the cellular texture is produced. The layer is separated into cells, where the substance is immobile. The motion of the substance takes place along the edges of the cells. The motion is in the clockwise and the counter-clockwise direction. It is interesting to note that such texture is observed only for p-azoxyphenetol: p-azoxyanisole and also smectic liquid crystals of ethyl-p-azoxybenzoate and ethyl-p-azoxycinnamate do not produce cellular texture. An important practical conclusion of these investigations is that by changing the intensity of ultrasound it is possible to obtain thin layers of liquid crystals of different transparency. When simultaneously the ultrasonic and the electric fields are applied to a p-azoxyphenetol specimen along with a set cellular texture and vortex motion of the substance along the cell walls the occurrence of sections with

threads is observed. With increase of the electric field intensity vortices appear, but the parallel arrangement of threads is disrupted by the action of the ultrasound.

Interesting data were obtained on the rate and the degree of absorption of ultrasound by liquid crystals [103-106]. It was established that these quantities vary anomalously at the point of conversion of isotropic liquid to liquid crystal. Such a change of the rate and the intensity of ultrasound in p-azoxyanisole becomes noticeable 2-3° prior to the transition point (135° C). This phenomenon may be explained by the occurrence of heterophase fluctuations near the point of transformation. Analogous behavior of the absorption and the speed of ultrasound was observed in cholesteric liquid crystals of cholesteryl benzoate (Fig. 63).

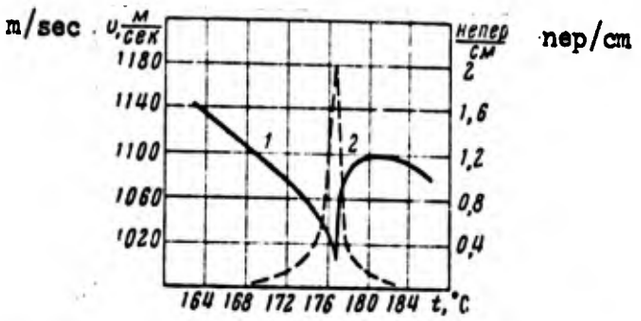


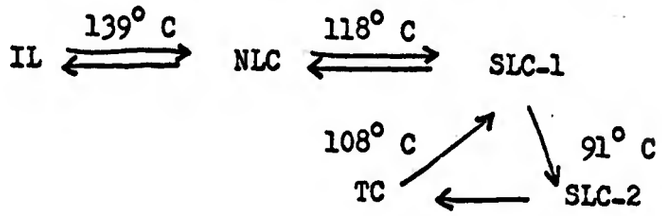

Figure 63. The velocity of ultrasound (1) and the coefficient of absorption of ultrasound (2) in cholesteryl benzoate near the transition point of liquid crystals to isotropic liquid.

## 5. Viscosity and Surface Tension

The viscosity of liquid crystals may be measured by the capillary method or by the measurement of damping of a disk suspended on an elastic thread and submerged into the liquid crystal. Let us note, that in the former case it is necessary to take into account the possibility of the decomposition of various liquid crystals at elevated temperature. For example, during heating of purified p-azoxyanisole in a liquid crystal mass the presence of dark particles is frequently observed, which interfere with the flow of liquid crystals along the capillary. In the Ubellode and Zud type viscosimeter, improved by Mikhaylov and Tsvetkov, a trap is present for catching foreign particles. In such a viscometer their effect on the rate of flow of substance from the capillary is excluded.

Figure 64 shows the relative viscosity of p-axozyanisole as a function of temperature [107]. It is apparent from the graph that there is linear dependence of viscosity on temperature both in isotropic liquid

and in the liquid-crystal phases. At the point of transition of the isotropic crystal into liquid crystals (135° C) the viscosity undergoes discontinuity [108-110]. An analogous discontinuity in the viscosity is observed during transition in the liquid-crystal phases. Thus, ethyl-p-(4-methoxybenzylidenediamino)-cinnamate has three liquid crystal phases (Fig. 65): one nematic and two smectic modifications (one of the latter is monotropic). The viscosity changes discontinuously during transitions from one liquid-crystalline phase into another. The scheme for phase transitions of this substance may be written as follows




Mikhaylov, Tsvetkov [107-110] and other authors measured the viscosity of liquid crystals in a magnetic and electric field. It was found that upon application of a magnetic field in a direction perpendicular to the capillary, in which the nematic crystal flows (p-azoxyanisole), the rate of flow decreases. When the field is applied in the longitudinal direction of the capillary the time of flow decreases. This indicates that there exists a viscosity anisotropy of liquid crystals, namely the viscosity coefficient is smaller in the direction of longitudinal molecular axes. The viscosity anisotropy may only be determined during slow flow of the liquid crystals. In the contrary case the orienting effect of the magnetic field is not apparent since the orientation of liquid crystals in the stream predominates.

The effect of the electric field on liquid crystals, flowing through a capillary, does not show anisotropy in the viscosity due to the occurrence of vortex motion of the liquid crystal substance between the electrode. The viscosity anisotropy, measured in a magnetic is quite significant [111]. Thus, for p-azoxyanisole at 122° C the following viscosity coefficients were found:

$\eta_1 = 0.024$, the molecules were parallel to the flow of liquid crystals in the capillary;

$\eta_2 = 0.092$, the molecules were parallel to the velocity gradient of the flow;

$\eta_3 = 0.034$, the molecules were perpendicular to the velocity vector and to the gradient vector of flow.

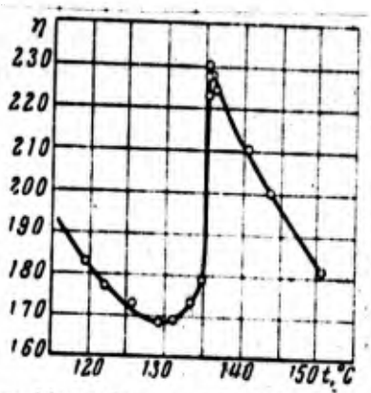



Figure 64. Relative viscosity of p-azoxyanisole as a function of temperature.

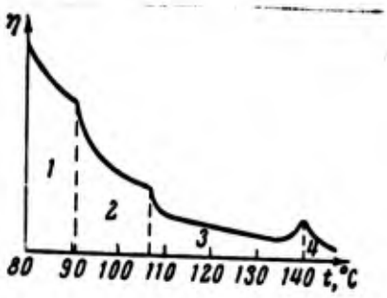



Figure 65. Relative viscosity of ethyl-p-(4-methoxybenzylidenediamine)-cinnamate as a function of temperature.
1. smectic phase (monotropic;
2. second stable smectic phase;
3. nematic phase;
4. isotropic melt.

The study of the viscosity anisotropy of smectic and cholesteric liquid crystals is difficult becuase these mesophases can be oriented only with great difficulty by the external interactions. The viscosity anisotropy can be determined only from qualitative observations, by studying the effects of the disruption of confocal texture during the reorientation in the homogenious liquid crystal layer. In the case of lyotropic liquid crystals of potassium oleate, for example, from confocal domains it appears as though a series of layers were originating from confocal domains (see Fig. 43), corresponding to Dupin cyclide surfaces. Smectic layers have a great freedom of motion when they are slipping over each other, reconstructed from confocal texture into a single crystal layer. The rearrangement of molecules in the direction perpendicular to the layers is difficult, consequently the viscosity in this direction is greater than in the direction parallel to the layers.

On the basis of all said thus far it is clear that investigation of viscosity, especially near the liquid crystal -- isotropic liquid transition and the theoretical interpretation of viscosity anomaly at this point is a real problem, the solution of which will enable us to penetrate deeper into the nature of the liquid crystal state.

The surface tension of liquid crystals has been investigated to an even lesser extent. Here we have only the investigation of the surface tension of nematic p-azoxyanisole, the results of these investigations, however, are contradictory. Ferguson and Kennedy [111], found that surface tension, measured by the capillary method) increases with increase of temperature, while for the isotropic crystal it decreases. This behavior is only apparent, since it probably is determined by the adhesive forces of the liquid crystal to the capillary tube. In order to exclude these forces, Naggiar [112] suspended a thin film of liquid crystal p-azoxyanisole in an opening of the supporting plate. The surface of the film was bent by the gravity force. By means of a microscope he was able to measure the curvature of the upper and of the lower surface of the film and its thickness. The surface tension coefficient was found from the relationship

$$2\sigma\left(\frac{1}{R_1}-\frac{1}{R_2}\right)=\rho g d_0,$$

where $R_1$ and $R_2$ are the radii of curvature in the center of the upper and the lower surfaces respectively, $\rho$ is the density of the liquid crystal, g is the acceleration of gravity and $d_0$ is the thickness of the film at the center. It was found that on increase of temperature from 116 to 134° C (the transition point to isotropic liquid) the surface tension decreases linearly from 39.5 to 37.4 dynes/cm, according to the equation:

$$\sigma = 52.1 - 0.110\ t \text{ (dynes )}.$$

One might say without a doubt that further investigations of the surface tension of liquid crystals of different types will yield valuable data from the practical standpoint regarding the surface active properties of liquid crystals. This is first of all applicable to liquid crystals which play an important role in the biological processes of living organisms.

## Chapter 4

## THE USE OF LIQUID CRYSTALS

### 1. Technical Uses of Liquid Crystals

Many substances in the liquid crystal state possess valuable electrical and optical properties. It is very significant that these properties change sharply as a function of temperature, wavelength, under the influence of external fields, etc. It is doubtless that many of the properties of liquid crystals have practical interest and some of them are already in use. Let us cite a number of examples.

The nematic lyotropic crystals are used in the production of light polarizers. If such a dichroic crystal is placed between two clear pieces of glass, previously rubbed in one direction, then one obtains a single crystal nematic film. The solvent evaporates with time and between the two pieces a thin film of oriented dichroic molecules is obtained, i.e. a light-polarizing material.

Cholesteric crystals found a very interesting application. Using these crystals a converter was constructed for transforming an infrared image into a visible image. This converter is successfully used for the visual detection of a gas-laser beam at 3.3 wavelength [113]. The principal element of this device is a film of cholesteric liquid crystals placed on a thin glass membrane. The membrane absorbs infrared radiation of the laser and transmits the heat to the liquid crystal layer. The color of the liquid crystal film (in the reflected light) depends on the temperature, therefore during illumination of the shell with white light a visible image of the infrared radiation is obtained. Let us remember that for transformation of the infrared radiation into visible ordinary converters are used which incorporate photoelectronic emissions or phosphorescing substances with extremely complex and extensive electronic circuitry. The simplicity of the above described device and its low cost make liquid crystal converters incomparably more economical than the complex apparatus previously used.

The color of cholesteric liquid crystals depends on temperature and it may be used for temperature measurement [114]. From a mixture of cholesteric substances one can produce temperature indicators from -20 to +250° C interval. The indicator is a thin flexible film of liquid crystal enclosed between two polymeric films. Such a substance may be applied to the circuit of a part for recording the temperature gradients in different directions. This method may be used for detection of structural defects in opaque objects: due to nonuniform thermal conductivity defects cause different color effects in the liquid crystal films.

Cholesteric liquid crystals (or their mixtures) are extremely sensitive to the presence of vapors of different chemicals. The presence of an extremely small quantity of vapor may change the structure of liquid crystals and consequently affect its optical properties by changing its color. By means of a liquid crystal it is possible to establish the presence of vapor in the air when its concentration is only a few parts per million. This method is of extreme practical value [114].

Liquid crystals are used in scientific investigations. Thus, during the investigation of nuclear magnetic resonance preliminary experiments have shown [115-124] that nematic liquid crystals can be successfully used as solvents during the investigation of high resolution NMR spectra. In this case the NMR spectra yield more complete information regarding the structure of dissolved molecules than spectra obtained by other methods.

The new explanation of the detergent action on soiled surfaces, found by means of liquid crystals, is also of great interest. It appears that an important here is played by the swelling process of the foreign matter in the soap-water system, which was established by Lawrence [43]. The basic change of the concept regarding the action of soap enables us to introduce changes into the technology of production and the use of cleansing agents.

An important direction in the practical use of liquid crystals is their use in the supercooled state. Two methods are available for the vitrefication of liquid crystals: 1) synthesis of substances which possess at the same time both the ability to form liquid crystals and the ability of vitrefying; 2) addition to the liquid crystal substance of special additives which fix the mesomorphic state and prevent the transition to the solid-crystal state. At present there are some substances known which can be vitrefied upon cooling. They include $\alpha$-benzeneazo-(anisal-$\alpha'$-naphthylamine). However, thus far the drawback of such substances is that with time (although it may be very long) they still crystallize. In addition, this process is accelerated with the increase of temperature to 40-50° C, which is very inconvenient from the practical standpoint. We know of stable substances also (for example cerebron), which preserve their vitrefied liquid-crystal state at 100° C, and higher for an indefinitely long period of time. These, however, have rather weak mechanical properties.

It should be noted that not any less important than the production of vitrefied crystals is the development of methods for their use. The mobility of the structure, and its rapid changes under the use of external fields is one of the most valuable properties of liquid crystals. However, the majority of substances which produce liquid crystals can exist in the liquid crystal state only at very high temperatures: of the order of 80° C and higher. This means that the devices where liquid crystals may be used there must be thermostated. Even now, however, substances are known which exist in the liquid crystal state at relatively low temperatures. For example, mona-2.4-dienoic acid exists in the form of nematic liquid crystals at 23-49° C. Let us also keep in mind the lyotropic liquid crystals, the crystallization point of which is even lower.

The region of the existence of the liquid crystal may be significantly expanded by means of isomorphic impurities. Unfortunately, the work in this area has thus far been conducted very sluggishly, although the purpose and the ways of carrying out the work are quite apparent.

The most promising material with respect to the practical utilization is single-crystalline mesomorphic substance. Here the situation is much better than with the use of supercooled crystals. The main problem is reduced to the orientation of the specimen by means of external interaction: electric or magnetic fields, solid surfaces, stretching (orientation with subsequent vitrefication of specimens).

## 2. Medical and Biological Uses of Liquid Crystals

Many substances of biological origin may have liquid-crystal structure. For example, myosin is a protein which enters the composition of the contractile substance in the muscle tissues (myofibrils). It forms lyotropic liquid crystals. Collagen, contained in the supporting tissue (bones, tendons) and in the brain, is close in its structure to nematic liquid crystals. The lyotropic liquid crystals, obtained from desoxyribonucleic acid, display the primary role in transmitting the inheritance information, and many polypeptides (for example poly-$\gamma$-benzyl-L-glutamate) and enzymes (trypsin). Numerous lipoids are capable of forming liquid crystals. For example, a mixture of kerasin and lecithin with insignificant wetting forms lyotropic smectic liquid crystals.

Cholesterol and particularly its esters present a great interest. They are frequently found in the organism in the liquid-crystal state, particularly in the form of liquid-crystal spherulites. This spherulite may be large (1.1 - 1.3 mm in diameter) or small (1-2 $\mu$ in diameter). The fine liquid-crystal spherulites are found particularly frequently in the blood after the intake of food containing fats.

Liquid crystals of esters play an extremely important role in the metabolism of living organisms, in particular, in the organism of man. The concentration of liquid crystals in the organism increases rapidly in the case of certain pathogenic processes. The deposition of liquid crystals in the tissues of an organism destroys epithelial cells, causing the growth of cells of mesenchymic origin and the occurrence of granulomatous tumors. Such a reaction is determined not by the chemical nature of the cholesterol compound (these compounds are not toxic), but by the fact that they exist in the liquid-crystal state, which in turn has a destructive effect on living cells.

According to the opinion of a Soviet pathologist S. S. Khalatov [125], the principal cause of the occurrence of liquid crystal deposits of cholesteryl esters in the organism is diathesis -- the specific constitutional predisposition of the organism to the formation of liquid crystals which circulate in the blood. Diathesis is most pronounced in 30-50 year old people. The increases amount of cholesterol and its compounds is observed during injuries of the brain (the most labile cholesterol storage, during insufficient excretion of cholesterol by the intestines and in the case of certain other illnesses. When the excessive concentration of cholesterol compounds (hypercholesterinemia) is combined with the constitutional predisposition of the organism to the cholesterin illness the cholesterin compounds circulate in the blood in the liquid crystal state. When liquid crystals penetrate the mesenchymic cells they irritate them and the cells begin to accelerate their reproduction. This leads to anisotropic adiposis of the organ (xanthomatosis). The following ailments belong to the xanthomatosis class (according to Khalatov): skin xanthomas, xanthomatosis of the aorta and arteries, anisotropic adiposis of the spleen and Kupffer cells of the liver, and cloudiness of the cornea with "age."

Thus far we have spoken only of the dark side in the behavior of liquid crystals in the organism, but it appears this is only one side of the problem. Many structural formations of completely healthy cells and even organs are in the form of liquid crystals. It should be noted that the brain is essentially a complex liquid-crystal system. The duramater in the brain consists primarily of cerebrosides, phosphatides and glycerides in a lyotropic liquid crystal state. In the white substance of the brain and in the nervous system tracts liquid crystals play the role of dielectrics. They form myelinic membranes around the nerve fibers (neurons) and this membrane (one of the most ordered biological structures) possesses all those properties which are typical for smectic liquid crystals. The myelinic membrane is anisotropic and it is very well visible in polarized light with crossed nicols (Fig. 66).

It was possible to see the alternating smectic layers of the myelinic membrane of the nerve by means of electron microscopy (Fig. 67). They consist of the protein and lipoid molecules.

The analyses in polarized light show that paraffin chains of lipoid molecules are oriented radially and the longitudinal axes of protein molecules are tangentially located with respect to the fiber axis. The average is in the identicity period (the distance between two centers of neighboring layers) on the electron micrograph is equal to 120$\mathring{A}$, and that obtained by means of x-ray structural analysis is 170$\mathring{A}$ (for the nerves of amphibia) and 180-185$\mathring{A}$ (for the nerves of mammals). The noncoincidence of their values of the identicity period results from the fact that it changes somewhat in the course of the preparation of the nerve specimen for electron microscopy.

Many structural elements of cytoplasm have similar structure to smectic crystals. For example, organellas of the cell which exist in the inner element of the rod in the retina have a structure similar to smectic crystals. Their structure is formed by the submicroscopic platelets stacked in a "pile." The analyses in polarized light show that the outer members of these rods consist of the transverse protein layers alternating with layers of longitudinally oriented lipoid molecules.

The smooth and the transversostriated muscle fibers also have liquid crystal structure, as a result of which they can stretch and contract without destruction.

From the standpoint of liquid crystal structure interesting objects are spermatozoa consisting of elongated heads and a lower appendage -- the tail. The head of the spermatozoa displays strong double refraction (0.05), which is almost a factor of 5 greater than it is for quartz (0.009). The optical sign is negative which indicates the similarity with cholesteric mesophase. Their optical axes coincide with the longitudinal direction of the head. The tail displays weak double refraction, and its optical sign is positive. The liquid crystal spermatozoids (if it is possible to say) are very stable. It is easier to destroy them than to convert them to the crystalline state.

The abundance and the important role of liquid crystals in living tissues is not surprising. The principal activity of living tissue is metabolism, i.e. continual absorption and excretion of substances from the surrounding medium. Liquid crystals are ideal formations for such an activity: they are absorption active, they can dissolve many substances even of different molecular structure (in contrast to crystals which dissolve only isomorphic substances, without changing at the same time its liquid crystal form. The structural complexity of liquid crystals along with the easy replacement of molecules in them creates a necessary condition for the rapid and easy exchange of molecules and for the retention of molecules in the lattice. The correctly arranged elements of liquid crystals produce an excellent medium for the action of intracellular catalysts, especially complex, for example catalysts of growth and reproduction. Due to their excellent dielectric properties paracrystalline [illegible] invaluable in cell membranes during the formation of intracellular [illegible]

heterogenic planes. They regulate electromotor relationships between the cell and the medium, as well between the individual cells and tissues, convey the necessary inertness to the component parts of cells and protect the cell from the action of the enzymes. Under appropriate conditions the liquid crystals may swell and then again shrink without the loss of their liquid-crystal state. This property is especially important since they counteract the mechanical activity of cells accompanied by the contraction and followed by relaxation.

The shape of liquid crystals is most convenient for biological processes. It incorporates both the stability to the external interaction and combines the extraordinary plasticity and flexibility. The liquid crystal fiber formations possess significant strength, which is necessary for the formation of the supporting fibers. It is necessary to add to all these properties that liquid crystals possess high sensitivity of the mesophase to all intracrystalline processes. The mesophase reacts to these processes instantaneously. All this explains why liquid crystals are found in the most important functional parts of the living cells.

It is interesting to note that the liquid crystal structure is also found in certain formations of plant cells. As an example let us point out the structure of chloroplasts -- the formations which are associated with the photosynthesis reaction. The chloroplasts of the corn mesophyll have platelet structure similar to smectic liquid crystals. In addition to this chloroplasts contain sharply outlined sections (faces). In these faces platelets are packed more densely than regularly thus producing a striated structure with the identicity period of the order of 136$^{\circ}_{A}$. This structure is very similar to the structure of myelinic cell membranes.

An extremely important role is played by the study of liquid crystals in order to solve the problems of viruses. It is known that the viruses of tobacco mosaic, cucumber viruses 4 and 3, potato viruses X and Y and others, possessing elongated form, form lyotropic liquid crystals. In dilute aqueous solutions of these viruses strong double refraction is discovered. At higher concentrations of virus liquid crystal tactoids are formed which precipitate to the bottom in the form of a liquid-crystal mass.

The above discussion convinces us that the study of the liquid crystal state is effective not only with respect to useful utilization of liquid crystals in technology. Undoubtedly these investigations will aid in penetrating the secrets of biological processes and the characteristics of the behavior of the organic world.

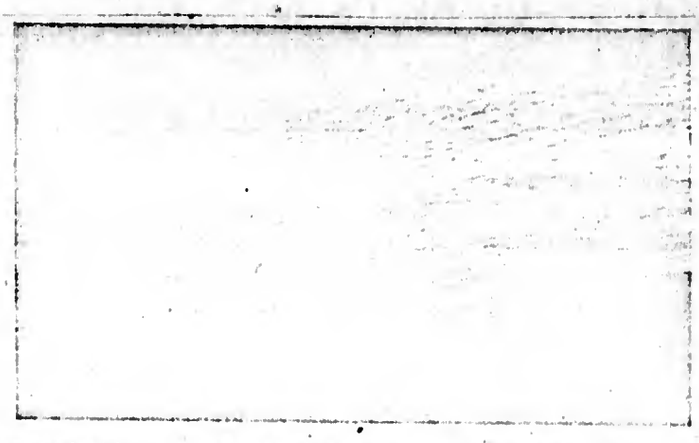


Figure 66. The sciatic nerve of a frog in polarized light. Many interwoven nerve fibers are visible which display double refraction.

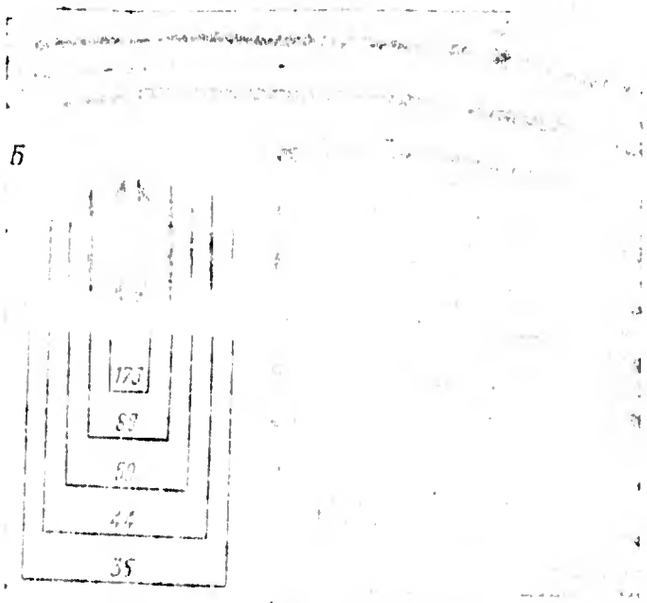



Figure 67. Electron micrograph of a transverse cut of the myelinic nerve membrane (850,000 x).

## Synthesis of Certain Liquid Crystal Producing Substances

### p-Azoxyanisole (Bogoslovskiy's method)

Five hundred ml of 99-100% methanol are placed into a round bottom flask with a reflux condenser and then gradually with external water cooling 500 g of finely cut metalic sodium is added to it. When the last portions of sodium are added (in order to accelerate the formation of sodium methylate) the flask is heated on a water bath to 65-70° C. The thus produced sodium methylate is immediately mixed with 50 g of p-nitroanisole (the melting point is 53° C) and the mixture is heated on the water bath (without mixing) for 6 hours at the boiling point of methanol (65° C). The produced brown solution is poured into 100 ml of water. A lemon-yellow crystalline product is precipitated out which should be washed in a Buchner funnel with 300 ml of cold water and dried at 60-70° C. The melting point of the product is 116.5 and 133° C (in this temperature region nematic liquid crystals are formed). In order to obtain extremely pure substance the produce is recrystallized from benzene.

### p-Axozyphenetol (Bogoslavskiy's method)

One hundred and thirty ml of 96% ethanol are placed into a two necked flask and then 10 g of finely cut metallic sodium are added in small portaions. After the formation of sodium methylate 10 g of 4-nitrophenetol are added to the hard solution. The nitrophenetol must be ground into a powder. It is rapidly dissolved upon mixing. Following this 5 g of hydrazine hydrate are added rapidly to the solution with frequent shaking and the mixture is heated on a steam bath. This produces boiling of the reaction mass accompanied from the very beginning by the liberation of gas and the formation of foam. Following 25-30 minutes the brown solution is poured into 500 ml of cold water. A bright yellow crystal precipitate is formed. The precipitate is filtered, washed several times with cold water and dried. The product melts at 135° C and 164° C. During recrystallization from benzene the melting points are elevated to 136 and 167° C respectively (nematic liquid crystal phase).

### Anisaldazine

13.5 g of anisic aldehyde are dissolved in dilute ethanol and 7 g of hydrazine hydrochloride are added to it. The mixture is heated on a steam bath. Soon thereafter anisaldazine crystals begin to precipitate from the solution. Upon completion of the reaction (20-30 minutes) the product is filtered and recrystallized from benzene. The purified anisaldazine is in the nematic liquid crystal state at 179-183° C.

## Cholesteryl acetate

5 g of cholesteryl are mixed with 7.5 g of acetic anhydride in a flask with a reflux condenser. The mixture is heated on a sand bath. The mixture must boil for 2 hours after which it must be cooled. The crystalline cholesteryl acetate is precipitated out. Its melting point is 114° C. For better purification of the product it can be recrystallized from a mixture of alcohol and ether. Upon supercooling of the isotropic solution monotropic liquid crystals of cholesteric type liquid crystals are produced.

## Cholesteryl cinnamate

5 g of cholesteryl and 10 g of cinnamic acid (cinnamic acid is taken in excess) are mixed and heated in an open container on a sand bath or on an oil bath to 200° C. The mixture is held at this temperature for 4-5 hours and then cooled in air. The dark brown reaction mass crystallizes completely. Following this it must be ground to a powder and boiled in alcohol to free the excess cinnamic acid and then filtered. The boiling must be repeated 2-3 times. The product is recrystallized from a large volume of alcohol-ether mixture. At 156-197° C cholesteryl cinnamate exists in the liquid crystal state.

## Cholesteryl caprinate

5 g of cholesteryl and 10 g caproic acid (the acid is added in excess) are placed in an open flask and heated on the oil or on the sand bath at 150° C for 4-5 hours. The mixture is cooled and the solid reaction mass which is produced is ground to powder. To free the excess acid the mixture is boiled in alcohol and after cooling it is filtered. The boiling and filtration must be repeated 2-3 times. Upon heating to 82.5° C cholesteryl caprinate produces cholesteric liquid crystals which at 90.6° C melt to form isotropic liquid. Upon cooling to 90.6° C cholesteric liquid crystals reappear again and they exist down to 78° C. Following this the preparation forms monotropic smectic phase which exists down to 53° C. At this temperature the substance crystallizes.

## Ethyl p-azoxybenzoate (Maier and Dalem method)

17g of p-azoxybenzoic acid are mixed with an aqueous solution of sodium hydroxide (5 g of NaOH). A dilute nitric acid solution is added until neutrality is attained. To this solution an aqueous solution of silver nitrate is gradually added (25 g of $AgNO_3$). The mixture is boiled

for several minutes and then cooled. The precipated silver salt is filtered out on a Buchner funnel, washed several times with cold ethanol and then with ether. The yield of silver salt is 28 g. To this light sensitive silver salt a mixture of ethyl iodide with benzene is added and it is boiled for 1 hour on a steam bath with the reflux condenser. The reaction mass is cooled and filtered. It is well to wash the precipitate with hot benzene and to dry it. The final product produces smectic liquid crystals in the 113.5 - 120.5° C temperature interval.

## α-Benzeneazo-(anisal-α'-naphthalamine)

14.3 g of α-naphthalamine is dissolved in ethanol and mixed with 14g of diazobenzenechloride in water (the solution of diazobenzenechloride is obtained by means of one of the generally described procedures). [illegible] sodium acetate is added to the mixture until congo red color ceases to turn blue. The obtained paste is filtered by suction on a Buchner funnel and washed with a large quantity of water (for the removal of chloride ions). The dark red mass is recrystallized from a small volume of [illegible], filtered and dried. The crystals are placed into a [illegible] methanol and 13.7 g of anisic aldehyde are added to it. The mixture is heated on a steam bath. 20-30 minutes later crystals precipitate from the solution and the mixture becomes thick. The product is filtered by suction in a Buchner funnel and recrystallized from aqueous acetone. The produced orange-red crystals metl (151° C) to form isotropic liquid. Upon cooling the substance produces monotropic nematic liquid crystals which vitrefy.

## Lyotropic potassium oleate liquid crystals

These crystals are obtained upon evaporation of water-alcohol solution of potassium oleate which is sold under the name "liquid potassium soap." The medical "green soap" also exists in the liquid crystal state (smectic type). Potassium oleate may be easily prepared (according to A. B. Mlodzeyevskiy): 10 $cm^3$ of oleaic acid are poured into a test tube to which 9 $cm^3$ of potassium hydroxide are added. The contents of the test tube are stirred with a glass rod. A layer of yellow precipitate of potassium oleate is formed above the level of the water. It is removed from the test tube by siphoning.

## Liquid crystals from the cholesterol mixture (Mlodzeyevskiy method)

By heating a mixture of cholesterol with glycerin in a test tube or between the slide and the cover glass one may obtain smectic type liquid crystals. Under the microscope between crossed nicols myelinic forms are obtained which have very beautiful interference coloration.

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