THE MESOMORPHIC STATE

LIQUID CRYSTALS

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Received May 22, 1957

CONTENTS

I. Introduction 1050
II. Nomenclature 1051
III. Hypotheses as to the nature of the nematic structure 1053
IV. The structure of the mesomorphic state 1054
  A. The smectic structure 1056
  B. The nematic structure 1067
  C. The cholesteric structure 1071
V. Molecular structure of substances which form the mesomorphic state 1074
  A. Aromatic type compounds 1075
    1. Basic structural requirements of aromatic type molecules 1075
    2. Effect of atomic grouping in the molecule on the mesomorphic character. 1075
    3. Effect of polarity of end group on the nematic-liquid point; effect of change of central group on the nematic-liquid point 1077
    4. Changes in molecular structure 1078
      (a) Molecular structure and the nematic structure; homologous series that represent both nematic and smectic structures—only one end group of the molecule changes 1079
      (b) Comparison of end groups with an equal number of links but with different kinds of atoms 1080
      (c) Effect of central group on crystal-mesomorphic, smectic-nematic, smectic-liquid, and nematic-liquid points; change of nematic-liquid point in the homologs of a series 1081
    5. Influence of substituents in certain molecules on the mesomorphic character; position of attached side groups 1084
    6. Convergence of smectic and nematic curves 1087
  B. The cholesteryl compounds; position and number of double bonds 1088
  C. Aliphatic compounds of mesomorphic character 1088
  D. Formation of the mesomorphic state without heat 1091
VI. Optical constants of the nematic structure 1092
VII. Viscosity of the nematic structure 1095
VIII. Dielectric constant of the nematic structure 1100
  A. Background of earlier reviews on dielectric constant 1100
  B. More recent developments in dielectric constant measurements 1101
IX. X-ray studies of the mesomorphic state 1107
X. Other observations 1114
  A. Preparation 1114
  B. Light scattering 1115
  C. Surface tension 1116
  D. Calorimetric measurements 1117
  E. Refractive index 1118

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F. Spectral observations 1119
G. Orientation effects 1120
H. Polymesomorphism 1122
I. Reactions in the mesomorphic state 1123
J. Electrical conductance 1123
K. Proton magnetic resonance 1124
L. Streaming potential 1125
M. Polarimetry 1125
N. Miscellaneous observations 1127
XI. Mixed liquid crystals 1131
XII. Lyotropic mesomorphism 1135
A. General 1135
B. Soaps 1136
1. Lyotropic soap systems 1136
2. Soaps in organic liquids 1138
C. Ionic and nonionic detergents 1139
D. Lyotropic mesomorphism of dyes 1141
XIII. Biological systems 1141
XIV. References 1147

I. INTRODUCTION

When certain solids (e.g., *p*-azoxyanisole) are heated they do not pass directly into the liquid state but adopt a structure which has properties intermediate between those of a true crystal and those of a true liquid. On reaching a certain temperature the solid undergoes transformation into a turbid condition that is both birefringent and fluid, the consistency varying with different compounds from that of a paste to that of a freely flowing liquid. At a higher temperature, the turbid condition is converted into the true liquid. As the liquid cools these changes take place in reverse order; however, some supercooling may occur when the transition temperatures are reached, as in the case of ordinary crystallization.

A birefringent fluid can also be formed when certain compounds are treated with a controlled amount of water or other polar solvent. These birefringent systems are formed with certain rather large molecules (e.g., sodium stearate); they are also found in some biological systems. The properties of this birefringent fluid resemble those of the birefringent fluid formed by heating certain solids.

Reinitzer (331) was the discoverer of the "liquid-crystalline" phenomenon, while Lehmann (218) first described the property of liquid crystallinity. In 1889 Lehmann (220) found that cholesteryl benzoate, when heated, first formed a turbid system that would flow as readily as oil but still retained many of the characteristics of crystals. Soon after this initial discovery Lehmann found that ammonium oleate and *p*-azoxyphenetole (219) were examples of substances that may exist in the "mesomorphic state." The early literature of the field contains some interesting debates between Reinitzer and Lehmann concerning priority on a number of important observations concerning the properties of liquid crystals. These are recorded in papers by Reinitzer (332) and Lehmann (227–229).

There are two books of note written on liquid crystals: namely, *Chemische Kristallographie der Flüssigkeiten* by Vorländer (433) and *Chemische Morphologie* *der Flüssigkeiten und Kristalle* by Weygand (442). Each book summarizes the work of the author in the field of liquid crystals. Both Vorländer and Weygand had the same goal in their study of liquid crystals; they attempted to define the constitutional pecularities which a molecule must possess to form the mesomorphic state.

Brauns (42) collected under one cover 172 abstracts of papers and books which were published between 1881 and 1931. These abstracts cover papers dealing with organic compounds in inanimate matter and the role of liquid crystals in living processes. Oseen (307) authored a small book on the theory of the formation of liquid crystals.

Two extensive symposia have been held to discuss liquid crystals; the papers presented at these symposia were published in *Zeitschrift für Kristallographie* (387) and *Transactions of the Faraday Society* (388).

Some brief reviews in journals, summaries as chapters of books, and small booklets or pamphlets have appeared but there has been no general review of recent origin. These reviews or summaries vary in length and importance; some of them are devoted only to a summary of the work of one researcher, while others deal with a small area of the field. The reviews and summaries of Lehmann (223, 231, 232, 239–246), Vorländer (427, 428, 430), Kast (196), Bragg (40), and Friedel (106, 107) are the most extensive and informative. Other brief reviews are by Garner (117, 118), Mayr (267), Stumpf (379), Pope (322), Chaudhari (68), Mauguin (265), Schenck (356), Rinne (335), Randall (327), Weygand (445), and Chatelain (66). The review by Schenck covers the years 1905–1909. Stumpf's review (379) is a résumé of the work done on liquid crystals after the earlier review of Schenck (356) and covers the years 1910–1918. The paper by Rinne (335) is a review comparing the morphological, chemical, thermal, and optical characteristics of sperma and of liquid crystals. However, none of these reviews are exhaustive. In some cases this is by choice of the author, who was interested in only one aspect of the subject; in other cases the author chose to discuss or emphasize only his own research in the field.

An effort has been made in this article to summarize the literature on the mesomorphic state and to bring into one review article the different methods that have been used to attack the problem of the properties of this state. Through the papers reviewed in this article and those reviewed in the articles and books listed above, an attempt has been made to cover the literature on the mesomorphic state. A number of the topics in this article have not been considered in the review articles or books mentioned above. For those topics that have been reviewed previously, the present review briefly summarizes the previous writings and then covers the literature from the date of the previous review to the present. The literature has been covered through 1955, with some additional references of later date.

II. Nomenclature

Lehmann was the first to suggest the name *liquid crystals* for those substances which are liquid in their mobility and crystalline in their optical properties. The first property (liquid) suggests that the substances in this phase are readily disturbed though the phase may be readily renewed, while the latter property (crystal) suggests some degree of arrangement of the component molecules. The term *liquid crystals* is simple and suggestive and has been used throughout the literature since the time when it was suggested by Lehmann; hence it has been used as the subtitle to this article and on occasion throughout this review. Friedel (106, 107) has argued that the name *liquid crystals* is not a good one because the substances are neither perfect crystals nor perfect liquids. He proposed the name *mesomorphs* or *mesoforms*, terms which are more logical since the properties to be described are intermediate between other properties that are well defined. A related term *mesomorphic state*, which the authors consider preferable, has been used in the title of this article and throughout the review. The name *paracrystals*, proposed by Rinne (338) for this class of compounds, has been used on occasion in this review. Other names that have been proposed for the mesomorphic state are discussed by Rinne (338).

Most compounds that exhibit the mesomorphic state can be classified by two structures which have been designated as *smectic* and *nematic*. The term *smectic* (soaplike) was coined by Friedel (104) from the Greek σμεγμα, meaning grease or slime. The smectic structure is stratified, the molecules being arranged in layers with their long axes approximately normal to the plane of the layers. The term *nematic* was coined by Friedel (104) from the Greek νημα, meaning *thread*. The term is used literally to describe the threadlike lines which are seen in the nematic structure on microscopic observation. In the nematic structure the only restriction on the arrangement of the molecules is that the molecules preserve a parallel or nearly parallel orientation. A third structure has been described in the literature—namely, the cholesteric—so called because it is shown mainly by cholesteryl derivatives. More details are given on the properties of these structures in Section IV.

The mesomorphic state can be prepared from solids either by thermal processes or by means of "solvents." Using the nomenclature of Friedel (106), Lawrence (214), and Jelley (182), *thermotropic mesomorphism* refers to the production of the mesomorphic state by means of heat in contrast to *lyotropic mesomorphism*, which has been defined as the process for preparation of the mesomorphic state by solvation.

Two terms have appeared in the literature describing those crystalline solids which yield the mesomorphic state on heating. *Smectogenic* is a name applied to solid-state anisotropic molecules that may be arranged in parallel layers or with the molecules of adjacent layers imbricated and which on heating give the smectic structure. *Nematogenic* is a name applied to solid-state anisotropic molecules that will lead to the nematic structure on heating. In this article the term *mesomorphic substance* will refer to a substance that yields the mesomorphic state by a thermal or lyotropic process.

The literature on the mesomorphic state has much confusion in the terminology used for designating the temperatures at which phase transformations take place. The temperature at which the crystal lattice collapses has been called

TABLE 1

Nomenclature for temperatures representing equilibrium between structures

Equilibrium Between Structures	Nomenclature	Abbreviated Nomenclature
Crystal ⇄ mesomorphic state (smectic or nematic structure)	Crystal - mesomorphic point	C-M point
Crystal ⇄ smectic structure	Crystal - smectic point	C-S point
Crystal ⇄ nematic structure	Crystal - nematic point	C-N point
Smectic structure (1) ⇄ smectic structure (2)	Smectic (1) - smectic (2) point	S_1-S_2 point
Smectic structure (2) ⇄ smectic structure (3)	Smectic (2) - smectic (3) point	S_2-S_3 point
Smectic structure ⇄ nematic structure	Smectic - nematic point	S-N point
Mesomorphic state ⇄ liquid	Mesomorphic - liquid point	M-L point
Smectic structure ⇄ liquid	Smectic - liquid point	S-L point
Nematic structure ⇄ liquid	Nematic - liquid point	N-L point

either the melting point or the transition point, while the temperature at which the true liquid is obtained has been referred to as the clarification point, clearing point, transition point, or melting point. In this review the authors have adopted the terminology for phase transformations listed in table 1.

III. HYPOTHESES AS TO THE NATURE OF THE NEMATIC STRUCTURE

A theoretical interpretation of the mesomorphic state has intrigued many physicists and chemists since its discovery in 1888. There can be found in the literature exchanges of arguments for and against two hypotheses that evolved out of the data that were interpreted. Even today there is no one theoretical interpretation of the mesomorphic structure that completely explains all of the experimental data. However, of the two hypotheses that have been proposed, namely the swarm hypothesis and the distortion hypothesis, the swarm hypothesis is the more widely accepted.

First, brief mention will be made of the distortion hypothesis as it was proposed by Zocher (464). Zocher expanded on his hypothesis in several other later papers. Only a few of Zocher's papers will be listed here, since these listings, in turn, will direct the reader to others. Zocher's papers (466, 468, 469) are especially concerned with an interpretation of the effects of a magnetic field on the nematic structure. The assumptions that Zocher made to derive equations for his theory of distortion in a magnetic field are: (*1*) the entire nematic structure under observation tends to take up such a position that the axial direction at every point is the same; (*2*) any force acting so as to disturb the state (under 1) where the directions are uniform causes a distortion in the nematic structure in which the direction changes continuously until a restoring force of an elastic nature holds the applied force in equilibrium; and (*3*) the positions of the units in the nematic structure initially assumed at the surfaces of solid bodies (e.g., glass) are almost unchangeable by application of an external force (magnetic field). Even though Zocher (467) applied the distortion hypothesis with some degree of success to the effects of a magnetic field on the nematic structure, the hypothesis has its limitations when one attempts to interpret the properties of light extinction and wall effects. Furth and Sitte (114) argued that the distortion and swarm hypotheses emerge as the swarm dimensions decrease. The reader is referred to their article and to one by Zocher (469) in which he argues that the two hypotheses do not have the same physical significance.

According to the widely accepted swarm hypothesis, which was initially proposed by Bose (33, 34), the molecules in the mesomorphic structure are not oriented in the same direction throughout the whole medium but are grouped in aggregrates or swarms. The molecules in the swarm lie parallel or approximately so, but in a direction that is random to the molecules of other swarms in the medium. From this point of view the structure resembles a mass of small crystals rather than a single crystal, but with this difference that, owing to the mobility of the molecules, the swarms do not remain constant in size but are continually exchanging molecules with one another and with the optically isotropic medium; the arrangement of the swarms is not a rigid one and is subject to mechanical deformation.

A number of investigators have developed mathematical interpretations of the swarm hypothesis. The reader is directed to several important papers by different authors. Since none of these mathematical developments have fully explained the varied properties of the mesomorphic structure, this section will be limited to a summary of the important aspects of the properties of the mesomorphic structure that can be explained by the swarm concept. Key references to mathematical theory are those by Oseen (308–310), Ornstein (303–304), Ornstein and Kast (305), and Tsvetkov (404). The interested reader is referred to these references for mathematical details.

The swarm hypothesis explains the turbid appearance of the mesomorphic structure as being due to the scattering of light by the swarms. The hypothesis also accounts for the fact that the orienting effects produced by applied electrical and magnetic fields on the nematic structure are much larger than would be expected if the molecules were acted on individually by the fields. If the mesomorphic structure is grouped into swarms, each will be oriented as a unit, and since its moment (length × charge) will be much greater than that of a single molecule, the effect of applied fields will be much increased. Calculation of the average diameter of a swarm on the basis of the effect of a magnetic field gives a value of the order of 10^{-6} cm., which is equivalent to a swarm content of approximately 10^5 molecules (305).

Also, the swarm hypothesis can explain the effect of surfaces of contact of the mesomorphic structure with solids (e.g., glass containers) where the swarms are oriented to a depth of a few hundredths of a millimeter (305). The hypothesis can account for the double refraction of the structure as well as for its diamagnetic and dielectrical anisotropy.

The smectic structure is not interpreted in terms of either the distortion or the swarm hypothesis. Evidently no hypothesis or theory has been proposed to explain the smectic structure.

IV. THE STRUCTURE OF THE MESOMORPHIC STATE

The transitions from the completely ordered solid crystal through the smectic and nematic structures to the true liquid may be outlined as follows:

1. Three-dimensional crystal. Apart from vibration, the centers of gravity of all lattice units are fixed; rotations are not possible.
2. Crystal with rotating molecules. The centers of gravity of all lattice units are fixed; rotation about one or more axes is possible. Example: butyl halides (4).
3. Smectic structure. The centers of gravity of the units (molecules) are mobile in two directions; rotation about one axis is permitted.
4. Nematic structure. The centers of gravity of the units (molecules) are mobile in three directions; rotation about one axis is permitted.
5. True liquid. The centers of gravity of the units are mobile in three directions; rotation about three axes perpendicular to one another is possible.

For a given compound, the temperature limits between which the mesomorphic structure is stable are definite values which vary slightly with pressure in accordance with the Clausius–Clapeyron equation (173). At the N-L point the mesomorphic and liquid states exist in equilibrium with one another; at the C-M point the crystalline and mesomorphic states can exist together. For some compounds, by rapidly cooling the melt, a mesophase is formed which is metastable with respect to the crystalline state under all conditions. For some lyotropic systems, by rapid evaporation of the solvent, a mesophase is formed which is metastable with respect to the crystalline state under all conditions. The mesophase is thus in a monotropic relationship to the crystalline state.

An interpretation of the reason for the existence of the mesomorphic state may be suggested by the molecular structures of the compounds which assume it. The structures of these compounds are discussed in Section V. It has been found that compounds exhibiting mesomorphism have molecules that are elongated, and in some cases flattened as well, and which possess one or more polar groups. The shape of the molecules favors a parallel alignment to one another, like logs in a river or a bundle of pencils; in the crystalline state they are arranged in this way and are held together by attachments through the polar groups as well as by the unspecific van der Waals attraction. If this is the arrangement in the crystalline state, it is not surprising that in going from the solid to the liquid the transformation is by stages, i.e., the weaker bonds break first, leaving the molecules with some degree of freedom of relative movement, before sufficient thermal energy has been acquired to overcome in any great degree the tendency for them to set themselves parallel to one another. Thus the system becomes fluid but remains birefringent because of the preferred orientation of the molecules.

Almost all the compounds that form the mesomorphic state can be classified by the two structures designated as smectic and nematic. The smectic structure is stratified, the molecules being arranged in layers with their long axes approximately normal to the planes of the layers. In the nematic structure the only restriction on the arrangement of the molecules is that the molecules preserve a parallel or nearly parallel orientation. Many mesomorphic substances show either the smectic or the nematic structure exclusively, but there are some substances that can exhibit both structures, the smectic followed by the nematic. Also, a few substances have been shown to exist in more than one smectic phase

Liquid state

⇅ N-L point

Nematic structure

1. Molecules parallel but not stratified
2. Positive optical sign
3. No optical rotatory power

Cholesteric structure

1. Arrangement of molecules unknown
2. Negative optical sign
3. Optically active

⇅ S-N point

Smectic structure

1. Molecules parallel and in layers
2. Positive optical sign
3. No optical rotatory power

⇅ C-S point

Crystalline state

Mesomorphic state

FIG. 1. Relationship between stability ranges of crystalline, mesomorphic, and liquid states.

and several systems have been reported which exhibit neither the smectic nor the nematic structure (19, 86, 340). Some of these mesomorphic structures observed recently (86, 340) will require further study before they can be designated accurately. In all of these structures the temperature ranges of stability of the different phases are sharply defined. In the literature a third common structure has been described—namely, the cholesteric—so called because it is shown mainly by cholesteryl derivatives. As discussed later in this section, some research workers consider this structure a special type of the nematic structure.

The relationship between the stability ranges of the different structures for substances that show the mesomorphic state is given in figure 1, together with some properties of each. This representation assumes that the substance goes through both smectic and nematic structures.

A. THE SMECTIC STRUCTURE

The special feature of this structure is its stratification. In each stratum the molecules are arranged side by side, the thickness of a stratum being approximately the length of the molecule. Each stratum or sheet is flexible and would straighten out if bent. Since the molecules in a sheet are parallel to one another, a sheet that could be considered suspended in space free from gravity would take the form of a perfectly flat surface. The thickness of the sheets of ethyl *p*-azoxybenzoate in the smectic phase as determined by x-rays is 19.9 A., while in the solid crystal the spacing is 16.2 A. (103). The difference is due to the inclination of the molecules in the solid as compared to a perpendicular arrangement in the liquid crystals. This repeat distance in the smectic structure is just what would be expected from the arrangement illustrated in figure 2a. In a compound such

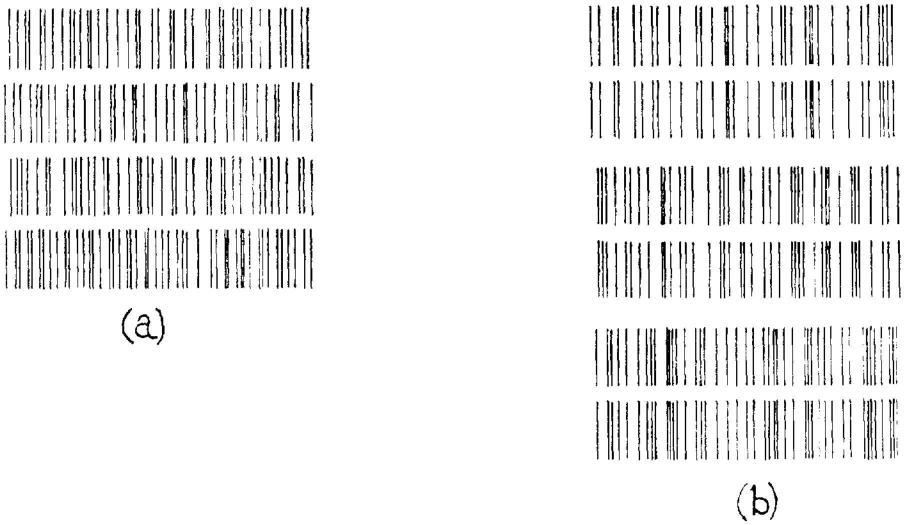

FIG. 2. Schematic arrangement of molecules in the smectic structure: (a) single layers; (b) double layers.

as thallium(I) stearate (157) the molecules in the smectic structure are double layers, as illustrated in figure 2b.

If a number of the strata were put together like the leaves of a book, one could envision the end molecules on the face of one stratum adjusting themselves so that they are fitted in some characteristic pattern with the end molecules of the adjacent strata. In this arrangement and with a regular repetition in every direction in space, the solid crystals would be formed. In the smectic structure, the temperature is high enough to break the bonds between the sheets but there is not sufficient energy to break up the sheets themselves.

The sheets in the smectic structure can slide without hindrance from their neighbors. The sheets themselves do not behave like an individual crystal but may be considered as a two-dimensional fluid. A film of ethyl *p*-azoxybenzoate in the smectic structure stretched over a small hole in a plate gives the condition of parallel sheets. The resulting structure is optically homogeneous and said to be homeotropic. The homeotropic structure is formed when the smectic phase is formed on a surface with which it does not form strong local attachments or if a film of the smectic structure is stretched over a small hole. In polarized light the structure will show rings and with a quarter-wave plate it simulates the optical pattern of a positive crystal. Because the sheets are not properly adjusted to each other the full structure of the crystal is not realized. Observed in convergent light the smectic structure behaves like a positive uniaxial crystal with the optic axis at right angles to the strata. The random side-to-side spacing of the molecules gives the uniaxial character of the structure.

An interesting example of the homeotropic structure, which indicates its stratification, is the *Grandjean terraces* (*gouttes à gradins*). The Grandjean terraces (144) are illustrated in figure 3 and a photograph of this structure is given in figure 4.[2] The steps in the structure can be inclined in any direction without pro-

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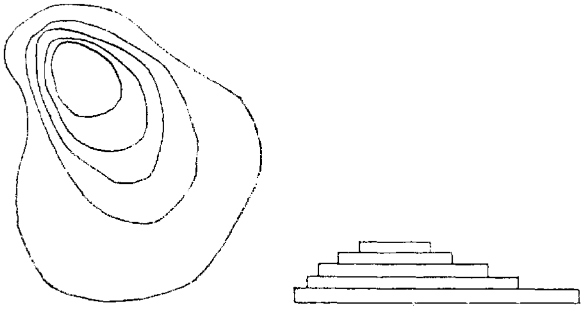
[2] Figures 4, 5, 9, 14, and 15 have been reproduced with the kind permission of Dr. A. S. C. Lawrence and the Royal Microscopical Society.

ducing any visible change. The thickness of the steps is visible, but it would appear that the thickness approximates a multiple of the length of the molecule. Under sufficient magnification the drops are optically homogeneous except that the layers are fringed by a chain of focal conics (considered later), indicating that the layers are contorted here. A probable explanation for these multiple layers may be that traces of impurities in the crystal establish dividing surfaces when the drop is in the process of formation. The reader is referred to Hartshorne and Stuart (155) and to Lawrence (215) for descriptions of various methods for the preparation of Grandjean terraces and other homeotropic structures of mesomorphic nature.

When the smectic structure is formed from cooling the liquid or from solution, it frequently first appears as nonspherical, characteristic, elongated shapes showing evidence of focal conic structure. These particles have been termed *bâtonnets* (little rods or batons) by the French workers in the field; when two bâtonnets meet they fuse together. Figure 5 is a photograph of these particles.



(a) Top Section (b) Cross Section

FIG. 3. Schematic illustration of Grandjean terraces

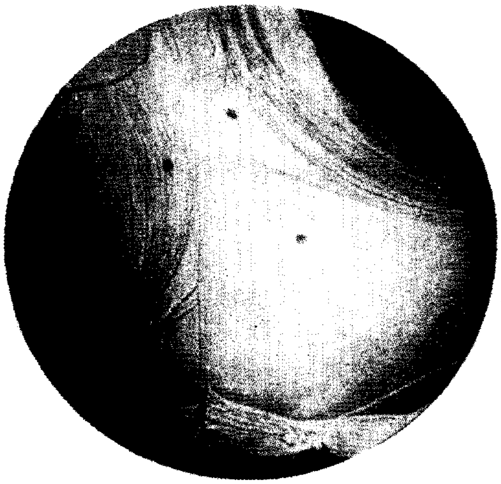


FIG. 4

FIG. 5

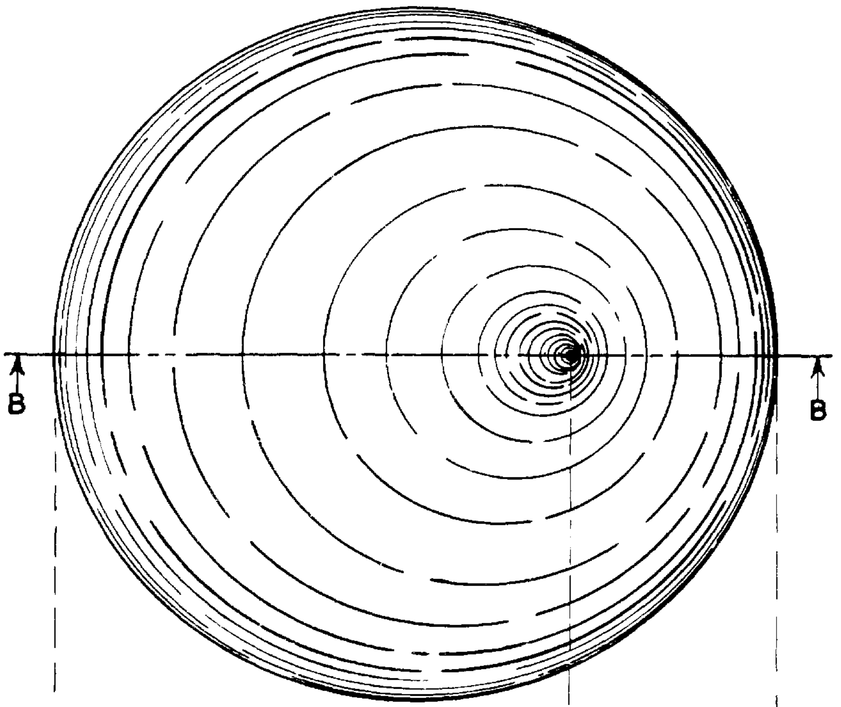
FIG. 4. Smectic structure, showing layer structure (Grandjean terraces). From Lawrence (215).

FIG. 5. Smectic structure separating from the liquid state as bâtonnets. The compound is ethyl *p*-azoxybenzoate. From Lawrence (215).

When the smectic structure is supported between glass plates the strata in the smectic structure are crumpled. Attachments between the substance and the glass are strong, and at different points these attachments compel the strata to take different directions. These directive centers of attachment require the general arrangement of the sheets in the body of the melt to accommodate themselves to the enforced conditions of the glass attachments. Also, as the associations of molecules (swarms) are formed at various points in the structure, when the liquid passes into the smectic structure, it is necessary for the molecular associations to be fitted to one another as they grow and meet. The contortions of the strata by contact with the glass plates bring about optical pecularities of the smectic structure. The forms which the strata assume and their effect upon the transmission of light have been discussed by different workers. The surfaces of the strata form series of cyclides, the properties of which were described by Dupin (84). Bragg (40) has done a splendid job of describing the chief properties of the cyclides as they are related to the smectic structure. Further discussions of Dupin's cyclides may be found in books of mathematics such as that by Hilbert and Cohn-Vossen (164).

From the microscopic observation of the smectic structure between glass surfaces, it is concluded that the strata form series of parallel curved surfaces. Dupin cyclides have the property that both sheets of their surface of centers degenerate into curves. Also, these surfaces may be defined as the envelopes of a family of spheres tangent to three fixed spheres. It may also be pointed out that each sphere of the family of spheres that envelopes a cyclide is tangent to the line of curvature of the cyclide. The torus is an example of a cyclide. Its surface of centers consists of the axis of rotation together with the circle traced out by the center of the generating circle during the rotation. All cones and cylinders of revolution are cyclides. In this case one part of the surface of centers is the axis of rotation and the other part is at infinity. For all other cyclides, the surface of centers consists of two conics which are in general an ellipse and a hyperbola.

To form an idea of the arrangement of the cyclides, a simple case is one in which the cyclides have uniform diameter and the ellipse becomes a circle and the hyperbola becomes the axis of the circle. The cylides are intersected at right angles by every straight line that meets both circle and axis. In this special case the straight lines that meet both circle and axis are perpendicular to the strata and therefore are parallel to the long dimension of the molecule. If we now go from this simple case to the more general one in which the circle becomes the ellipse, every straight line that meets both ellipse and hyperbola is normal at all points to a series of surfaces. If any two points on the hyperbola are taken and straight lines are drawn from each of them to every point on the ellipse, a region bounded by two cones is included which can be divided by Dupin cyclides into series of sheets of uniform thickness. At all points on the surface of the space the sheets are perpendicular to the generator of the cones. The reader is referred to Bragg (40) for further discussion and illustration of these statements. An example of a cross section of a Dupin cyclide is shown in figure 6. This figure illustrates the cyclides degenerating to a point. A half-cyclide is represented in figure 7, showing the principal cross-section. It can be seen that the circular cross-section



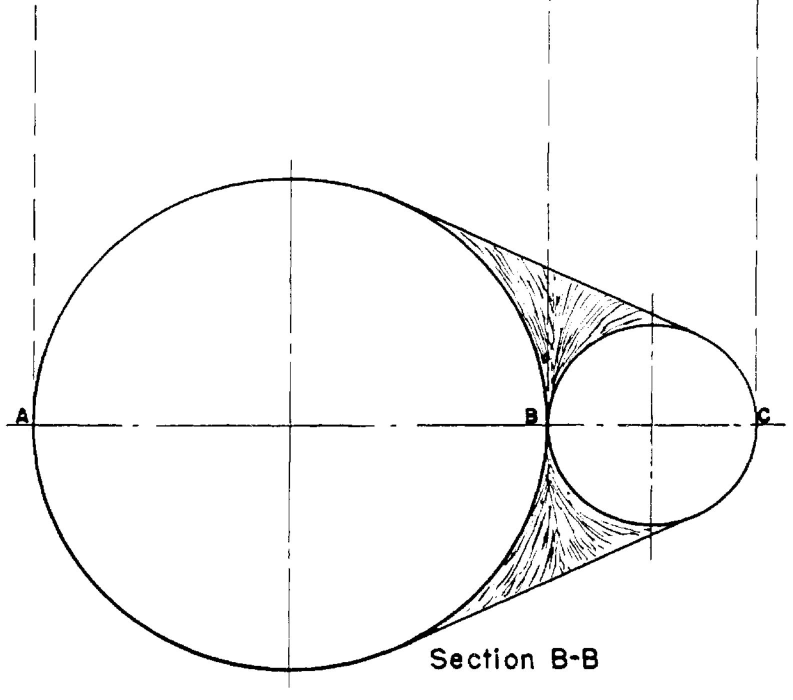


FIG. 6. (Upper section). Cyclide in plan
FIG. 7. (Lower section). Half-cyclide, showing principal cross-section

varies in diameter from a maximum *AB* to a minimum *BC* and that this cross-section occupies diametrically opposite positions on the cyclide.

The geometric basis of the focal conic structure is illustrated in figure 8. It consists of a family of parallel, equally spaced cyclides, shown in section (elevation view) in figure 8a and in another section (plan view) in figure 8b. The

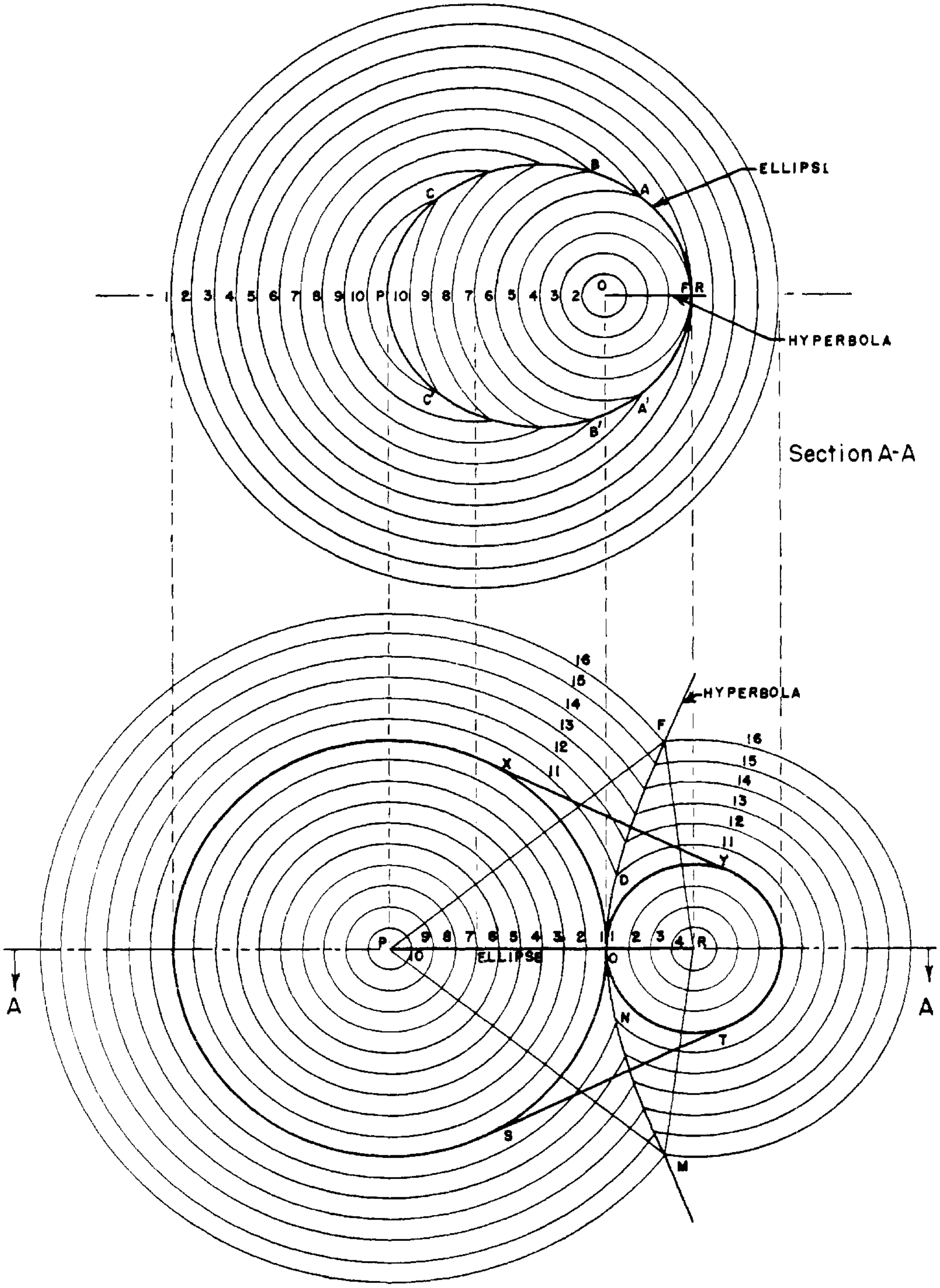


FIG. 8. (a) Lower section: elevation view of cyclides in section. (b) Upper section: plan view of cyclides in section.

common centers in the principal cross-sections are *P* and *R*. Lines in the same cyclide bear the same numbers, as 1,1; 2,2; 3,3; etc. Cyclide No. 1 may be considered as the starting point in the discussion. In cyclide No. 1 the radii of the principal sections are *PO* and *OR*, with point *O* representing the point in figure 6. Lines XY and ST in figure 8a are the "top" and "bottom" boundaries in the half-cyclide of figure 7. The first four cyclides (Nos. 1, 2, 3, 4) are similar to those represented in figures 6 and 7, but in No. 5 the radius of the minor principal cross-section has shrunk to a point (R) and above No. 5 the cyclides are incomplete, the cross-section shrinking to points AA', BB', CC' (see figure 8b) before the full circuit of the hollow ring can be made. Thus, instead of being rings they are crescents. The points A, B, C, R, etc. of figure 8b lie on an ellipse of which O is one of the foci and P and R are the vertices.

The cyclides outside No. 1, i.e., 11, 12, 13, etc. (figure 8a), have no central hole but only a "dimple" above and below, e.g., D and N (cyclide No. 11) and F and M (cyclide No. 16) (figure 8a). The points M, N, D, F, etc. lie on a hyperbola of which O is a vertex and R is a focus.

The locus of the vertices of the circular cones of revolution passing through a given ellipse is a hyperbola which passes through the focus of the ellipse and lies in a plane perpendicular to the plane of the ellipse. Conversely, the locus of the vertices of circular cones passing through the hyperbola is an ellipse. Thus F is the apex of a cone of revolution of PRF in which RF and PF lie on diametrically opposite sections of the cyclides. Similarly M, N, and D are the apices of cones of evolution MRP, NRP, and DRP, respectively, and the ellipse is a section of all these cones. The ellipse and the hyperbola are described as focal conics. Dupin's cyclides are surfaces which are drawn at right angles to all the straight lines that pass through both conics.

The mathematical relationship between the focal conics is as follows:

$$\left.\begin{aligned}\frac{x^2}{a^2}+\frac{y^2}{b^2}&=1\\ z&=0\end{aligned}\right\}\text{ for the ellipse}$$

$$\left.\begin{aligned}\frac{x^2}{c^2}-\frac{y^2}{b^2}&=1\\ y&=0\end{aligned}\right\}\text{ for the hyperbola}$$

The condition that each passes through the focus of the other is

$$c^2 = a^2 - b^2$$

These relationships are discussed in books on differential geometry (97).

Dupin's cyclides have the property that any pair of surfaces is equally separated everywhere; this makes it possible for the surfaces to coincide with the surfaces of sheets of uniform thickness. Agreement between theory and experiment leads to the conclusion that the smectic structure is arranged in such a manner that the strata take the form of Dupin's cyclides. Since there are other geometric arrangements of sheets of uniform thickness, there must be a justification for the preference of cyclides. This is based on energy considerations. The strata in the smectic structure must, while obeying the boundary conditions, arrange themselves so that the potential energy of the system is a minimum. This requirement is met with the cyclides which have the lowest potential energy

FIG. 9. Smectic structure of ethyl *p*-azoxybenzoate. From left to right: crystalline solid; pseudomorph of solid; smectic, focal conic structure; liquid state. From Lawrence (215).

of the possible arrangements. Bragg (40) has considered other geometric forms and concluded that only the Dupin cyclides meet the structural requirements of the smectic structure. The most direct evidence for the focal conic structure in the smectic phase is that the outline of the ellipse and hyperbola can be seen as dark lines when the structure is examined under the microscope. Figure 9 is a photograph that shows this structure. The location of the ellipse and hyperbola in the structure (as can be seen in figure 8) represent optical discontinuities in the medium; they are the loci of points at which the strata undergo a sharp change in direction.

The simplest representation of the focal conic structure is the so-called polygonal structure. This structure is generally obtained in fairly thick and not too viscous systems. Friedel (104) described the preparation of this structure in detail. A microscopic examination of the system that shows this polygonal structure reveals a number of irregular polygonal areas which may have any number of sides and in each of which there appears a family of ellipses which are tangential to the sides of the polygon and to each other. The spaces between larger ellipses are occupied by smaller ellipses and so on. Figure 10 represents an imaginary case showing the larger ellipses in a four-sided polygon, *RSTU*, and portions of the ellipses in neighboring polygons. In this structure all major principal axes of all the ellipses in a given polygon pass through one point, *P*. A second observation is that if the upper surface of the preparation between the glass sur-

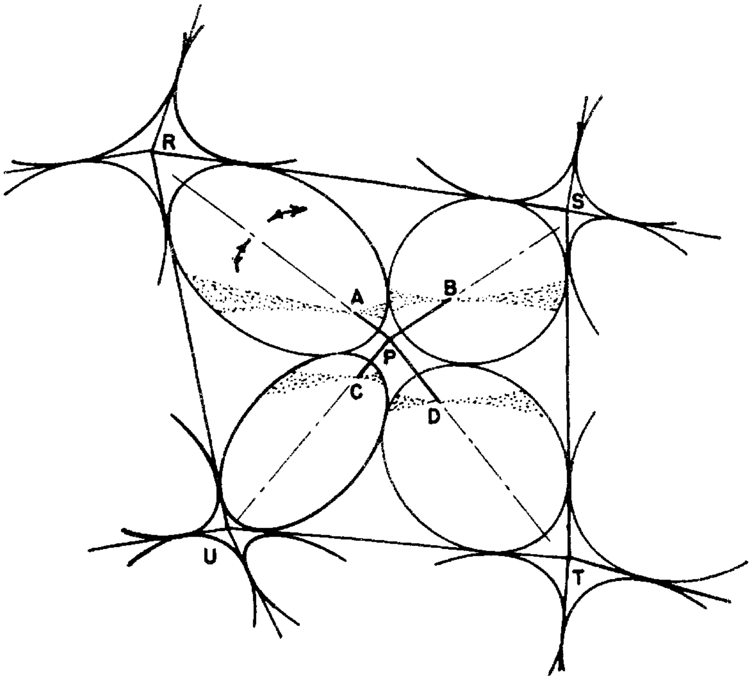


FIG. 10. Polygonal structure (upper surface focused); analyzer only

faces is focused and the analyzer (without the polarizer) is inserted, each ellipse is seen to be crossed by a straight brush, the direction of which is parallel to the vibration direction of the nicol. The narrowest part of the brush coincides with one of the foci of the ellipse (*A*, *B*, etc. in figure 10).

If the focus of the microscope is altered from the upper to the lower surface it will be observed that (*1*) each ellipse has as its partner one branch of a hyperbola which lies in the vertical plane containing the major axis of the ellipse and which meets the ellipse at the focus crossed by the dark brush (*A*, *D*, etc. in figure 10), and (*2*) the hyperbolas belonging to ellipses in the same polygon will all meet in the lower surface at one point *X*, which is directly below the point of intersection of the major axes of the ellipses. This point of intersection of hyperbolas is a common corner in the system of polygonal areas on the lower surface which is now in focus. The polygon edges which radiate from this point intersect at right angles the projections of the edges of the polygon on the upper surface to which the hyperbolas belong. These are illustrated in figure 11. Thus *XY*, *XZ*, *XG*, and *XH* intersect at right angles the projection of *ST*, *RU*, *UT*, and *RS*.

The experimental observations may be explained as follows. The medium may be divided into pyramids and wedges or tetrahedrons, the base of the pyramids being the polygons observed in the upper and lower surfaces which are under examination. Take the block of material represented by figure 12, which may be considered as consisting of an inverted pyramid *RSTUX*, two erect pyramids *UWZXH* and *TZVGX*, and three tetrahedrons *UZTX*, *URXH*, and *TSXG*. The base *RSTU* of the inverted pyramid corresponds to the polygonal structure in figure 10 with the apex of the pyramid, *X*, corresponding to the point similarly labeled in figure 11.

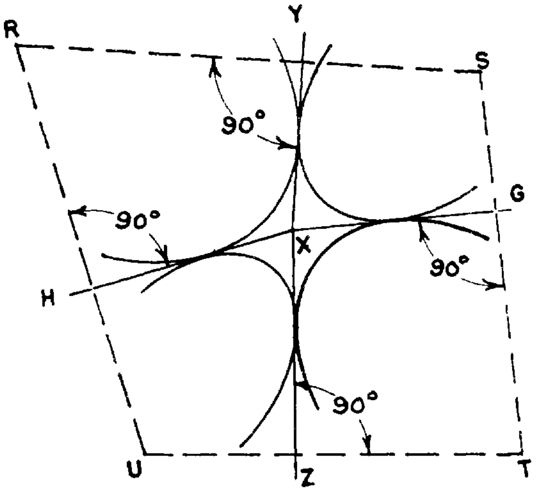


FIG. 11. Polygonal structure (lower surface focused)

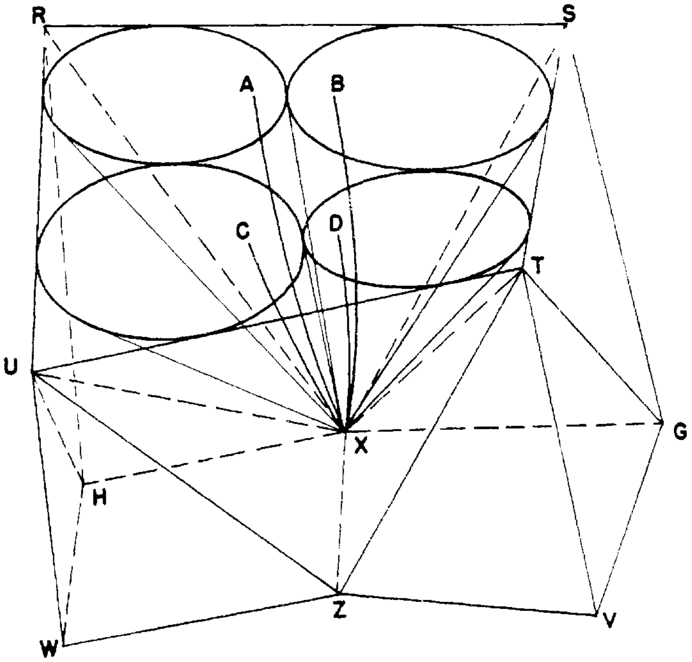


FIG. 12. Polygonal structure

Each pyramid contains a family of cones of revolution which touch one another along common generators. The elliptic bases of the cones rest on the base of the pyramid (see figure 12). The hyperbolas which bear a focal conic relationship to these ellipses come together at the apex of the pyramid. For example, in figure 12 the four largest cones with elliptic bases are represented along with their hyperbolas AX, BX, CX, and DX.

Figure 13 represents the continuity of strata in focal conic structure. The upper section of the drawing represents a section of the smectic structure in the plane of the ellipses. AO, BO, $A'O'$, and $B'O'$ represent the hyperbolas that pass

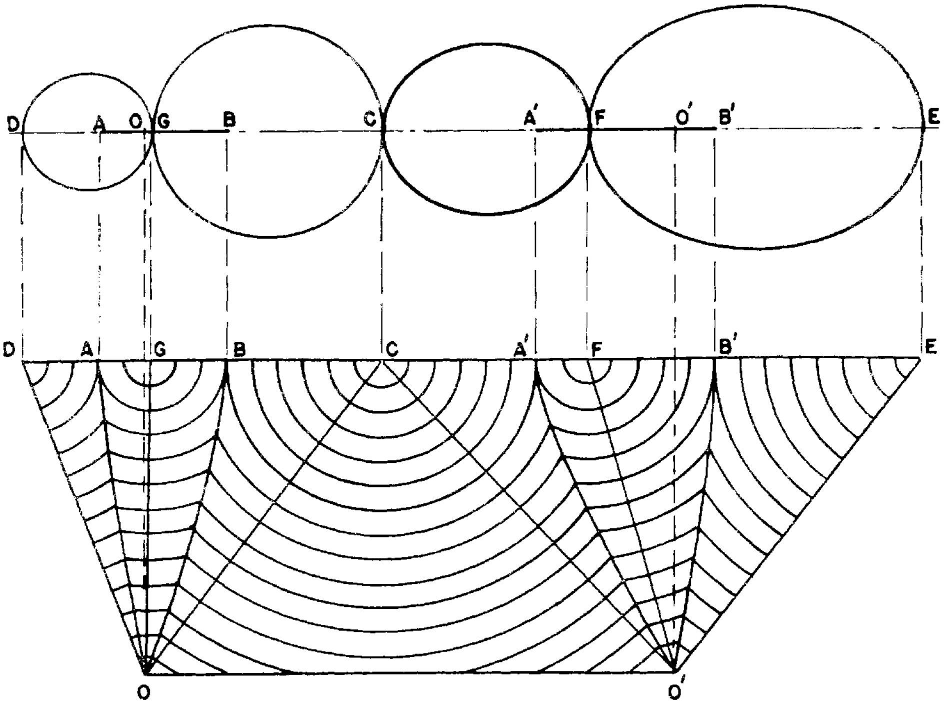


FIG. 13. Continuity of strata in focal conic structure

through the foci A, B, A', and B' of the ellipses, respectively. In this focal conic structure the plane of the hyperbola is perpendicular to the ellipse. DOC and $EO'C$ are cones belonging to different pyramids. It can be seen from figure 13 that the cyclides of one cone $EO'F$ pass continuously into the cyclides of the other cone $CO'F$. Even though the representation in figure 13 is for only a few lines of contact between cones, it is assumed that each pyramid is completely filled with cones, small ones in the crannies between the larger ones at least down to the limit set by intermolecular distance; then the strata of each cone will at every point on its surface be continuous with the strata of some other cone except at the surface of the pyramid, where they are continuous with those of the tetrahedral regions.

It is impossible by direct observation to prove that the pyramids are completely filled with cones. Ellipses smaller than the limit of the microscopic resolution cannot be observed, but it may be concluded with some confidence that the presence of any other type of structure would involve discontinuities in the strata in addition to those at the hyperbolas.

The pairs of polygon edges which are at right angles to one another and represented in figure 11 by XG, XH, ST, and RU are each composed of an upper and lower edge of a tetrahedron. Reference to figure 12 will make this clear. It may be concluded that the edges are parts of focal conic curves, i.e., in each pair one edge is part of an ellipse and the other part of a hyperbola. The cyclides corresponding to these curves will be continuous with those of the cones on the surfaces of the neighboring pyramids. A single section is shown in figure 13. OCO' is a section of a tetrahedron, and its cyclides, based on the edges OO' and C, are continuous with those of the cones $CO'F$ and COG. Lines CO' and CO, respectively, are the lines of contact between the cone and the tetrahedron.

The dark brushes across each ellipse in the polygonal section, when it is observed in polarized light, may be explained as follows. The long axes of the molecules are everywhere at right angles to the strata. If the analyzer is inserted into the microscope and the microscope is focused on the upper surface of the preparation, ordinary light entering the medium is resolved into extraordinary and ordinary rays. The extraordinary rays vibrate in the plane containing the ray and the optic axis of the medium, i.e., in the direction of the long axis of the molecule. Owing to the curvature of the strata, the inclination of the optic axis varies continuously from point to point throughout the preparation. Grandjean (145) showed that, as a result of curvature, the ray will be deviated and will follow a curved path. Consequently, few of these rays reach the objective of the microscope. The propagation of ordinary rays which vibrate at right angles to the long axes of the molecules is not affected by the curvature of the strata. Therefore, the ordinary rays are primarily responsible for the formation of the image. The long axes of the molecules lie along lines joining the hyperbola to the ellipse, i.e., along lines PF, RF, OP, etc. in figure 8a, and the vibration directions of the emerging ordinary rays are at right angles to these radial lines. Vibration directions of some of the rays are shown in figure 10. It can be seen that rays emerging on the radial lines which are parallel to the vibration direction of the analyzer will be extinguished.

If the lower surface of the preparation is focused and the polarizer is used (analyzer omitted), the extraordinary rays are deviated as before while the ordinary rays appear only where the molecules are not parallel to the vibration direction of the polarizer. Thus each ellipse shows a brush parallel to this direction.

B. THE NEMATIC STRUCTURE

The nematic structure has none of the conic structure nor the Grandjean terraces of the smectic structure. It has no stratification but does possess some interesting optical properties and has some degree of molecular arrangement. The properties of the nematic structure indicate that the molecules are parallel, or nearly parallel, to one another but are not in layers. It can be concluded that the substance owes its mobility to the facility with which the molecules can be drawn past one another while retaining a strong tendency to acquire or retain a parallelism between the long dimensions of the molecules and the direction of drawing.

Bernal and Crowfoot (17) studied the crystal structure of solid *p*-azoxyanisole and *p*-azoxyphenetole by x-rays and found that the molecules in the solid lie parallel to one another but cannot be clearly separated into layers. This crystal pattern has been described as imbricated; however, it must not be inferred that all nematic substances have an imbricated structure in the crystalline state. There are not many x-ray data available on the crystalline state of solids that form the mesomorphic state, so no general statement can be wisely made about crystalline arrangement versus mesomorphism. However, it appears that with a layer arrangement of molecules in a crystalline state, the substance can exist as a smectic structure as well as a nematic one.

When the nematic preparation is placed between glass surfaces, the molecules in contact with the glass tend to be attached sideways to the surfaces. The orientation of the molecules in the bulk of the phase appears to be governed by those sticking to the glass surface. The effect of surfaces on orientation of the swarms in the nematic structure has been the object of much study. Some of these studies are presented in Section X,G. The influence of the surface on the orientation of swarms can be demonstrated as follows: a microscopic slide and a cover glass are treated briefly with hydrofluoric acid and washed and dried without touching the surfaces. The hydrofluoric acid treatment gives a roughened glass surface and many points of contact for the swarms. A molten liquid-crystalline substance, such as *p*-azoxyanisole, is allowed to run between the slide and cover glass by capillary action. If the edge of the film is inoculated with a grain of the crystalline substance, relatively large crystal plates are obtained on cooling the system. If the preparation is now heated to convert it to the mesomorphic state, each plate assumes the nematic structure with the orientation of the molecules in each plate controlled by the surface which it contacts. The orientation of the molecules on the top surface is different from the corresponding orientation on the face below. However, the preparation is now fluid and it is birefringent (uniaxial positive) and uniform in optical properties. If this preparation is cooled and carefully handled, the cover glasses can be twisted a little and the plates adhering to the top and bottom surfaces separated.

If the cover glass is moved sideways carefully and the preparation of the nematic structure observed under a microscope, there appears an effect which indicates that the boundaries of the uniform plates are doubled. This is because the molecules in the top layer are attached to the cover glass and move with it while those on the bottom layer remain attached to the lower glass; the molecules in the bulk of the preparation adjust themselves to the shearing effect. If a polarizer of the microscope is set parallel to the molecules on the lower surface, the analyzer, in order to obtain extinction, is not set perpendicular to the polarizer but at some other angle dependent upon the amount of displacement of the molecules in the system. If the cover glass is rotated, the nematic structure is forced to take on a twisted structure. This causes the structure to rotate the plane of polarization of light, i.e., the structure appears as if it were optically active.

If the nematic structure is heated just inside the liquid state and cooled again to the nematic structure, the pattern of nematic plates as described above is reproduced. This may be explained by reasoning that the molecules at the glass surfaces remain oriented while in the liquid state, and that when the system is cooled, they direct the molecules in the preparation into their original arrangements.

Zocher and Ungar (474) made a study of the nematic structure in converging polarized light and at thicknesses up to 1 mm. It was concluded that the parallel

FIG. 14

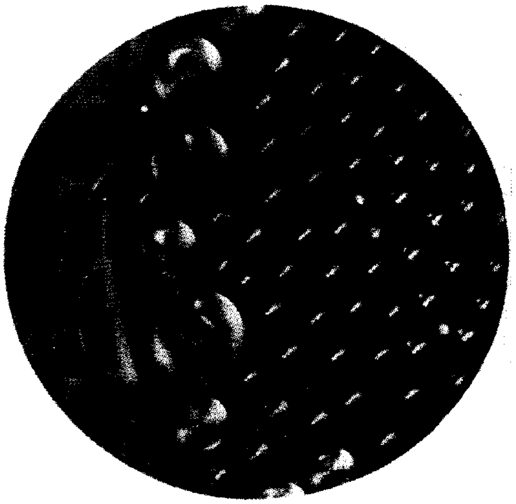


FIG. 15

FIG. 14. Nematic structure, showing from left to right: crystalline solid; nematic structure; liquid. From Lawrence (215).

FIG. 15. Spherical "drops" formed as the nematic structure separates from the liquid. From Lawrence (215).

orientation of the molecules extends from one glass surface to the other, right through the preparation in these thin sections.

If a substance possessing mesomorphic properties is cooled suddenly from the liquid state to the nematic structure, the preparation becomes full of complicated vortices and intertwinings. Among these are the fine lines or threads from which the structure derives its name. The threads are lines of discontinuity giving rise to optical effects. The photograph of the nematic structure in polarized light and showing these threads is given in figure 14. These threads are most frequently found in preparations that are relatively thick and on glass surfaces that have not had special treatment in their preparation. The threads appear to be partly or wholly anchored to the glass but for the most part they freely follow the movement of the fluid, continually changing their length and shape. In some cases they disappear without leaving a trace. The threads appear to be due to discontinuities in the structure, but the nature of the discontinuity is a matter of doubt. The discontinuity may be a line toward which the long axes of the molecules are directed in a radial manner. Or again, the discontinuity might be a line around which the medium is circulating, corresponding to a vortex ring, perhaps hollow and vacuous, around which the molecules are circulating. The long axes of the molecules are then tangential to circles normal to, and centered on, the lines of discontinuity. The discontinuity may be due to both structural patterns. In any case, the lines can be looked upon as axes about which the medium is structurally built.

If one takes two successive photographs of the nematic structure as quickly as possible after it has formed, so as to avoid changes due to continuous motion of the liquid, one observes differences between the two photographs in that the threads that look narrow and clear in one photograph are blurred or distorted in the other; otherwise the photographs are identical. The same effect can be obtained by allowing the substance to crystallize between glass surfaces before the thread structure is established. On observation through an analyzer (no polarizer) it will be seen that parts of the field are brighter than others. In the brighter parts the threads are well-defined lines, while in the darker parts they are blurred. If the threads are the axes about which the medium is structurally built, the above phenomenon can be explained on the basis that the extraordinary rays passing near a thread are deviated by the curvature of the structure and for the most part do not meet the microscope objective. The ordinary rays are not deviated because they vibrate at right angles to the long axes of the molecules. The vibration directions of the emerging rays are dependent upon the orientation of the molecules which adhere to the upper glass surface, and the orientations at the surface are dependent upon the previous arrangement of the molecules in the solid crystal. If the orientation of the long axes of the molecules at the glass surface is perpendicular to the angles of the vibration direction of the analyzer, the ordinary rays that reach the eye will not be deviated as they pass near the thread; thus the threads will be in sharp outline in the brightly illuminated area. However, if the orientation of the long axes of the molecules at the glass surface is parallel to the vibration direction of the analyzer, only extraordinary rays will pass and the images will be blurred because these rays are deflected out of their course by passing near the threads. The intensity of the light will be low and the images thus are distorted. This phenomenon was studied in considerable detail by Zocher and Birstein (470).

When the nematic structure is formed by cooling the liquid, it first appears in "drops" that are spherical. These anisotropic "drops" are shown in figure 15. It can be seen that each "drop" shows a cross and that the arms of all the crosses are parallel to the principal planes of the nicols in the microscope; these observations indicate a spherulitic type of structure. There is an indication that the molecules in the drop either radiate from the nuclear point in the center of the drop or are arranged along concentric circles as if there were a vortex. Either arrangement would account for the cross. If the preparation is rotated with respect to the nicols, the crosses do not move. The drop is therefore independent of surface attachments and is floating freely in the body of the liquid.

The molecules in the nematic structure are oriented by electrical and magnetic fields. This indicates a greater degree of freedom of movement of the molecules in the nematic structure than in the smectic structure. Once the smectic structure has been formed, the magnetic and electrical fields, of the strength that have been used in studies reported in the literature, do not affect it. With an electrical field, the molecules in the nematic structure set themselves with their long axes perpendicular to the electrical lines of force while the molecular axes are set parallel to the magnetic flux lines in a magnetic field. Viewed along the lines of force of the magnetic field, the nematic structure appears clear.

The electrical moment of a swarm is of the order of 10^5 times that of an individual molecule. The diamagnetism of the nematic structure leads to a similar value of the size of the swarm. More information on these facts may be found in Sections VI and VIII.

C. THE CHOLESTERIC STRUCTURE

The cholesteric structure has certain characteristics that are markedly different from the smectic and nematic structures. The structure is found especially with cholesterol and its derivatives but a few other substances, e.g., amyl cyanobenzalaminocinnamate, show this property. The characteristic properties of the cholesteric structure may be summarized as follows:

1. It is optically negative, while smectic and nematic structures are optically positive. The optically negative character is probably connected with the broad sterol portion of the molecule.
2. The structure is optically active and shows strong rotatory power.
3. When illuminated with white light, the most striking property of the cholesteric structure is that of scattering the light to give vivid colors. The color of the scattered light at a particular angle to the surface of the film is dependent on (*a*) the substance, (*b*) the temperature, and (*c*) the angle of the incident beam.
4. In the structure, one circularly polarized component of the incident beam is completely unaffected. For the dextro structure it is only the circularly polarized beam with counter-clockwise rotating electrical vector which is reflected (the sign of rotation refers to an observer who looks in the direction of the incident light). Levo structures have the reverse effect.
5. Electrical vectors of the incident and reflected light rotate in opposite directions (see sign of rotation in 4 above). For ordinary substances the direction of rotation is unaffected by reflection.
6. The mean wavelength of the reflection band depends on the angle of the incident beam (angle between the surface and the incident beam). The relationship can be described approximately by the Bragg diffraction equation. The apparent reflections occur on layer spacings of about 2000 A. (146).
7. When the structure fills a wedge-shaped space, bright and dark lines appear which follow the lines of equal thickness. Some researchers interpret these dark lines as intersections of structural layers in the medium. The spacings of the dark lines agree with the spacings found in the experimental methods mentioned in paragraph 6 above.

The cholesteric structure in some respects resembles the smectic and nematic structures. For example, cholesteryl cinnamate on cooling from the liquid state will first form a confused appearance of a focal conic structure. With a slight mechanical disturbance the medium takes a form which reflects light of brilliant colors. The color is temperature dependent, being a vivid green at higher temperatures and golden-bronze at lower temperatures.

Friedel (104) suggested that the cholesteric structure was a special kind of nematic structure. His main points of argument were as follows: (*1*) Some mesomorphic substances show both the smectic and nematic structures; some show both the cholesteric and smectic; but no substance has been found to exhibit both cholesteric and nematic. (*2*) When certain mixtures of dextrorotatory and levorotatory cholesteric substances are heated, the cholesteric properties slowly disappear and the nematic structure takes over. The change does not show any discontinuity.

Friedel (106) summarized the optical rotation of the cholesteric attraction as follows: a dextro structure will rotate the plane of polarization of the incident light to the right when the wavelength is less than that of the light scattered at maximum intensity (perpendicular to the surface); the incident light is rotated to the left when its wavelength is greater than this. For the levo structure, levorotation occurs when the incident light is of shorter wavelength than that scattered at maximum intensity and dextrorotation when the wavelength is greater.

An interesting characteristic of the cholesteric structure is that the scattered light is circularly polarized, being either dextro- or levorotatory. A further interesting property is that if the incident light is circularly polarized in the same sense as that normally scattered by the substance, i.e., if right-handed circularly polarized light is directed at a dextro substance, it is scattered without change of sense, which is contrary to what is normally found for the reflection of circularly polarized light. If the incident circularly polarized light is of opposite sense, the light is then transmitted without change of sense.

Gaubert (125) studied mixtures of cholesteryl compounds and different acids. Cholesterol and succinic, cinnamic, or anisic acid gave optically negative crystals, while compounds such as succinimide and the tartaric acids gave positive crystals.

It was the belief of the Friedels (107) that substances possessing the nematic structure can be made to form stratified cholesteric structures by the addition of asymmetric molecules. Friedel (105) reported that small amounts of cholesteryl acetate in *p*-azoxyanisole gave levorotation, decreasing in a normal manner with increasing wavelength. The systems were not circular-dichroic over the entire range of the conditions that he studied. For example, a mixture composed of 40 parts of *p*-azoxyanisole to 1 part of cholesteryl acetate gave a rotation of 265 in revolutions per millimeter at 100°C. and 505 mμ, while the rotation was 125 revolutions per millimeter at 125°C. and 635 mμ. Upon doubling the cholesteryl acetate concentration Friedel found that the specific rotation decreased by about one-half; this shows that the concentration of the cholesteric structure itself and not the concentration of the asymmetric units is responsible for the unusual rotation values.

The effect of temperature and the angle of observation relative to the illuminating beam on the color of the scattered ray is illustrated by such systems as a mixture of approximately 55 per cent cholesteryl benzoate and 45 per cent of cholesteryl acetate or by pure cholesteryl cinnamate. With the cinnamate, Royer (345) found that the reflected colors are displaced toward the red as the melt is cooled from the liquid through the cholesteric structure. Further discussion of this phenomenon can be found in the paper by Gaubert (129). The reflected color with the acetate and benzoate mixture is violet at the upper limits of the mesomorphic structure. The colors vary successively from violet to red as the temperature decreases. In all cases the illuminating white light and the observation are normal to the surface. If the direction of observation is oblique to the preparation, the wavelength of the light reflected decreases with increase in obliqueness of the angle of observation.

The optical rotation of the cholesteric structure has been studied most recently by Mathieu (263) and Levy (248). Mathieu's results may be summarized as follows: (*1*) The scattered radiations form a spectral band of 0.020 μ in width; the intensity passes through a maximum towards the center of the band and for this wavelength, λ_0, the scattered light is circularly polarized. (*2*) In this spectral band of light the transmitted light is elliptically polarized; the light becomes circularly polarized if the thickness of the cholesteric layer is sufficient. (*3*) The rotative ability does not attain any infinite value but is reversed, taking a null value for the wave length λ_0.

The last of these points resolves the two different points of view about the rotative ability of the cholesteric structure. One view (107) was that the rotatory power changed in sign while taking on some infinite values, and the other view (377) was that the rotatory power of the cholesteric structure is similar in the vicinity of some wavelength, λ_0, to that of the rotatory power of ordinary optically active liquids in the vicinity of certain absorption bands.

The values that Mathieu (263) obtained for the rotation of the cholesteric compounds that he studied are of the order of 1000° per millimeter. The largest values reported for organic molecules in a homogeneous medium is a specific rotation of about 300° per millimeter (284).

Levy (248) measured the natural rotation and ellipticity of cholesteryl oleate in a perpendicular and parallel magnetic field using a wavelength of 5460 A. and between the temperatures of 37° and 43°C. The strength of the magnetic field was 24,600 gauss. For any given temperature, the rotation increased slightly under the influence of both a perpendicular and a parallel field as compared to no field; generally, the ellipticity increased with temperature, reaching a limiting value around 42°C. The experimental findings fit the theoretical developments reported by Levy (247).

Grandjean (143) studied the orientation of the cholesteric structure of cholesteryl esters on ionic salts. When the cholesteric structure of cholesteryl caprate is introduced into the cleavage cracks of crystals, the optical axis of the liquid becomes oriented and parallel with respect to the crystalline surface. With rock salt, cleavage (001), the direction of the optical axis of the structure is that of the diagonals of the face of the cube. In the case of cholesteryl benzoate, and of the ammonium and trimethylammonium oleates, the orientation of the axis of the cholesteric structure is normal to the cleavage plane.

De Vries (439) gives a theoretical treatment to the phenomenon of the rotatory power of the mesomorphic state, with a main concern for the derivatives of cholesterol. He assumed that the molecules are arranged in a special way so that

TABLE 2

Typical examples of compounds showing a single mesomorphic structure

Compound	Structure	Temperature Range
		°C.
Ammonium oleate	Smectic	Room temperature
Ethyl *p*-azoxybenzoate	Smectic	114–120
Ethyl *p*-azoxycinnamate	Smectic	140–250 (ca.)
p-Azoxyanisole	Nematic	116–133
Anisaldazine	Nematic	168–182
Cholesteryl benzoate	Cholesteric	146–178.5
Amyl cyanobenzalaminocinnamate	Cholesteric	92–105

the electric axes rotate screwlike. It does not matter whether this molecular arrangement occurs in small steps (as has been thought by practically all workers in the field) or continuously. When the axes make one revolution over a thickness, p, then light in a region $\lambda = pn$ will be reflected (n = refractive index). The second important parameter is the value of the double refraction, $\alpha = (n_2 - n_1)/n$, where $n = (n_1 + n_2)/2$. From p and α all optical properties can be calculated. De Vries pointed out that no accurate data for testing the theory were available, but that on a qualitative basis the agreement is satisfactory with experiment. Evidently the work of Mathieu (263) was not known to this author.

V. MOLECULAR STRUCTURE OF SUBSTANCES WHICH FORM THE MESOMORPHIC STATE

A characteristic structure of a molecule that will show the mesomorphic state cannot be defined easily. Mesomorphism is found in aromatic, aliphatic, and multi-ring compounds. An illustration of a simple aliphatic compound showing liquid crystallinity is 2,4-nonadienoic acid, while the simplest aromatic compounds are *p*-propoxybenzoic acid, *p*-butylbenzoic acid, and *p*-methoxycinnamic acid. Examples of compounds showing a single mesomorphic structure and their temperature ranges of mesomorphism are given in table 2. Typical compounds showing more than one mesomorphic phase are: (*1*) cholesteryl pelargonate:

$$\text{Crystalline} \xrightleftharpoons{78^\circ} \text{smectic} \xrightleftharpoons{79^\circ} \text{cholesteric} \xrightleftharpoons{90.5^\circ} \text{liquid}$$

(*2*) ethyl anisal-*p*-aminocinnamate:

$$\text{Metastable crystal} \xrightleftharpoons{83^\circ} \text{smectic 1} \xrightleftharpoons{91^\circ} \text{smectic 2} \xrightleftharpoons{118^\circ} \text{nematic} \xrightleftharpoons{139^\circ} \text{liquid}$$

Smectic structure 1 and the metastable crystalline modification are found on cooling smectic phase 2 if all traces of the stable crystalline form are absent.

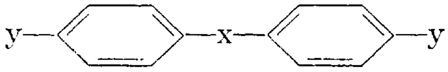
There are generally only one or at most two mesomorphic modifications of a given compound. However, Weygand (444) found *n*-octoxybenzal-*p*-propylaniline to be a substance that exhibits four liquid-crystalline modifications.

A. AROMATIC TYPE COMPOUNDS

Aromatic compounds will be considered first, since they make up the largest group of known compounds exhibiting mesomorphism. Bernal and Crowfoot (17) proposed that an aromatic molecule to show mesomorphism must possess the following structure: (*1*) the molecules must be geometrically anisotropic and either rod-shaped, flat, or lath-shaped; (*2*) there must not be more than one group in the molecule with a high dipole; and (*3*) the molecules should contain moderately active groups such as —CCl, —COC—, —CH=N—, and $—OCO_2—$ toward the extremities of the molecule. The structural requirements listed by Bernal and Crowfoot may be considered as the basic requirements for the mesomorphic structure of aromatic type molecules.

1. Basic structural requirements of aromatic type molecules

A summary of the basic structure of aromatic type compounds can be given by use of the general formula:



Summarized in table 3 are the listings of the composition of the central group, x, the type of compounds represented for the particular x, and a typical example of that type. Table 3 is divided into symmetrical and unsymmetrical molecular structures. In table 4 the types of end groups, y, are summarized. Neither of these tables is meant to contain an exhaustive listing of all the groups reported in the literature. However, the tables may be considered as an extensive listing of the known aromatic types of compounds exhibiting mesomorphism. The general plan of classification is patterned after Weygand (442).

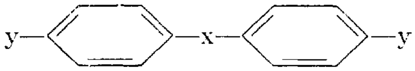
2. Effect of atomic grouping in the molecule on the mesomorphic character

The effect of different atomic groups in a molecule can be illustrated by the characteristic molecules shown in table 5. The first portion of the table deals with unsymmetrical molecules and illustrates the effect of the change in C-N and N-L points with a rearrangement of the end groups. The second portion of the table illustrates the effect of the change of arrangement of the central group on the C-N and N-L points while the end groups remain fixed. No effort has been made to accumulate all possibilities to be found in the literature to illustrate the effect of atomic grouping in the molecule; however, these illustrations are typical of this particular phenomenon.

The substitution of the methoxyl group for the nonpolar phenyl group gives practically no change in the N-L point, while the exchange of two polar groups gives a pronounced change in the N-L point (as much as 20°C.). Examination of table 5 shows that a change of the atomic groupings in a molecule with a strong central dipole such as the azoxy group in these few compounds listed here does not result in much change of the N-L point. However, in the case of the weaker dipole such as the azo group, a change in the arrangement of the central grouping gives a large change in the N-L point (as much as 40°C.). The data for table 5 are from Foote (96) and Kast (197).

TABLE 3

Composition of central group in aromatic type molecules showing the mesomorphic state



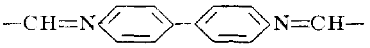
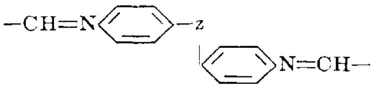
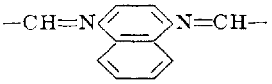
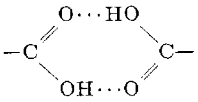
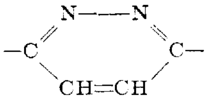
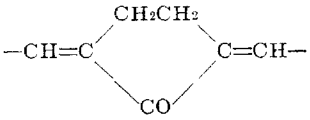
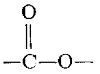
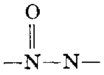
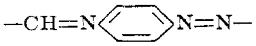
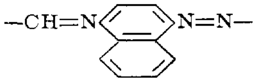
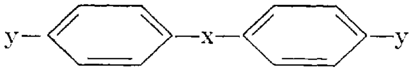
x = Central Group	Type	Typical Example
	Symmetrical molecules	
—	Biphenyl	*p*, *p*′-Diethylbenzidine
$-CH{=}CH-$	*trans*-Diphenylethylene	*p*, *p*′-Diacetoxystilbene
$-C{\equiv}C-$	Diphenylacetylene	*p*, *p*′-Diacetoxydiphenylacetylene
$-N{=}N-$	*trans*-Azobenzene	*p*-(*p*-Acetoxyazo)benzoic acid
$-CH{=}CH-CH{=}CH-$	Diphenylbutadiene	*p*, *p*′-Dimethoxydibenzalbutadiene
$-CH{=}N-N{=}CH-$	Dibenzalazine	*p*, *p*′-Dimethoxybenzalazine
	Dibenzaldiphenyldiamine	Dibenzalbenzidine
	Dibenzaldiphenyldiamine derivatives	1, 2-(Dibenzal-*p*, *p*′-diaminodiphenyl)ethane
	Dibenzalnaphthalenediamine	*p*, *p*′-Dimethoxydibenzal-1, 4-naphthalenediamine
	Carboxylic acids (double molecule)	*p*-Butylbenzoic acid (double molecule)
	Diphenylpyridazine	*p*, *p*′-Butyldiphenylpyridazine
	Dibenzalcyclopentanone	*p*, *p*′-Diethoxybenzalcyclopentanone
	Unsymmetrical molecules	
$-CH{=}N-$	Benzalaniline	*p*-(*p*-Cyanobenzal)anisidine
 $-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-$	Phenyl ester of benzoic acid	*p*-(*p*-Methoxybenzoxy)benzoic acid
 $-\overset{\mathrm{O}}{\overset{\|}{\mathrm{N}}}-\mathrm{N}-$	Azoxybenzene	*p*-Azoxyanisole
	Benzal-*p*-aminoazobenzene	Anisal-*p*-aminoazobenzene
	Benzal-1-aminonaphthalene-4-azobenzene	Anisal-1-naphthylamino-4-azobenzene

TABLE 4

Composition of end group in aromatic type molecules showing the mesomorphic state



y = End Group	Type	y = End Group	Type
$CH_3(CH_2)_n$—	Normal alkyl	$CH_3(CH_2)_nOCO$—	Carboxylic acid ester
$(CH_3)_2CH(CH_2)_n$—	Branched alkyl	$CH_3(CH_2)_nCOO$—	Phenol acid ester
$CH_3(CH_2)_nO$—	Alkoxy	CN—	Cyano
$CH_3O(CH_2)_nO$—	Oxygen-broken alkoxy	NO_2—	Nitro
Cl, Br, I	Halogen	NH_2—	Amine, substituted amine

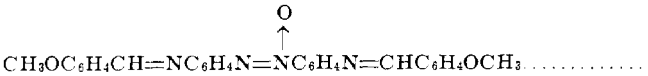
TABLE 5

Effect of atomic grouping on crystal-nematic and nematic-liquid points

Change in arrangement of unsymmetrical end groups

Compound*	Crystal-Nematic Point	Nematic-Liquid Point
	°C.	°C.
$C_6H_5C_6H_4CH{=}NC_6H_4OCH_3$	186	176
$CH_3OC_6H_4CH{=}NC_6H_4C_6H_5$	161	177
$CH_3COOC_6H_4CH{=}NC_6H_4OCH_3$	112	128
$CH_3OC_6H_4CH{=}NC_6H_4OCOCH_3$	81.5	108
$CNC_6H_4CH{=}NC_6H_4OC_2H_5$	115	132
$C_2H_5OC_6H_4CH{=}NC_6H_4CN$	105	124

Change in arrangement of central group

Compound*	Crystal-Nematic Point	Nematic-Liquid Point
	°C.	°C.
 $CH_3OC_6H_4CH{=}NC_6H_4N{=}\overset{\overset{O}{\uparrow}}{N}C_6H_4N{=}CHC_6H_4OCH_3$	185	292
 $CH_3OC_6H_4N{=}CHC_6H_4N{=}\overset{\overset{O}{\uparrow}}{N}C_6H_4CH{=}NC_6H_4OCH_3$	226	>295
$CH_3C_6H_4CH{=}NC_6H_4N{=}NC_6H_4N{=}CHC_6H_4CH_3$	190	285
$CH_3C_6H_4N{=}CHC_6H_4N{=}NC_6H_4CH{=}NC_6H_4CH_3$	228	>297
$CH_3OC_6H_4CH{=}NC_6H_4N{=}NC_6H_4N{=}CHC_6H_4OCH_3$	220	>300
$CH_3OC_6H_4N{=}CHC_6H_4N{=}NC_6H_4CH{=}NC_6H_4OCH_3$	257	>340

* All benzene rings are joined in the para position.

3. Effect of polarity of end group on the nematic-liquid point; effect of change of central group on the nematic-liquid point

For any given basic molecular structure it is generally found that an increase in the polarity of the end groups decreases the N-L point. An exception to this is found in the case where the central group is a carboxyl group. The polarity of the central group, keeping the end groups fixed, also influences the N-L point of the compound. At present it is not proper to make a sweeping statement about polarity of the central group versus N-L point. Factors (e.g., resonance) other than polarity enter into the structural features of the molecule.

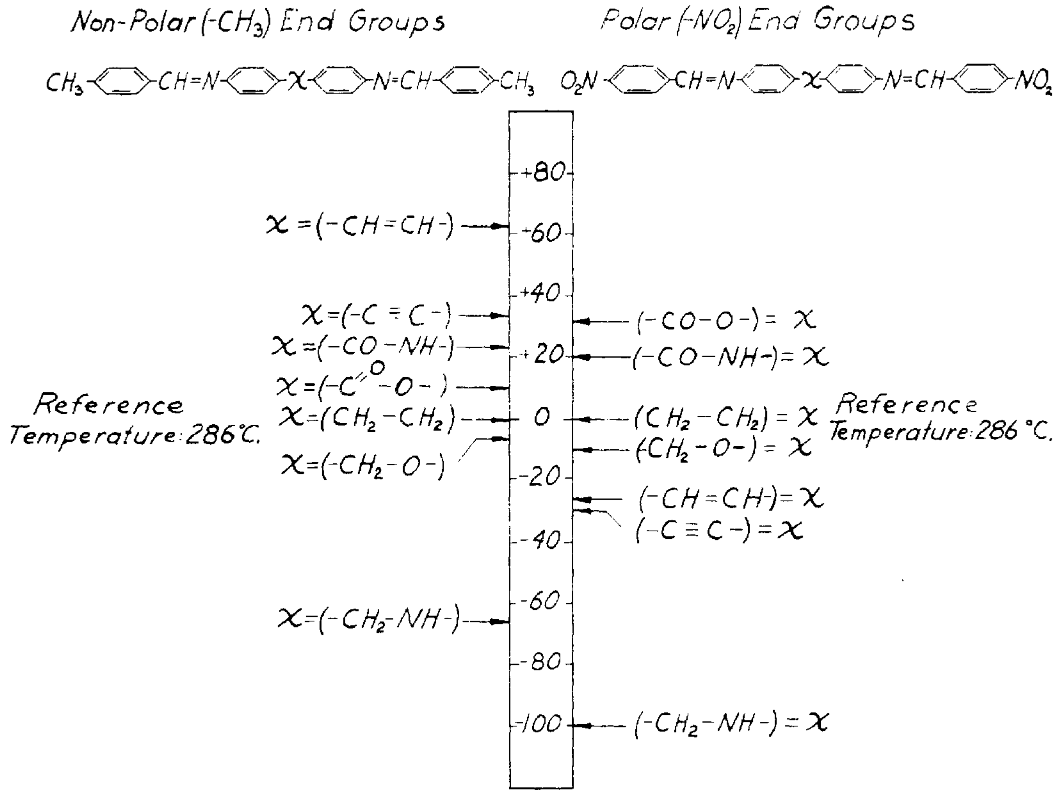
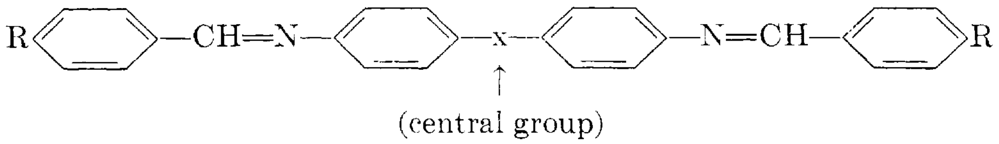


FIG. 16. Effect of polarity of end group on the nematic-liquid point; effect of change of central group on the nematic-liquid point.

Assembled in figure 16 are the N-L points of a series of compounds fashioned around the basic structure:



The end groups (R) in one case are nonpolar and in the second case polar. An illustration of the change in the N-L point with a change in the central grouping for a fixed set of end groups can also be observed in figure 16. This aspect of the central grouping is discussed further in the next section.

4. Changes in molecular structure

This section deals with compounds that exhibit both the nematic and the smectic structures. It presents examples of investigations that have been made in which the researchers have carried out systematic studies (*a*) on the change of the C-M, S-N, S-L, or N-L point in a homologous series, (*b*) on the effect of the change of the central group in a molecule on the C-M and N-L points, and (*c*) on the influence of the kind and number of substituents on an aromatic nucleus on the mesomorphic character. The examples given here are in some

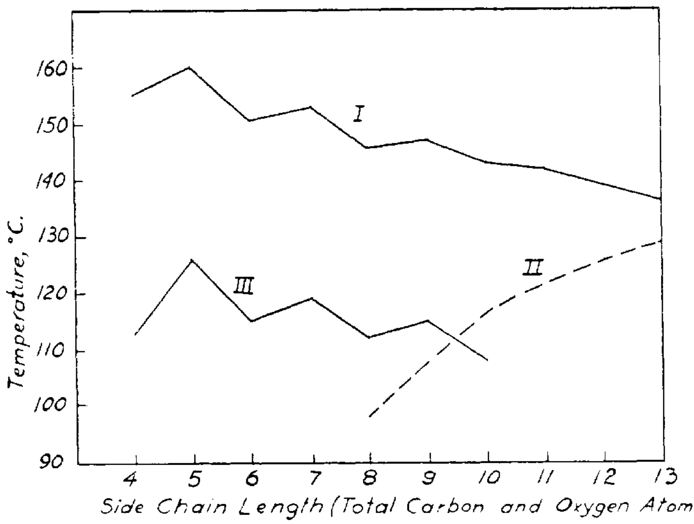


FIG. 17. Nematic-liquid and smectic-nematic points versus side-chain length for the *p*-*n*-alkoxybenzoic acids and the nematic-liquid points for the *p*-*n*-alkylbenzoic acids. Curve I, N-L points for the *p*-*n*-alkoxybenzoic acids (Gray and Jones (151)). Curve II, S-N points for *p*-*n*-alkoxybenzoic acids (Gray and Jones (151)). Curve III, N-L points for *p*-*n*-alkylbenzoic acids (Weygand and Gabler (450)). 4 = *n*-butyl, 5 = *n*-amyl, etc. for alkyl groups and 4 = *n*-propoxy, 5 = *n*-butoxy, etc. for alkoxyl groups.

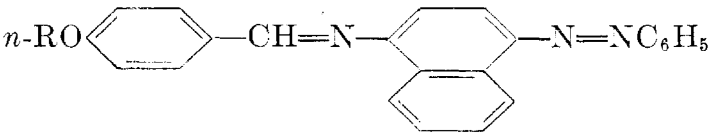
cases the only ones available, while in other cases other examples could be cited. All of the studies attempt to relate mesomorphism with molecular structure.

(a) Molecular structure and the nematic structure; homologous series that represent both nematic and smectic structures—only one end group of the molecule changes

The alkylbenzoic acids and the alkoxybenzoic acids furnish an interesting series of compounds for comparison of the effect of change of C-M and N-L points in a homologous series. Effect of the change of the end groups on transition temperatures can also be observed in these series. These series of compounds represent both the nematic and the smectic structures. Vorländer considered the benzoic acid derivatives as representative smectic type compounds. In figure 17 the N-L points of the benzoic acid derivatives are plotted against the chain lengths of the alkyl or alkoxy groups. Also included in figure 17 is the plot of the S-N points versus chain length. It is noted that for the lower-molecular-weight members of the series the apices in the curves I and III occur at the odd-numbered chain members and that the curves tend to flatten out as the molecules become larger. The data for the alkylbenzoic acids are from Weygand and Gabler (450), while those for the alkoxybenzoic acids are from Gray and Jones (151). The general slope of curves I and III is negative; the general slope of curve II is positive. Both of these plots are representative of most homologous series that have been studied.

A homologous series (451) which shows a pronounced regularity when the

N-L points are plotted against the length of the end chain is that of the benzalnaphthylaminoazobenzene compounds,



The N-L points alternate regularly and equally strong between 85° and 100°C.; no increasing or decreasing tendency is noticed. Branching of R will lower the N-L point; the isopropyl derivative, for example, has an N-L point of 11°C. compared to 88°C. for the normal compound. In the case of the isoamyl derivative the N-L point is 78°C., which is close to that of the *n*-amyl derivative (89°C.).

Some of these benzalnaphthylaminoazobenzene compounds show unusual properties in retardations in the transformations from crystalline solid to true liquid and vice versa. For example, the isobutyl derivative melts at 106°C. and will solidify glass-clear if kept at its melting point for a long period of time and then cooled rapidly to 0°C. This glass-clear product is stable for several days if kept at 0°C. As the glass-like material is warmed to 16°C. it becomes cloudy after several minutes at this temperature and changes into the mesomorphic state. The mesomorphic state clears sharply at 22°C. This transformation takes place in the range of the supercooled melt.

(b) Comparison of end groups with an equal number of links but with different kinds of atoms

The compounds chosen to illustrate this comparison are the *p*-alkoxybenzal-*p*-alkoxyanilines. These compounds were studied by Weygand and Gabler (448). The results of their studies are summarized in table 6. Some of the phase transformations illustrated in table 6 are carried out in the supercooled melts, as can

TABLE 6

Transition temperature of p-alkoxybenzal-p'-alkylanilines, p-alkoxybenzal-p'-alkoxyanilines, p-(p-alkoxy)alkoxybenzal-p'-(p'-alkoxy)alkoxyanilines, and p-(p-alkoxy)alkoxybenzal-p'-alkylanilines

Weygand and Gabler (448)

Compound	Crystal-Mesomorphic Point*	Smectic Transitions		Nematic-Liquid Point
	°C.	°C.	°C.	°C.
n-$C_9H_{19}OC_6H_4CH{=}NC_6H_4CH_3$ (I)	73	74	70	76
n-$C_9H_{19}OC_6H_4CH{=}NC_6H_4CH_2CH_3$ (II)	65	77	74	—
n-$C_9H_{19}OC_6H_4CH{=}NC_6H_4OCH_3$ (III)	108	—	—	96
n-$C_9H_{19}OC_6H_4CH{=}NC_6H_4CH_2CH_2CH_3$ (IV)	51	84	79	—
n-$C_9H_{19}OC_6H_4CH{=}NC_6H_4OCH_2CH_3$ (V)	101.5	84	79	115
n-$C_3H_7OC_6H_4CH{=}NC_6H_4OC_3H_7$-*n* (VI)	133	—	—	107
$CH_3OCH_2OC_6H_4CH{=}NC_6H_4OCH_2OCH_3$ (VII)	47	—	—	—
n-$C_4H_9OC_6H_4CH{=}NC_6H_4OCH_2CH_3$ (VIII)	105.5	—	—	129.5
$CH_3CH_2OCH_2OC_6H_4CH{=}NC_6H_4OCH_2CH_3$ (IX)	64	—	—	—
n-$C_3H_7OC_6H_4CH{=}NC_6H_4OCH_2CH_3$ (X)	125	—	—	123.5
$CH_3OCH_2OC_6H_4CH{=}NC_6H_4OCH_2CH_3$ (XI)	80.5	—	—	—

* Applies to the melting point where mesomorphism is not present.

be seen by the temperatures for some of the transitions. Compounds IV and V have two smectic forms with transformation points at the same temperatures of 84° and 79°C. Compound V also has an N-L point at 115°C. In the next lower homologs, compound II has two smectic transitions at 77°C. and 74°C., while compound III has lost its smectic properties but does have an N-L point at 96°C. Figure 18 diagrammatically represents these observations and includes the theoretical N-L points for compounds II and IV.

If this structure is altered by replacing the alkyl of the alkoxy group in the *p*-alkoxybenzal-*p*-alkoxyanilines with an ether (i.e., RCH_2CH_2O— with $ROCH_2O$— or $ROCH_2CH_2OCH_2$—) the N-L point will be lowered, or the mesomorphic structure disappears entirely. Data from Weygand, Gabler, and Bircon (452) to illustrate this fact are given in table 6. For comparison, observe the pairs VI and VII, VIII and IX, and X and XI. For example, compounds VI and VII have the same number of carbon atoms in the side chains but compound VII does not exhibit a nematic structure.

(c) Effect of central group on crystal-mesomorphic, smectic-nematic, smectic-liquid, and nematic-liquid points; change of nematic-liquid point in the homologs of a series

The first series of compounds chosen for this illustration are the azoxyphenol, azophenol, and azomethinephenol ethers studied by Weygand and Gabler (446, 449). The C-M and N-L points are given in table 7.

The N-L points for the azophenol ethers and the azomethinephenol ethers are obtained by melting the compounds and then slowly cooling them. All plots of chain length versus the N-L point of the azoxy-, azo-, and azomethinephenol ethers give curves with apices at the odd-numbered chain lengths (even number

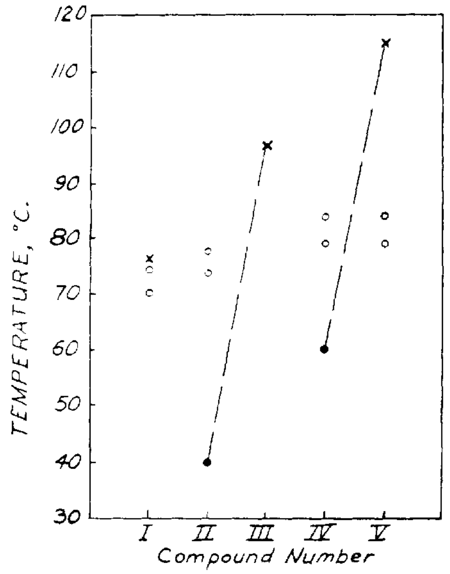


FIG. 18. Transformation points for some *p*-*n*-alkoxybenzal-*p'*-alkylanilines and *p*-alkoxybenzal-*p'*-alkoxyanilines (Weygand and Gabler (448)). × = nematic points; ○ = smectic points; ● = theoretical nematic points.

TABLE 7

Equilibrium temperatures and phase transitions for the azoxyphenol, azophenol, and azomethinephenol ethers

Weygand and Gabler (446, 449)

Side-chain length: 2 = methoxy, 3 = ethoxy, 4 = *n*-propoxy, etc.

Side-Chain Length	Azoxyphenol Ethers			Azophenol Ethers			Azomethinephenol Ethers	
	C-M point	N-L point	S-N or S-L point	C-M point	N-L point	S-N or S-L point	C-M point	N-L point
	°*C.*	°*C.*	°*C.*	°*C.*	°*C.*	°*C.*	°*C.*	°*C.*
2	116	134	—	165	(110)	—	146	99
3	134	168	—	159	150	—	149	143
4	116	122	—	146	(112)	—	133	(107)
5	107	134	—	135	124	—	125	121
6	82	119	—	113	108	—	113	105
7	81	127	72	102	114	—		
8	74	122.5	92	102	109	97		
9	76	124.5	106	98	—	—		
10	77	121	113	103	107	99		
11	78	123	119.5	106	—	107		
12	78	—	120.5					
13	82	—	122					

of carbon atoms). As is generally observed, the maximum differences in the N-L points are with the lower-molecular-weight compounds and this difference decreases as the molecular weight increases.

A plot of N-L, S-N, and S-L points versus number of linked atoms in the end groups is shown in figure 19 for the azoxyphenol ethers, alkoxybenzoic acids, alkoxycinnamic acids, and alkoxyazines (361, 446). Note that the N-L point curves are all similar and that the S-N and S-L point curves take on a positive slope for all the series except the alkoxyazines. For example, in the case of the azoxyphenol ethers the slope of the smectic line is positive, while with the alkoxyazines the slope is negative (or perhaps zero). The smectic curve for the azophenol ethers is the more general type. In both cases the N-L point and S-N and S-L point curves approach each other, and in the higher homologs no nematic structure is observed.

Mention should be made of the work of Gray, Hartley, Ibbotson, and Jones (149) on mesomorphism and the chemical constitution of certain mono- and dianils of the benzene, biphenyl, fluorene, and fluorenone series. Data in table 8 represent mesomorphism versus chemical constitution for the monoanils and dianils of *p*-(*n*-alkoxy)benzylideneamino derivatives of biphenyl, fluorene, and fluorenone. The data show the change of the transformation temperatures with change in the central structural group.

For the monoanils the average transition temperatures indicate the order of decreasing thermal stability, with respect to both structures (nematic and smectic), to be fluorene, biphenyl, fluorenone. In the case of the dianils the order is biphenyl, fluorene, and fluorenone. The authors (149) attribute the differences within the monoanil and dianil types and between the two types to such factors as molecular geometry and polarizability. These workers attempt to relate the

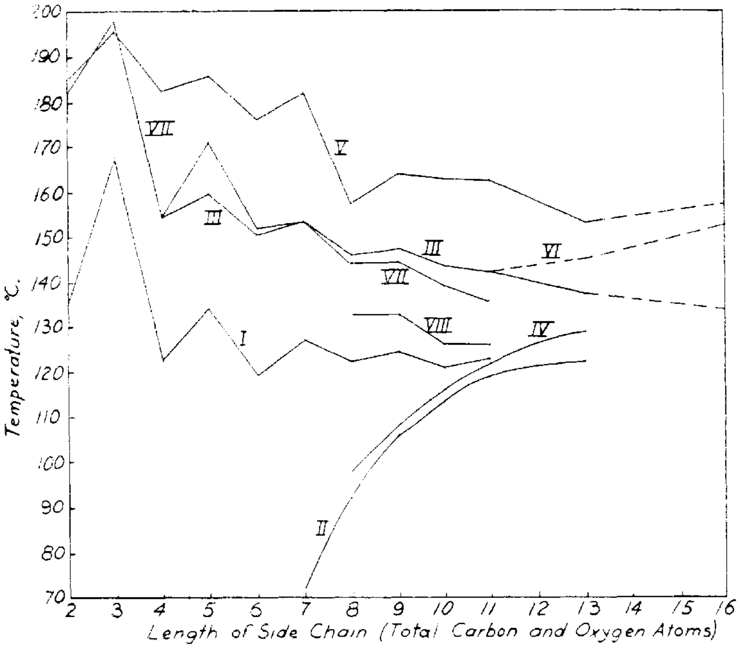


FIG. 19. Smectic-nematic, smectic-liquid, and nematic-liquid points versus side-chain length for azoxyphenol ethers, alkoxybenzoic acids, alkoxycinnamic acids, and alkoxyazines. Curve I, N-L points for *p*-azoxyphenol ethers (Weygand and Gabler (450)). Curve II, S-N or S-L points for *p*-azoxyphenol ethers (Weygand and Gabler (449)). Curve III, N-L points for *p*-*n*-alkoxybenzoic acids (Gray and Jones (151)). Curve IV, S-N points for *p*-*n*-alkoxybenzoic acids (Gray and Jones (151)). Curve V, N-L points for *p*-*n*-alkoxycinnamic acids (Störmer and Wodary (375)) and Bennett and Jones (13)). Curve VI, S-N points for *p*-*n*-alkoxycinnamic acids (Bennett and Jones (13)). Curve VII, N-L points for *p*-*n*-alkoxyazines (Shaw (361)). Curve VIII, S-N points for *p*-*n*-alkoxyazines (Shaw (361)). 2 = methoxy, 3 = ethoxy, etc.

TABLE 8

Transition temperatures of mono- and dianils of fluorene, fluorenone, and biphenyl

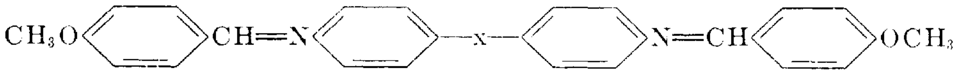
Gray, Hartley, Ibbotson, and Jones (149)

Average transition temperature (°C.) (C_7–C_{10} end group)	Monoanils from				
	Fluorene		Biphenyl		Fluorenone
Smectic to nematic structure	166°	$\xrightarrow{10.6°}$	155.4°	$\xrightarrow{82.1°}$	73.3°
Nematic to true liquid structure	186.4°	$\xrightarrow{24.5°}$	161.9°	$\xrightarrow{22°}$	139.9°

Average transition temperature (°C.) (C_7–C_{16} end group)	Dianils from				
	Biphenyl		Fluorene		Fluorenone
Smectic to nematic structure	313°	$\xrightarrow{16.2°}$	296.8°	$\xrightarrow{43.2°}$	253.6°
Nematic to true liquid structure	345°	$\xrightarrow{24°}$	321°	$\xrightarrow{24.2°}$	296.8°

TABLE 9

Effect of change of the central group of dianisalbenzidine on the crystal-nematic and nematic-liquid points



x	Crystal-Nematic Point	Nematic-Liquid Point	x	Crystal-Nematic Point	Nematic-Liquid Point
	°C.	°C.		°C.	°C.
No group or atom	253	>345	$-OCH_2CH_2O-$	209	298
$-CH_2-$	Not liquid-crystalline		$-NHCH_2CH_2NH-$	187	241
$-CH_2CH_2-$	171	312	$-COOCH_2CH_2OCO-$	183	197
$-CH_2CH_2CH_2-$	Not liquid-crystalline		$-OCOCH_2CH_2COO-$	183	266
$-CH_2CH_2CH_2CH_2-$	156	270	$-C_6H_4-$	290	320
$-CH_2CH_2CH_2CH_2CH_2-$	Very small liquid crystallinity		$-O-$	Not liquid-crystalline	
$-CH{=}CH-$	230	>360	$-S-$	Not liquid-crystalline	
$-C{\equiv}C-$	235	251	$-NH-$	239	<239
$-CH_2O-$	209	298	$-Hg-$	209	285
$-\underset{\underset{O}{\|}}{C}-O-$	206	>310			

mesomorphic character of these compounds to recent interpretations of the structure of fluorene and fluorenone.

The effect of change of the central group between the central benzene nuclei of dianisalbenzidine was studied by Vorländer. His findings, presented in table 9, are compiled from his many papers on liquid crystals (for example, 431). A complete bibliography of Vorländer's works is included in a memoir to him written by Weygand (445).

Vorländer (432) made a comparable study of a large number of derivatives of $C_6H_5CH{=}NC_6H_4xC_6H_4N{=}CHC_6H_5$. The central groups studied in this series were comparable to those given in table 9 and the results were similar. The structural influence of different groups on the end phenyl groups was also discussed.

5. *Influence of substituents in certain molecules on the mesomorphic character; position of attached side groups*

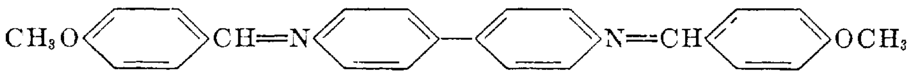
The work of Wiegand on dianisalbenzidine and its derivatives illustrates the effect of substitution into different positions of the diphenyl portion of the molecule. Table 10 summarizes the findings of Wiegand (456).

Gray and Jones (152) have made a study of the mesomorphism and constitution of *n*-alkoxynaphthoic acids. They found for the unsubstituted alkoxynaphthoic acids that the 4- and 5-*n*-alkoxy-1-naphthoic acids and the 7-*n*-alkoxy-2-naphthoic acids exhibited no mesophases, whereas the 6-*n*-alkoxy-2-naphthoic acids are mesomorphic. They attributed these characteristics to the fact that the 5,1 and 7,2 acids are not rod-shaped, since the axes of the carboxyl and alkoxy groups are not in line. This is especially true when the dimer is con-

TABLE 10

The effect of substituents on mesomorphic character of the dianisalbenzidine derivatives

Wiegand (456)



Compound	Crystal-Nematic Point	Nematic-Liquid Point
	°C.	°C.
Dianisalbenzidine	252–253	>345
2,2′-Dichlorodianisalbenzidine	215–216	320–321
3,3′-Dichlorodianisalbenzidine	148–149	>340
2,2′,6,6′-Tetrachlorodianisalbenzidine	217–219 (m.pt.)	None
2,2′-Dimethyldianisalbenzidine	172–173	307–308
3,3′-Dimethyldianisalbenzidine	180–181	353
2,2′,6,6′-Tetramethyldianisalbenzidine	212–213 (m.pt.)	None

sidered. The 4,1 acid is essentially linear but is also very broad. Also, if a dimer forms, the two naphthalene rings may cause such imbrication in the molecule that the closest packing in the crystal lattice is not one in which the molecules lie parallel. Mesomorphism of the 6,2 acid is to be expected, since the individual molecule and the dimer are both long and rod-shaped.

Substituents in the alkoxybenzoic acids and the 6-alkoxy-2-naphthoic acids influence the mesomorphism of these acids. Gray and Jones (150, 152a) studied the *m*-alkoxybenzoic acids and the α-6-alkoxy-2-naphthoic acids. The results of their findings are summarized in table 11. In the alkoxybenzoic acids the bromo and nitro derivatives do not show mesomorphism. Among the various facts to be noted in table 11 is that with an increase in the size of the halogen atom, the smectic structure appears at a greater length of the side chain.

The position of the dianisal groups in the naphthalene nucleus in dianisalnaphthyldiamines determines whether the compounds are mesomorphic in character. Wiegand (457) found the results summarized in table 12.

Those molecules that are rod-shaped or most nearly rod-shaped are mesomorphic in character, while those that are not rod-shaped do not possess liquid crystallinity.

Work on the *p*-alkoxycinnamic acids and their halogen derivatives will be mentioned. Störmer and Wodary (375) found that the allocinnamic acids did not show mesomorphism, while the trans stable form gave the mesomorphic structure. Bennett and Jones (13) studied these same cinnamic acids extensively and reached the same conclusion concerning mesomorphism.

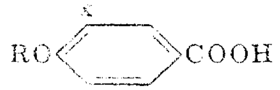
In the study of cis and trans isomers the work of Weygand and Lagendorf (454) on the *cis*- and *trans*-1,2-dibenzoylethylenes should be noted. The effect of halogen substitution on the mesomorphism of the *trans*-*p*-(*n*-alkoxy)cinnamic acids has been studied very recently by Gray, Jones, and Marson (153). It was found that the chloro- and bromo-*trans*-4-*n*-alkoxy-3-halogenocinnamic acids showed mesomorphism but with less of a mesomorphic transition temperature than the comparable *p*-(*n*-alkoxy)cinnamic acids. The iodine derivatives were found to be nonmesomorphic. The plots of the mesomorphic transition tem-

TABLE 11

Influence of substituents on the mesomorphism of alkoxybenzoic acids and 6-alkoxy-2-naphthoic acids

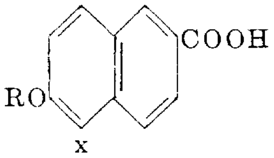
Gray and Jones (150, 152a)

Alkoxybenzoic acids,



x	Length of n* at First Appearance of				
	Nematic structure	Smectic structure	Smectic structure only	Maximum phase length	Value of n* at maximum phase lengths
				°C.	
H	3	7	18	57	10
F	8	9	16	16	16
Cl	8	8	—	4.5	16

6-Alkoxy-2-naphthoic acids,



x	Length of n* at First Appearance of				
	Nematic structure	Smectic structure	Smectic structure only	Maximum phase length	Value of n* at maximum phase lengths
				°C.	
Cl	3	6	16 and 18	42	6
Br	3	7	16 and 18	40	7
I	4	8	16 and 18	25	8
NO_2	9	12	—	1.5	10

* n = number of carbon atoms in alkoxy side chain.

TABLE 12

Molecular structure versus mesomorphism of the dianisalnaphthyldiamines

Wiegand (457)

Compound	Crystal-Nematic Point	Nematic-Liquid Point
	°C.	°C.
Dianisal-1,4-naphthylenediamine	182.5–184	262–263
Dianisal-1,5-naphthylenediamine	196	282.5
Dianisal-2,6-naphthylenediamine	188.5–189.5	354–356
Dianisal-1,7-naphthylenediamine	142–143 (m.p.)	None
Dianisal-2,5-naphthylenediamine	133–134 (m.p.)	None
Dianisal-2,7-naphthylenediamine	204–206 (m.p.)	None

peratures of the chloro-substituted *trans-p-(n-*alkoxy)cinnamic acids versus the length of the side chain are given in figure 20. Mesomorphism does not show up in these substituted acids until the hexoxy derivative. With unsubstituted *trans-p-(n-*alkoxy)cinnamic acids the methoxyl group shows mesomorphism. A comparison of the average temperature change of mesomorphic transitions

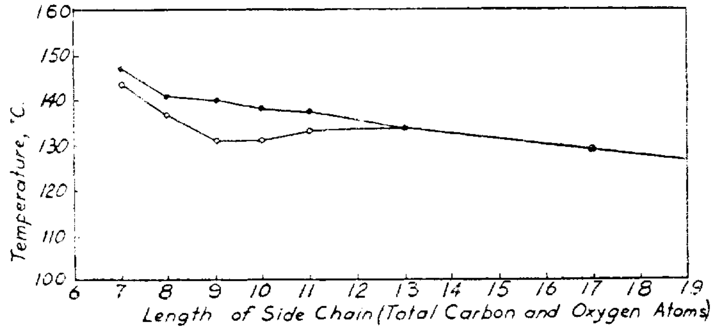


FIG. 20. Smectic-nematic, smectic-liquid, and nematic-liquid points versus chain length for the *trans*-4-*n*-alkoxy-3-chlorocinnamic acids (Gray, Jones, and Marson (153)). ● = nematic points; ○ = smectic points. 2 = methoxy, 3 = ethoxy, 4 = *n*-propoxy, etc.

TABLE 13

Temperature changes of mesomorphic transitions of certain trans-alkoxycinnamic acids

Gray, Jones, and Marson (153)

3-Substituent in the *p*-(*n*-alkoxy)cinnamic acids	H	Cl	Br
Average mesomorphic-liquid transition temperature, °C. (C_{12}–C_{18})	160.5°	129.8°	123.8°
Decrease in transition temperature from unsubstituted acid		30.7°	36.7°

through substitution in the 3-position of the *trans*-alkoxycinnamic acids is given in table 13.

Gray, Jones, and Marson attribute the decrease in thermal stability when chlorine was substituted for hydrogen to two factors: first, the C—Cl dipole will increase the molecular polarization and the mesomorphic thermal stability, and secondly, the increase in molecular breadth due to the chlorine atom will increase the molecular separation, weaken the intermolecular forces maintaining the molecular orientation in the mesomorphic structure, and decrease the thermal stability. Bromine gave a slightly greater decrease than chlorine and with iodine the mesomorphism disappeared. The authors compare their findings on the *trans*-*p*-(*n*-alkoxy)cinnamic acids with their findings on the halogen derivatives of the alkoxynaphthoic and alkoxybenzoic acids. The results are comparable.

Vorländer (434) discussed the esters of both simple and complex alcohols and of the saturated phenyl fatty acids and saturated aliphatic mono- and dicarboxylic acids, esters of unsaturated carboxylic acids, and diphenyl paraffins. There is a collection of transformation temperatures for a large number of members of different homologous series of these different classes of compounds. Transition temperatures and chain length of the end groups are related.

6. Convergence of smectic and nematic curves

In a number of homologous series that have been studied it has been found that the S-N and S-L, and N-L points tend to converge at some high homolog of the series. Figures 19 and 20 represent this property. The S-N and S-L, and

N-L points versus length of side chain for *p*-azoxyphenol ethers, *p*-(*n*-alkoxy)-benzoic acids, and *p*-(*n*-alkoxy)cinnamic acids are plotted in figure 19. Figure 20 represents the S-N and S-L, and N-L points for the *trans*-alkoxy-3-chlorocinnamic acids. In all cases it can be seen that the smectic and nematic curves tend to converge. The reader is referred to Weygand and Gabler (451) for further discussion and illustrations of the convergence of plots of S-N and S-L, and N-L points versus length of side chain.

B. THE CHOLESTERYL COMPOUNDS; POSITION AND NUMBER OF DOUBLE BONDS

Wiegand (455) studied the relationship between spatial structure and the mesomorphic character of cholesteryl derivatives. The basic structures which he considered are given in figure 21. His results are summarized in table 14.

Also, Wiegand (455) compared the C-N and N-L points for the different positions of the double bond in cholesteryl benzoate and the different positions of pairs of double bonds in cholestadienyl benzoate. The results of his findings are summarized in table 15. The numbering of positions in the molecules is the same as in figure 21.

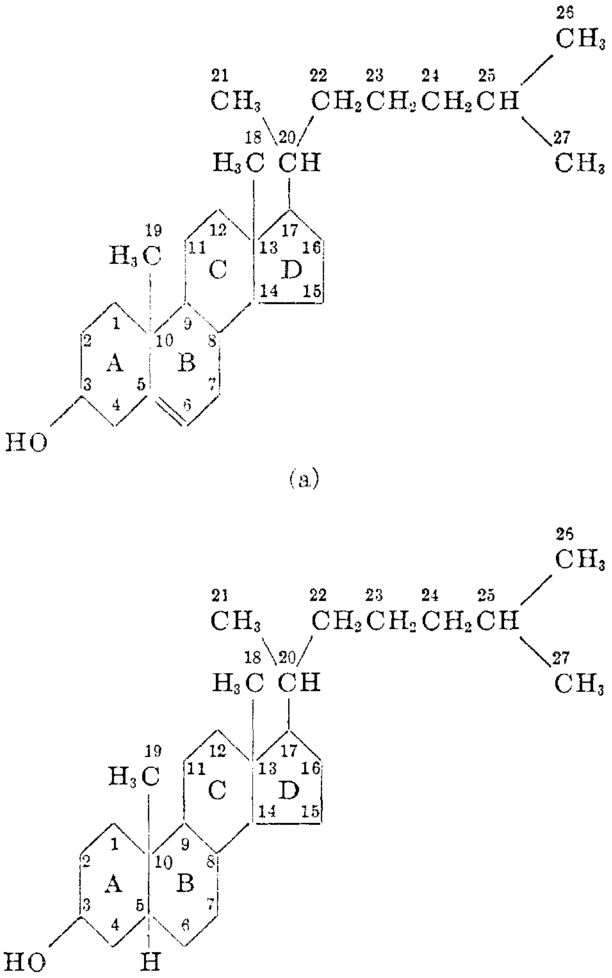
C. ALIPHATIC COMPOUNDS OF MESOMORPHIC CHARACTER

The list of aliphatic compounds that exhibit the mesomorphic structure is not nearly so large as that of the aromatic type. The monocarboxylic aliphatic acids and their salts are the compounds of this type that have been studied most extensively. Other aliphatic compounds such as esters and alcohols are to be found listed in tables in *International Critical Tables* (96) and Landolt-Börnstein (210). The aspects of the polymesomorphism of these compounds have been summarized by Weygand (443) and are briefly reviewed in Section X,H in this article.

The monocarboxylic aliphatic acids have been studied in some detail. The simplest aliphatic compound that exhibits mesomorphism is 2,4-nonadienoic acid (453). This compound has a C-N point of 23°C. and an N-L point at 49°C. In this same paper 2,4-undecadienoic acid, which has a C-N point at 32°C. and an N-L point at 58°C., is described (453).

Vorländer (429) concerned himself with the study of the sodium salts of a number of monocarboxylic acids, while Lawrence (214) reported on the ammonium salts of a number of these same acids. The changes in the mesomorphic state are reproducible but are often missed if the rate of heating is too fast. Vorländer's work on the salts of the monocarboxylic acids was not very critical, as can be seen from the work of Nordsieck, Rosevear, and Ferguson (299) on the transition points of anhydrous sodium palmitate.

The differences in refractive index and viscosity in the mesomorphic region of anhydrous salts are often quite small. The transition temperature is independent of the chain length but defined by the nature of the cation. Vold and Vold (425) as well as Vold, Rosevear, and Ferguson (423) showed that sodium palmitate passes through five states when the crystals are heated to the liquid. A somewhat



(a)

(b)

Fig. 21. Numbering of cholesterol and cholesteryl derivatives: (a) cholesterol; (b) cholestanol, rings A-B trans, OH in β-position; epicholestanol, rings A-B trans, OH in α-position.

TABLE 14

Relationship between spatial structure and mesomorphic character of cholesteryl derivatives

Wiegand (455)

Ester	Cholesterol		Cholestanol		Epicholestanol	
	Crystal-nematic point	Nematic-liquid point	Crystal-nematic point	Nematic-liquid point	Crystal-nematic point	Nematic-liquid point
	°C.	*°C.*	*°C.*	*°C.*	*°C.*	*°C.*
Benzoyl	149–150	178	136.5–137	155	104–105	No nematic structure
Anisyl	162.5–163	236	160–160.5	239	104.5–106	No nematic structure
4-Phenylbenzoyl	177–179	290	171–172	291	115–117	No nematic structure
4-Toluyl	179.5-180.5	241	171.5–172.5	225	91.5–92.5	No nematic structure
2-Toluyl	120–121	133	122–123	(108)	96–98	No nematic structure

TABLE 15

Effect of location of double bonds in cholesteryl derivatives

Wiegand (455)

Cholesteryl Benzoate			Cholestadienyl Benzoate		
Location of double bond	Crystal-nematic point	Nematic-liquid point	Location of double bond	Crystal-nematic point	Nematic-liquid point
	°C.	°C.		°C.	°C.
5, 6	149–150	178	5, 6; 7, 8	142.5–143	188
7, 8	157–158	176	6, 7; 8, 9	146	180
8, 9	147	174	7, 8; 14, 15	149–150 (m.pt.)	None
8, 14	115	140	8, 9; 24, 25	126–128	138
14, 15	169–171	None	14, 15; 24, 25	120–122 (m.pt.)	None

similar effect was found for sodium stearate by Vold, Macomber, and Vold (421), but Stainsby, Farnand, and Puddington (368) found fewer phases when using rigorously anhydrous conditions. Mesomorphic states have been termed waxy, neat, and middle soap, with the prefixes "super" and "sub" being applied when subdivisions of these phases have been distinguished.

Wirth and Wellman (463) have detected definite changes in dielectric constant associated with the mesomorphic phase transitions in anhydrous sodium palmitate.

Light transmission by alkali metal stearates in the mesomorphic state has been studied recently by Benton, Howe, and Puddington (15). The plot of per cent transmission versus temperature for the alkali metal salts shows sharp breaks in the curves at different transition temperatures. Such a plot shows two types of breaks in the curves, i.e., those transitions that are abrupt and those that are manifested by a change of slope in the curves. The authors point out that the latter minor changes are much more accurately determined by the optical method of light transmission than by the usual microscopic methods. The breaks in the curves indicate phase changes, but the authors point out that the optical method used in this study may not necessarily measure true thermodynamic transition temperatures, since a change in translucency may be due to causes other than a phase transition. However, in general, the agreement between the transition temperatures obtained by this convenient optical method check well with data obtained by other, sometimes more elaborate, methods. Results for comparison of transition temperatures by different methods are given in table 16.

With the exception of 10-methylstearate, it was found that the sodium salts of the substituted stearic acids show a much greater decrease in intensity of light transmitted at the neat-liquid transition temperature than through the normal stearates.

The densities of the alkali metal stearates in the mesomorphic state and of sodium stearates having substituents in the hydrocarbon chain have been measured over a temperature range of 25–380°C. by Benton, Howe, Farnand, and Puddington (14). Discontinuities in the density–temperature relationships indicate the transitions between the various mesomorphic forms in which these soaps

TABLE 16

Transition temperatures for sodium stearate

Benton, Howe, and Puddington (15)

Transition	Temperature			
	Vold (416)	Vold (416)	Stross and Abrams (376)	Benton, Howe, and Puddington (15)
	°*C.*	°*C.*	°*C.*	°*C.*
Curd 1 - curd 2	89	90	88–96	—
Curd 2 - subwaxy	114	117	112–118	—
Subwaxy - waxy	134	132	129–130	132
Waxy - superwaxy	—	167	—	165
Superwaxy - subneat	208	205	198	188 220
Subneat - neat	238	257	243–251 271–273	258
Neat - liquid	280	288	280	283

TABLE 17

Density–temperature relationships for sodium and potassium stearates

Benton, Howe, Farnand, and Puddington (14)

Phase	Sodium Stearate		Potassium Stearate	
	Temperature	Density	Temperature	Density
	°*C.*		°*C.*	
Curd and waxy	25–130	1.00–0.93	25–165	1.02–0.92
	135–190	0.91–0.87		
Subneat	195–258	0.86–0.82	165–265	0.92–0.84
Neat	260–283	0.81–0.795	270–353	0.83–0.77
Liquid	283–310	0.795–0.78	360–380	0.78–0.77

exist. Mesomorphism is found to be much less pronounced in the substituted stearates than in the normal soaps. Illustrative data on the normal sodium and potassium stearates are given in table 17.

Other references to studies of aliphatic monocarboxylic acids and their salts may be found in Sections IX and XII.

Several authors have interpreted certain polymeric forms as being mesomorphic. The work of Bunn and Garner (47) on nylon as well as the structural studies on polyamides in general has been interpreted by Kast (197) as representing polymeric forms that show mesomorphism. Figure 22 represents Kast's interpretation of the structure of the polyamides.

D. FORMATION OF THE MESOMORPHIC STATE WITHOUT HEAT

A number of compounds are known that form the mesomorphic state when a polar compound is added. The first of these compounds observed was bromophenanthrenesulfonic acid, which was studied by Sandquist (347). Since this report many compounds such as the salts of high-molecular-weight monocarboxylic acids, salts of high-molecular-weight naphthenic acids, and high-molecular-weight sulfonic acids and their salts have been reported. These compounds are discussed in Section XII.

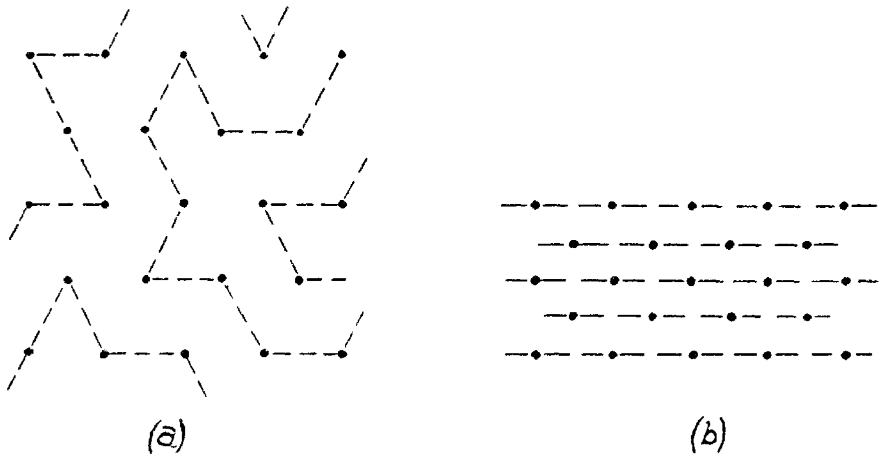


FIG. 22. Structure of polyamides: (a) smectic hexagonal structure; (b) crystalline monoclinic state.

VI. OPTICAL CONSTANTS OF THE NEMATIC STRUCTURE

p-Azoxyanisole has been the compound most studied in the measurement of optical constants of the nematic structure. The refractive index in the unoriented turbid medium cannot be measured, but the oriented state is optically clear enough to allow measurement of the two principal indices of refraction of *p*-azoxyanisole. The oriented uniaxial state can be obtained by the action of the walls of the container if the sections are thin or by the use of a moderate magnetic field. Chatelain (56) has obtained values for the refractive index of *p*-azoxyanisole at different temperatures using light of a wavelength of 546 mμ. In these studies Chatelain had his samples in thin layers between rubbed, parallel glass plates. The nematic structure behaved essentially like uniaxial crystals.

Later a prism-shaped glass container (314) was used and values of the refractive index were obtained for *p*-azoxyanisole, *p*-azoxyphenetole, and anisaldazine. The refractive indices were taken at two different wavelengths and were considered by Chatelain to be more precise than those obtained earlier. Values for the refractive index of *p*-azoxyanisole in the mesomorphic state at two different wavelengths and at different temperatures are given in table 18. The liquid at 136°C. has refractive indices of 1.644 at 589 mμ and 1.661 at 546 mμ.

The n_e was found to be much more strongly dispersed than n_0 and there was a difference in the absorption of two rays in visible light. With a layer 0.02 mm. (56) thick at 120°C. the ordinary ray was transmitted down to 422 mμ and the extraordinary ray only to 434 mμ. It can be seen that *p*-azoxyanisole in this state shows strong positive dichroism for blue light. Chatelain showed that sections up to 1 mm. thick can be prepared in an uniaxial state and that the wall action and magnetic field give exactly the same orientation effect on the molecules at a given temperature.

Recently Falgueirettes (91) made a study of the refractive indices for the nematic structure of *p*-butoxybenzoic acid. His results are summarized in table

TABLE 18

Refractive indices of p-azoxyanisole in the mesomorphic state

Pellet and Chatelain (314)

Temperature	589 mμ		546 mμ	
	n_0	n_e	n_0	n_e
°C.				
105	1.558	1.875	1.568	1.907
110	1.559	1.865	1.569	1.898
114	1.560	1.856	1.570	1.890
117	1.561	1.849	1.571	1.884
120	1.563	1.842	1.572	1.877
122	1.564	1.836	1.574	1.872
125	1.566	1.825	1.576	1.862
128	1.569	1.814	1.578	1.850
130	1.571	1.806	1.581	1.843
132	1.576	1.795	1.584	1.833

TABLE 19

Refractive indices of p-butoxybenzoic acid at different temperatures and different wavelengths

Falgueirettes (91)

Temperature	λ = 589 mμ		λ = 546 mμ		λ = 436 mμ		λ = 404 mμ	
	n_e	n_0	n_e	n_0	n_e	n_0	n_e	n_0
°C.								
143	1.619	1.449	1.627	1.452	1.663	1.465	1.684	1.472
149	1.615	1.449	1.621	1.452	1.659	1.465	1.681	1.472
153	1.606	1.450	1.614	1.454	1.652	1.467	1.674	1.474
157	1.600	1.451	1.606	1.455	1.644	1.469	1.663	1.477
159	1.591	1.453	1.598	1.456	1.632	1.472	1.651	1.480
160	1.580	1.454	1.588	1.457	1.621	1.473	1.636	1.481

19. For comparison, the liquid at 162°C. has refractive index values of 1.491 at 589 mμ, 1.495 at 546 mμ, 1.515 at 436 mμ, and 1.527 at 404 mμ.

Stumpf (378) made measurements of the refractive index of active amyl *p*-cyanobenzylideneaminocinnamate perpendicular to the optic axis and also parallel to the optic axis. Curves showing the variation of the refractive index with the wavelength of the incident light are convex to the wavelength axis; convexity becomes more pronounced as the temperature falls. This compound has the power of extremely strong elliptical polarization (about a thousand times that of quartz). The refractive indices at different wavelengths of light have been determined for ethyl *p*-ethoxybenzalamino-α-methylcinnamate and ethyl *p*-ethoxybenzalamino-α-ethylcinnamate (74). An interesting property of these compounds is that they are perfectly transparent to visible light.

The Verdet constant for the nematic structure for light travelling parallel to the optical axis apparently has not yet been measured. However, Vieth (409) found that the angle of rotation of light in a magnetic field varies markedly with the wavelength of the light. Likewise, flow birefringence of the nematic structure does not appear to have been measured.

It may also be pointed out that Kerr constants for the mesomorphic state do not appear to have been determined. However, using solutions of substances that form the mesomorphic state on heating, Tsvetkov and Marinin (405) evaluated the molar Kerr constant for the solute. For example, using benzene solutions, the molar Kerr constant for *p*-azoxyanisole was found to be 57.8, and dibenzalbenzidine gave a value of 1250.

The longitudinal depolarization of light by the nematic structure has been reported by Tsvetkov (399) and by Procopin (325). Tsvetkov avoided wall effects by adding 3 per cent methoxycinnamic acid to the *p*-azoxyanisole in the nematic structure. The depolarization, $D = \tan^2 \beta$, is complete in unoriented layers 1.25 mm. thick (the analyzer of the microscope setting for balance, with both fields black, is $\beta = 0$; in a measurement to restore balance, the analyzer must be rotated through the angle β). The depolarization of the structure decreases with increasing magnetic field strengths up to about 3000 oersteds and remains constant up to 22,000 oersteds (maximum field studied). At 3000 oersteds the depolarization is about 1 per cent. Tsvetkov studied both longitudinal and transverse magnetic fields with similar results. Procopin concluded from his studies that the size of the molecular aggregates (swarms) in the nematic structure of *p*-azoxyanisole was greater than 1 micron in diameter.

Procopin also studied beeswax and found that in the temperature range of 59° to 61°C. the beeswax depolarized light and produced high brightness in the field of observation just as *p*-azoxyanisole does in the nematic structure. Lanolin was found to depolarize light at room temperature, and it was found by Procopin (325) that this depolarizing effect decreases regularly with increase in temperature, disappearing entirely at 39°C., the melting point of lanolin.

The relationship between optical and magnetic properties of the nematic structure has been studied by a number of workers. Föex (95) found the principal magnetic susceptibilities of the solid crystals to be $\chi_1 = -0.665 \times 10^{-6}\text{g.}^{-1}$; $\chi_2 = -0.634 \times 10^{-6}\text{g.}^{-1}$; $\chi_3 = -0.408 \times 10^{-6}\text{g.}^{-1}$ with the average, $\bar{\chi} = -0.569 \times 10^{-6}\text{g.}^{-1}$ It can be seen that the solid crystal is not magnetically uniaxial; it is known that the crystal is not optically uniaxial. For the nematic structure the process of measurement orients the molecules parallel to the field, so that the quantity measured is properly $\chi_{\parallel}$. Just at the C-M point the magnetic susceptibility of the nematic structure was found by Föex to be $-0.457 \times 10^{-6}\text{g.}^{-1}$; the diamagnetic anisotropy increases as the temperature is raised, first rather rapidly, and then towards the N-L point (135°C.) discontinuously. Föex found the liquid state of *p*-azoxyanisole to have an average magnetic susceptibility value of $-0.545 \times 10^{-6}\text{g.}^{-1}$ at 134°C. and above. Tsvetkov (400) and Tsvetkov and Sosnovsky (407) developed a rotating magnetic field for the measurements of diamagnetic anisotropy of liquid crystals. The magnetic anisotropy ($\Delta\chi = \chi_{\parallel} - \chi_{\perp}$) for the oriented nematic structure was obtained for methoxycinnamic acid, *p*-azoxyanisole, *p*-azoxyphenetole, anisaldazine, *p*-acetoxybenzalazine, *p*-anisylideneaminoazobenzene, dibenzylidenebenzidine, and dianisylidenebenzidine. Tsvetkov and Sosnovsky combined their results for *p*-azoxyanisole with the value of $\chi_{\parallel}$ from Föex to obtain $\chi_{\perp}$ and $\bar{\chi}$.

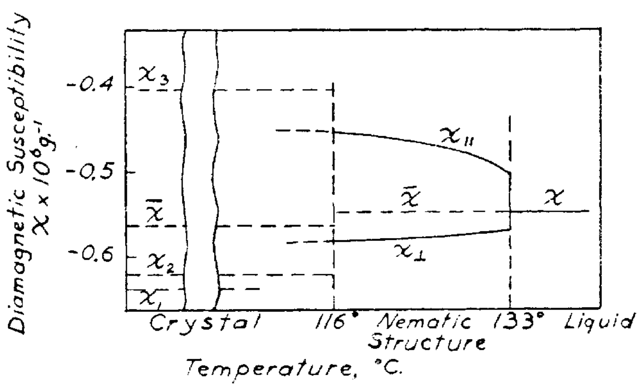


FIG. 23. Temperature dependence of diamagnetic susceptibilities of *p*-azoxyanisole in three phases (Tsvetkov (400) and Tsvetkov and Sosnovsky (407)).

The results are illustrated in figure 23. It can be seen from the figure that the magnetic anisotropy takes a sharp drop at the C-N point, gradually falls off through the range of the nematic structure, and vanishes in the liquid. Tsvetkov and Sosnovsky also showed that the magnetic anisotropy is proportional to the number of benzene rings in the molecules. Tsvetkov (402) used the data that he obtained in evaluating $\Delta\chi$ in the rotating magnetic field to obtain values of viscosity. The values obtained were found to agree with those obtained by other methods.

VII. VISCOSITY OF THE NEMATIC STRUCTURE

Schenck (353) made the first study of the viscosity of the mesomorphic state. His studies were made by the capillary-flow method and were done on cholesteryl benzoate and *p*-azoxyanisole. Both compounds showed sharp breaks at the N-L point in the viscosity versus temperature curves. Eichwold (87) found a comparable sharp break at the N-L point in the viscosity versus temperature curves for *p*-azoxyanisole, *p*-anisalazoxyphenetole, and *p*-methoxycinnamic acid. Becherer and Kast (11) studied the viscosity of *p*-azoxyanisole between 115° and 145°C. according to the Helmholtz method. Results of their findings are similar to those of Schenck, who used the capillary method. Becherer and Kast found that the viscosities versus temperature curves of the mesomorphic state and the liquid state lie on parallel straight lines and that the transition between the two lines occurs suddenly at the N-L point for *p*-azoxyanisole (135.2°C.). A plot of the data from Becherer and Kast (11) is shown in figure 24.

Bose and Conrat (35) made a study of the viscosity of anisaldazine over a temperature range of 163° to 194°C. and under conditions in which they controlled the temperature within a few tenths of a degree. The capillary-flow method used by Bose and Conrat gave results that showed a decrease in viscosity with rising temperature up to 180°C. where the viscosity was a minimum, thereafter increasing rapidly up to 182.8°C. (the N-L point) where the viscosity has its maximum value; the viscosity falls off regularly with further rise in temperature. Bose (33) studied the viscosity of anisaldazine by the capillary method under different pressures and found that Poiseuille's law holds only under small pressures.

Several investigators (22, 31, 32, 208, 312) have compared data on the viscosity of substances that exhibit the mesomorphic state with the viscosity of emulsions. All investigators present data or references to data to substantiate their conclusions. In general, the conclusions by these authors were that the mesomorphic state and emulsions show viscosity characteristics that are very similar. No attempts have been made in recent years, since the rapid growth of colloidal chemistry, to discuss the problem of relationship between the viscosity characteristics of the mesomorphic state and those of emulsions.

Several authors have discussed the viscosity of the mesomorphic state theoretically. Herzog and Kuder (163) concluded that the values for the experimentally determined viscosity could be traced to the translational and rotational motions of the swarms and reasoned theoretically from this point of view. Prior to this, Voight (413) reasoned that viscosity data that had been collected at the time of his articles gave no grounds for the swarm hypothesis. Schachenmeier (349) developed a mathematical theory for the viscosity coefficient of the mesomorphic state. It does not appear that anyone has applied the results of this study to experimental data.

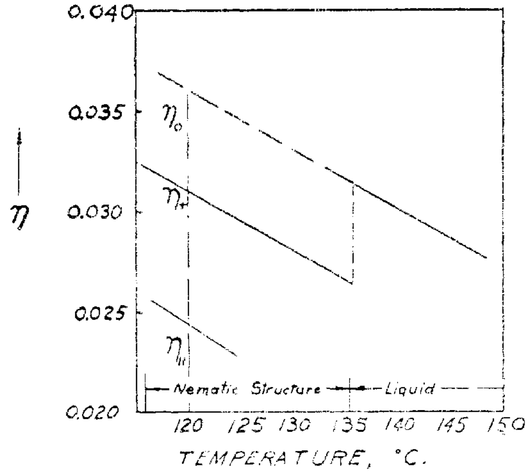


FIG. 24. Viscosity (η) of p-azoxyanisole versus temperature. The viscosity is in poises For η_0 the molecules lie arbitrary to the velocity gradient. For η_+ the molecules have their longitudinal axes in layers but the groups of molecules in the layers have arbitrary azimuth. For $\eta_{\parallel}$ the molecules stand perpendicular to the velocity gradient. $\eta_{\parallel}$ is from Eichwold (87) and η_0 and η_+ are from Becherer and Kast (11).

The most recent study of the viscosity of the mesomorphic state is by Peter (317) and Peter and Peters (318). The capillary-flow properties of p-azoxyanisole in the temperature range 119–154°C. and under the influence of shearing velocities from 60 to 18,000 cycles per second were studied. In the mesomorphic state, and under low shearing frequency, p-azoxyanisole exhibited little change in viscosity; above 10,000 cycles per second an isotropic liquid showing Newtonian flow was observed. Peter assigned a value of 2.9 kcal. per mole to the activation energy for the flow process in the mesomorphic state and a value of 5.6 kcal. per mole to the liquid. By measurement of the transmission of light, Peter established the frequency of orientation through the shearing stress in the mesomorphic state as well as the frequency of disintegration of the orientation. Both processes followed first-order kinetics. The rate constant for the orientation process was 0.8 sec.$^{-1}$ at 119°C. and at a shearing frequency of 1750 cycles per second. The disintegration constants at 119°C., 125°C., and 131°C. were found to be 0.110 ± 0.004 sec.$^{-1}$, 0.115 ± 0.007 sec.$^{-1}$, and 0.123 ± 0.005 sec.$^{-1}$, respectively. A relation between the viscosity of the nematic structure and the rate constants of the various orientation processes is deduced.

A few data are available on the viscosity of the mesomorphic state formed by the action of polar molecules on certain solids. Bastow and Bowden (7) observed the viscous flow of liquid films of 1 per cent ammonium oleate solutions; thin liquid-crystalline films showed pronounced rigidity. Other measurements of the viscosity of lyotropic mesomorphic systems are cited in Section XII; for example, see the articles by Hyde, Langbridge, and Lawrence (176) and Smith and McBain (364). Jelley (181) used spectrographic, ultramicroscopic, and streaming birefringence methods to study dispersions of 1,1′-diethyl-ψ-cyanine chloride in sodium chloride solutions and found the properties of these solutions to correspond to the nematic structure. Scheibe, Kandler, and Ecker (352) attributed the properties of these 1,1′-diethyl-ψ-cyanine chloride solutions to a reversible polymerization of the dye ions.

Powell and Puddington (323) used the capillary method of viscosity measurement to study the transition temperatures of anhydrous sodium stearate. From the viscosity data a new transition within the subneat phase was found at 225°C. and thixotropy was found over the range 211–298°C.; above 305°C. the flow is that of a Newtonian liquid.

The viscosity of mixtures of substances in the mesomorphic state has been studied by Pick (321), using mixtures of *p*-azoxyanisole and *p*-azoxyphenetole. No maximum was found on a plot of viscosity versus mole per cent of the constituents, but on the contrary the curve had a slight concave pattern.

The effect of an electrical field and of a magnetic field on the viscosity of the mesomorphic state has been studied by several different investigators. Björnstähl (23) used an oscillating-disk viscometer with connections for applying an electrical field perpendicular to the plates. The relationships between change in viscosity of *p*-azoxyanisole with change in applied voltage (both alternating and direct current) as found by Björnstähl are sketched in figures 25 and 26. *p*-Azoxyphenetole gave comparable results. Björnstähl concluded, in harmony with x-ray work by Kast, that the axis of the swarm is inclined parallel to the electrical field.

The experimental results of the effect of the perpendicular electrical field by Björnstähl have been verified by Mikhailor and Tsvetkov (283), using the capillary method; in addition, they found that a parallel electrical field reduced the time of flow when compared to a field-free capillary. Mikhailor and Tsvetkov interpreted their results as being due to a flow of the nematic structure caused by the field and not to a direct orienting effect of the field.

Björnstähl and Snellman (25), by using a simple Couette viscometer, ob-

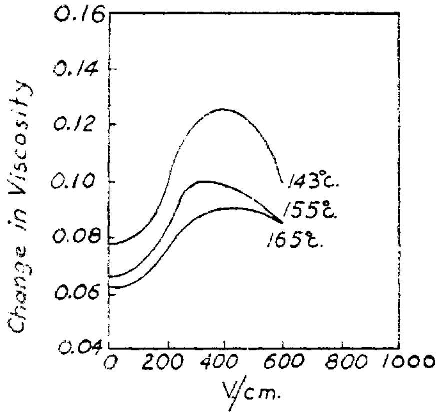


FIG. 25

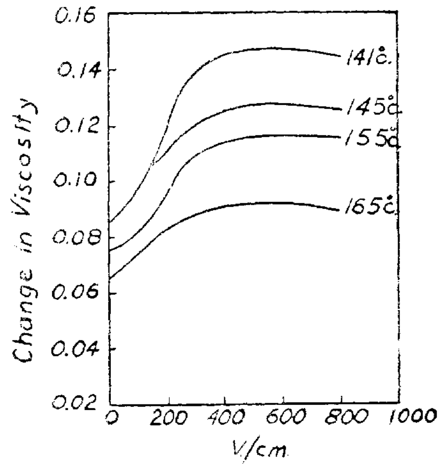


FIG. 26

FIG. 25. Change of viscosity of *p*-azoxyanisole with change in voltage (alternating current) (from Björnstähl (23)).

FIG. 26. Change of viscosity of *p*-azoxyanisole with change in voltage (direct current) (from Björnstähl (23)).

tained results showing that the increase in viscosity due to a direct electrical field was directly proportional to the square of the field strength and inversely proportional to the speed of rotation. The effect was found to be smaller with alternating fields, decreasing with increasing frequency. A plot of change in viscosity of *p*-azoxyphenetole at 145°C. against the square of the voltage of the applied field (direct current) is given in figure 27.

In a more recent study, Tsvetkov (403) concluded that an electrical field acts to orient the molecular axes parallel to the field, the effect being independent of the frequency, and secondly, that the field gives rise to a macroscopic motion of the liquid between the electrodes, diminishing with increasing frequency of the field. Tsvetkov found that in a transverse field parallel to the velocity gradient the increase in the flow time of *p*-azoxyanisole with increasing electrical field strength is smaller the higher the frequency. For direct current in a transverse field, the increase of flow time with increase in voltages takes place only above 10,000 volts per centimeter.

The first work on the effect of a magnetic field on the viscosity of the mesomorphic state was done by Neufeld (298), but his capillaries were only 0.09 mm. in diameter and the action of the field may have been impeded by the directive action of the wall of the capillary. Tsvetkov (401) found that the viscosity of *p*-azoxyanisole at 120°C. rises with the strength of the magnetic field up to about 10,000 oersteds and remains constant thereafter. Tsvetkov used values of the viscosity coefficient of *p*-azoxyanisole in a rotating magnetic field up to 2000 oersteds as a basis for his conclusion that the molecules are associated in groups with diameters of the order of 7×10^{-5} cm.

The most careful study of the effect of the magnetic field on the viscosity of the mesomorphic state was carried out by Miesowicz (280–282), whose results are summarized in table 20.

The swarms were oriented by means of a magnetic field of such a strength that the flow did not change their orientation. Tsvetkov and Michajlow (406) obtained values about 80 per cent of those obtained by Miesowicz. It appears that Tsvetkov and Michajlow did not reach the state of constant orientation of the swarms and that the flow of the liquid changed their orientation. The result is that their viscosity value lies between Miesowicz's η_1 and η_2. Becherer and Kast (11) evidently did not have constant orientation of the swarms and got viscosity values between Miesowicz's η_1 and η_3 (measurements were made parallel and perpendicular, respectively, to the direction of flow). The values obtained by Miesowicz for η_1 check those obtained by Eichwold (87); this would indicate that both were dealing with the orientation of molecules parallel to the direction of flow.

Miesowicz (282) concluded that other investigators had measured his η_1 value, which is the common value corresponding to the orientation of the molecules in the direction of flow; however, in the other values of viscosity, η_2 and

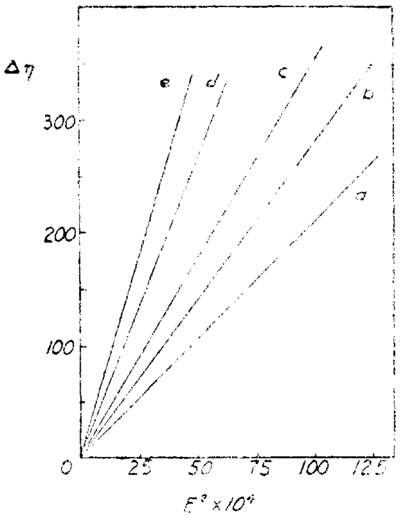


FIG. 27. Square of voltage (E) versus change in viscosity ($\Delta\eta$) of p-azoxyphenetole at 145°C The rotation velocities of the viscometer are: $a = 0.63$, $b = 0.43$, $c = 0.33$, $d = 0.20$, $e = 0.096$. From Björnstähl and Snellman (25).

TABLE 20

Viscosities of the nematic structure in the magnetic field

Miesowicz (282)

Substance and Temperature	Molecules Parallel to the Direction of Flow η_1	Molecules Parallel to the Gradient of Velocity η_2	Molecules Perpendicular to the Direction of Flow and to the Velocity Gradient η_3
p-Azoxyanisole, 122°C.	0.024 ± 0.0005	0.092 ± 0.004	0.034 ± 0.003
p-Azoxyphenetole, 144.4°C.	0.013 ± 0.0005	0.083 ± 0.004	0.025 ± 0.003

η_3, he concluded that the other investigators had not completely oriented the molecules in the nematic structure.

VIII. DIELECTRIC CONSTANT OF THE NEMATIC STRUCTURE

A. BACKGROUND OF EARLIER REVIEWS ON DIELECTRIC CONSTANT

The literature previous to 1931 has been reviewed by Lichtenecker (249) and by Kast (191). Lichtenecker gives a summary of the work on the dielectric constants of liquids and synthetic mixtures for the fifty years previous to 1926. Anisotropic systems are included in this summary. Kast gives a critical summary of the work done on liquid crystals up to 1931. Kast's survey is concerned with substances that have the nematic structure, which from their dielectric characters fall into two groups, i.e., symmetrical and unsymmetrical molecules. Anisaldazine represents the symmetrical molecules and ethyl *p*-ethoxybenzalamino-α-methylcinnamate the unsymmetrical molecules. Symmetrical molecules show a reduction in dielectric constant when a magnetic field is perpendicular to the plates of the condenser, and a small increase when parallel. The amount of change depends on the temperatures, the magnetic field strength, and the electrical field between the condenser plates. There is a small increase in the dielectric constant of unsymmetrical molecules when they are acted on by a magnetic field parallel to the electrical field. The differences have been attributed to the tendencies of the symmetrical and unsymmetrical molecules to set themselves parallel and perpendicular, respectively, to the condenser plates. Born (29) assumed self-orientation of the molecular dipoles to be responsible for the anisotropy and used the same theoretical treatment for determining dipole moment as had been used for calculations of paramagnetism. He (29) found a value for the dipole moment 50 per cent higher than that observed experimentally. It is apparent that use of dipole moment alone does not explain anisotropy. Kast (191) reported on the changes of dielectric constant with constant magnetic field and different electrical fields. By applying Langevin's formula for calculating the average electric moment of the swarms in the mesomorphic state, Kast found a moment approximately 10^5 times the value obtained by Erréra (88, 89) for the molecular moment. It was concluded from these studies that groups of dipoles must be present in the mesomorphic state. It cannot be assumed from this value that there are always 10^5 molecules which associate with oriented dipoles, since the strength of the external field was the only quantity used in arriving at the result.

The influence of electrical field strength on the dielectric constant was first studied by Jezewski (184), the results of whose findings are illustrated in figure 28. Kast (191) has interpreted these results by assuming that in the absence of a magnetic field the particles are parallel to the condenser plates; this is also true for the particles in the case of the perpendicular magnetic field. In these cases the decrease in dielectric constant should be due to the rotation of the molecules by the electrical field. The difference in the two curves might be due to the deflection of the current carriers, thus causing a turbulence, or to different

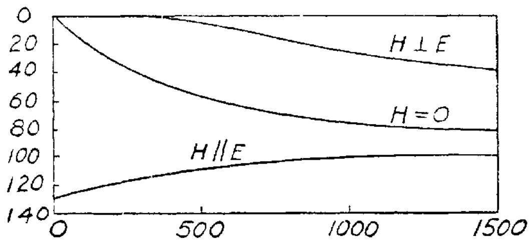


FIG. 28

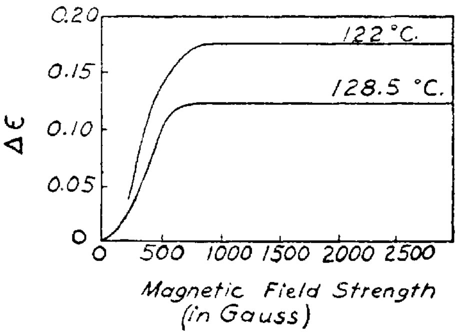


FIG. 29

FIG. 28. Influence of the electrical field alone or together with a longitudinal or transverse magnetic field on the dielectric constant. The compound used was *p*-azoxyanisole. $H \perp E$ = magnetic field perpendicular to the electrical field. $H = 0$, no magnetic field. $H \parallel E$ = magnetic field parallel to the electrical field. From Jezewski (184).

FIG. 29. Dielectric constant of anisotropic 4,4′-di-*p*-methoxyazoxybenzenes as a function of magnetic field strength. $\Delta\epsilon = \epsilon_{\text{transverse}} - \epsilon_{\text{longitudinal}}$. From Maier, Barth, and Wiehl (256).

frequencies. The parallel magnetic field first has to orient the particles perpendicular to the condenser plates; therefore the dielectric constant first decreases (195).

B. MORE RECENT DEVELOPMENTS IN DIELECTRIC CONSTANT MEASUREMENTS

Bhide and Bhide (21) measured the dielectric constant and absorption of *p*-azoxyanisole by the resonance method at frequencies of 1000, 3855, and 6480 kilocycles. There were abrupt changes in the dielectric constant as the mesomorphic state changed to the isotropic liquid, with the changes being more pronounced at the higher frequencies. This change in dielectric constant at the transition point checks with the observations of Kast (191). The absorption values showed a break at the transition temperature. According to Bhide and Bhide (21), the values of the dielectric constant for rising and falling temperatures below the N-L point were not coincident. Cholesteryl benzoate showed comparable effects on the change in dielectric constant but showed no absorption.

Ornstein, Kast, and Bouma (306) from a study of the dielectric constant measurements of benzophenone and *p*-azoxyanisole calculated the degree of orientation of the swarms, obtaining a maximum value of about 80 per cent.

Marinin and Tsvetkov (259), by means of the suspension method, studied the dielectric properties of *p*-azoxyanisole in motion through a capillary. The dielectric properties are found to vary with the velocity of flow, the strength of the applied magnetic field, and the temperature. At 119°C. and a rate of flow of 0.17 cm. per second the orienting effect is 20 per cent in a magnetic field of 3000 gauss and 59 per cent for 1000 gauss. With a rate of flow of 2.12 cm. per second the effects are 87 per cent and 93 per cent, respectively. The orienting effect falls linearly with temperature from 90°C. to 120°C. and then rapidly to zero at 135°C. (N-L point); the effect increases rapidly with increasing magnetic field up to 800 gauss and only slowly above 1000 gauss, the change in slope in the curve being almost independent of the temperature.

Maier (252) observed the change in dielectric constant in longitudinal and transverse magnetic field up to 5000 gauss. The ratio of transverse to longitudinal is found to be $-\frac{1}{10}$ instead of $-\frac{1}{2}$ as predicted. X-ray studies demonstrated that the difference is due to orientation of the swarms, largely by convection currents, in the absence of a field. Maier found that a horizontal temperature gradient of 0.1°C. per centimeter produces almost complete orientation of the swarms.

Funt and Mason (112) found no effect of shear on the dielectric constant of the mesomorphic state by use of a rotating cylindrical condenser. These investigators concluded that the oriented groups (swarms) are too small to be affected by the shear gradients used.

The dielectric loss of the mesomorphic state of *p*-azoxyanisole with change in temperature has been studied by means of a resonance-coupled circuit (36, 198). A plot of loss versus frequency shows a maximum. The maximum frequencies increased from 7×10^4 to greater than 2×10^6 Herty with a temperature increase from 118°C. to 124°C. A sharp maximum appeared at the C-N point of the *p*-azoxyanisole when a plot of the increase in maximum frequency with temperature was made. The maximal losses show a great temperature gradient which is difficult to interpret in the light of the Debye frictional dispersion theory. It has been shown (305) that in the absence of any external magnetic field the dielectric loss of *p*-azoxyanisole has a maximum at frequencies of the order of 1 megacycle. It was found that the dielectric loss in the mesomorphic state varied with temperature and also with frequency.

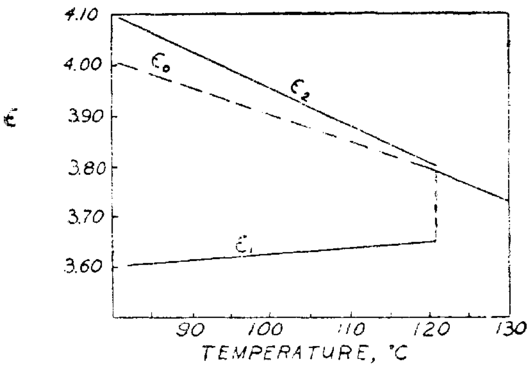
A recent study of dielectric constant has been done by Maier, Barth, and Wiehl (254). The change in dielectric constant

$$\Delta\epsilon = \epsilon_{\text{transverse}} - \epsilon_{\text{longitudinal}}$$

with increasing magnetic field strength increases rapidly up to 1000 gauss but $\Delta\epsilon$ is independent of field strength above 1000 gauss. These results are illustrated in figure 29. The variation of the principal dielectric constants of 4,4′-dipentoxyazobenzene with temperature is illustrated in figure 30. The magnetic field of approximately 1000 gauss was used to measure both ϵ_2 (field perpendicular to the condenser plates) and ϵ_1 (field parallel to the condenser plates). ϵ_0 is the dielectric constant in the absence of a magnetic field. The temperature dependence of the dielectric constant of the mesomorphic state is represented for the same compound by figure 31.

The swarms are considered to be ellipsoidal and are oriented by a magnetic field of about 1000 gauss. The temperature dependence in two directions of the axis of the ellipse is different. In one direction the dielectric constant increases with the temperature as in a solid and in the other direction the dielectric constant decreases with increasing temperature as in a liquid. The observations are explained by means of the positions of the dipoles of the compounds. By means of a modified Onsager theory it is possible to calculate the numerical value of the dipoles from the measurements.

The schematic representation of the electrical measuring fields for the meas-



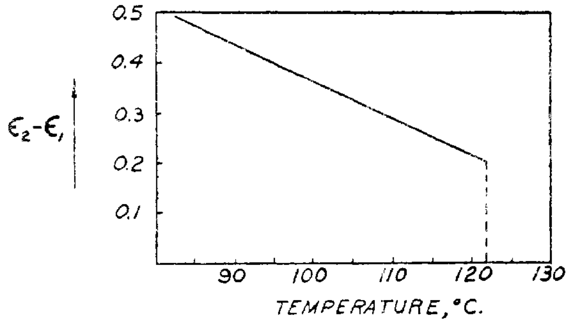


FIG. 30 FIG. 31

FIG. 30. The principal dielectric constants ϵ_1 and ϵ_2 of 4,4′-di-*n*-pentoxyazoxybenzene (Maier, Barth, and Wiehl (256)).

FIG. 31. Temperature dependence of dielectric constant of anisotropic 4,4′-di-*n*-pentoxyazoxybenzene (Maier, Barth, and Wiehl (256)).

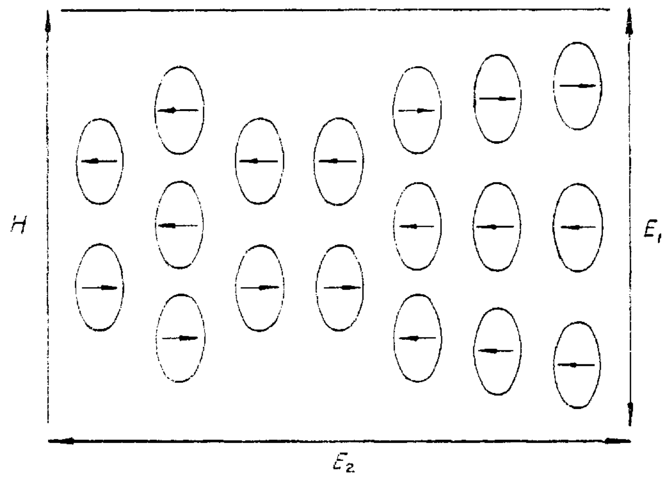


FIG. 32. Schematic representation of the electrical measuring fields for the measurement of the dielectric constants ϵ_1 and ϵ_2.

urement of the dielectric constants ϵ_1 and ϵ_2 may be given by figure 32. Here it is assumed that there is a strong dipole in the middle of the molecule. Field E_1 gives a measure of the principal dielectric constant ϵ_1, and E_2 gives the other principal dielectric constant, ϵ_2.

The molar electrical susceptibility σ is defined as

$$\sigma = \frac{\epsilon - 1}{4\pi} \frac{M}{\rho}$$

where ϵ = dielectric constant, M = molecular weight of the compound, and ρ = density of the compound.

Data from Maier, Barth, and Wiehl (254) on molar electrical susceptibility as a function of temperature for the principal dielectric constants of 4,4′-dipentoxyazobenzene are shown in figure 33. σ_2 corresponds to E_2 and σ_1 to E_1.

As pointed out in the section on molecular structure the N-L points when

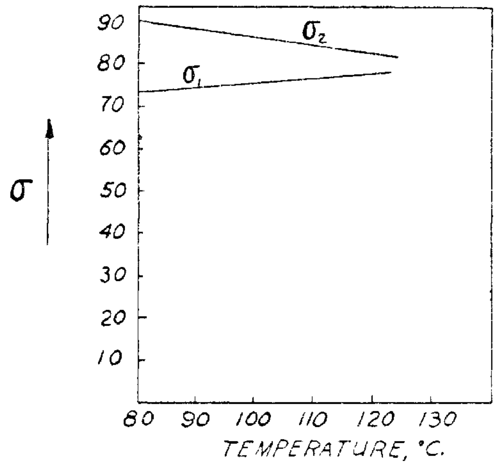


FIG. 33

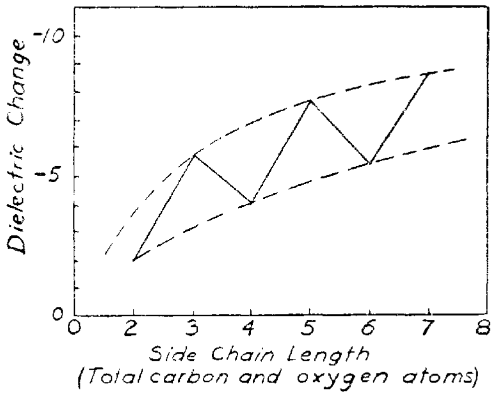


FIG. 34

FIG. 33. Molar electrical susceptibility (σ) of 4,4′-di-*n*-pentoxyazobenzenes (Maier, Barth, and Wiehl (256)).

FIG. 34. Change of dielectric constant of the mesomorphic state of the homologous series of *p*,*p*′-di-*n*-alkoxyaxozybenzenes (Maier and Baumgartner (254)). 2 = methoxy, 3 = *n*-propoxy, 4 = *n*-butoxy, etc.

plotted against chain length of the side chain in a homologous series give curves showing peaks and valleys at even and odd numbers of carbon atoms in the side chain, respectively. The change in dielectric constant with change in chain length of the side chain was studied by Maier (253) and by Maier and Baumgartner (255). The findings are comparable to those of plots of transition temperature versus chain length. The results of their findings are summarized in figure 34.

Two papers have appeared in which the authors have used evaluation of the Kerr constant as a means of studying the polarizability of the mesomorphic state. Tsvetkov and Marinin (405) evaluated the Kerr constant for *p*-azoxyanisole (I), *p*-azoxyphenetole (II), dibenzalbenzidine (III), anisal-*p*-aminoazobenzene (IV), ethyl *p*-azoxybenzoate (V), anisaldazine (VI), and *p*-acetoxybenzalazine (VII). Compounds III and IV have their dipole moments directed at small angles with the molecular axis, while compounds I, II, V, VI and VII have their optical axes perpendicular to the electrical field; the latter five compounds have a negative dielectric anisotropy. Negative dielectric anisotropy is exhibited by the mesomorphic state, the molecules of which have a dipole nearly perpendicular to the molecular axis, whereas substances with positive dielectric anisotropy are characterized by a small angle between the dipole moment and the molecular axis. In this case, dielectric polarization is due mainly to rotation of the molecular dipoles around the long axes of the molecules and the dielectric constant is greater than it would be if the liquid crystal were oriented parallel to the field. Also, Maier (253) has studied the effect of a static magnetic field on the dielectric constant of a homologous series of compounds which exhibit the mesomorphic state and has correlated the results with the electric dipole moments and polarizabilities. Tolstoi (393) attempted to answer the question of the permanent dipole moment relative to the molecule. Again, he used the evaluation of the Kerr constant to arrive at an answer. For *p*-azoxyanisole it was concluded that the dipole moment forms an angle of the order of 45° with the azoxy group. The dipole moment has a substantial component in the direction perpendicular to the axis of the molecule. This bears out the interpretation of Tsvetkov and Marinin (405) of the large electrical polarizability of *p*-azoxyanisole, which calls for the existence of a perpendicular component only; however, it is not inconsistent with a parallel component of the dipole moment. Tolstoi (393) reasoned that since a swarm as a whole has no dipole moment, then the molecules in it are disposed as frequently with the longitudinal component in one as in the opposite direction. An electrical field perpendicular to the axes of the molecules will tend to split the swarm at points where neighboring molecules have antiparallel components; consequently, the electrical field may result in a break up of an existing swarm pattern and bring about a new swarm array. This tendency to split will be especially strong between two clusters of molecules parallel within each cluster but antiparallel from one cluster to another.

The dielectric constant of the mesomorphic state of β-lactoglobulin in water has been measured (360) and the data for frequency versus dielectric constant at temperatures of 13.7°C., 16.6°C., and 20.0°C. obtained. Little change was found in the dielectric constant at the different temperatures. The data show a broader frequency range of dispersion and absorption and a smaller value of dielectric losses than is predicted by the Debye theory for a system characterized by a single relaxation time.

The influence of a magnetic field on the microwave dielectric constant of the mesomorphic state at a frequency of 15,300 megacycles per second has been observed (50, 51). It was found that the real part of the dielectric constant was greater in a magnetic field parallel to the microwave electrical field than with no field. Also, the results of the real part of the dielectric constant with the magnetic field of 2000 gauss perpendicular to the microwave field were found to be almost the same as for a zero field. These results are exactly opposite to those found by Jezewski (183) in his measurements of the low-frequency dielectric constant. Maier (253) interpreted Jezewski's results as indicating that the contribution of the permanent electric dipole moment, which is perpendicular to the axis of the molecule, is greater than the contribution from the induced polarization along the axis of the molecule. The results of Carr and Spence would indicate that at microwave frequencies the induced polarization yields the predominant effect. The microwave dielectric constant of the liquid shows no observable dependence on the magnetic field. This is in agreement with the optical measurements of Pellet and Chatelain (314) in that they observed no anisotropy for the index of refraction in the isotropic liquid. The dielectric loss of the mesomorphic state of *p*-azoxyanisole decreased in a static magnetic field parallel to the microwave electrical field and increased in a magnetic field perpendicular to the electrical field. Figure 35 shows the results of these measurements. It is clear from figure 35 that, regardless of the magnitude or orientation of the magnetic field, the dielectric loss increases as the temperature on the mesomorphic state increases. *p*-Azoxyphenetole gives similar results. The field dependence of the imaginary part of the complex dielectric constant is shown in figure 36. The general shape of this curve is very much like that observed by Miesowicz (282) for the field dependence of the viscosity.

Microwave dielectric loss in the mesomorphic state in *p*-azoxyanisole and *p*-azoxyphenetole is decreased by application of a magnetic field parallel to the microwave electrical field. If the magnetic field is suddenly turned off, a length of time varying from a fraction of a minute to a few minutes is required for the nematic structure to become optically homogeneous. This can be shown by measuring the change in dielectric loss after the magnetic field is turned off. Time to return to the zero-field distribution is dependent upon the temperature and decreases as the temperature increases.

By suddenly reversing an externally applied magnetic field of about 200 gauss it can be shown that the aligning effect of the magnetic field is entirely due to the diamagnetic nature of *p*-azoxyanisole and *p*-azoxyphenetole. Under the conditions of measurements by Carr and Spence about 1 min. was necessary to produce alignment in the nematic structure when the field was turned on. If the alignment were due to a permanent magnetic moment, the molecules or swarms would have turned over when the field was reversed and while turning over would pass through a state of random orientation. Because of the long time required for the alignment to take place, this random distribution would have caused a change in the dielectric loss as the magnetic field was reversed. Reversing the magnetic field showed that there was no turning over of the "particles", a result which implies that the magnetic moment in the nematic structure is induced.

Mann and Spence (258) studied the entry of microwaves into the nematic

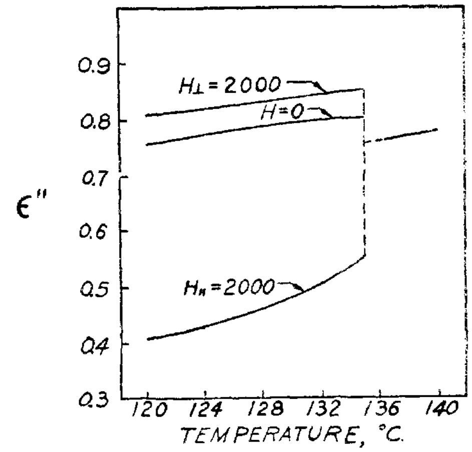


FIG. 35.

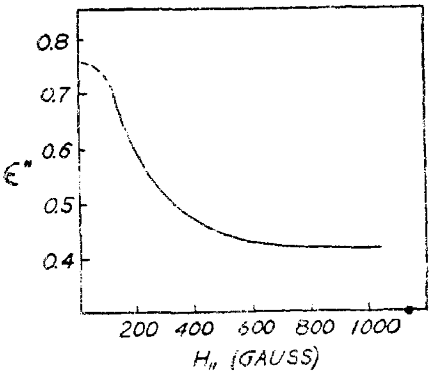


FIG. 36.

FIG. 35. Dielectric loss (ε'') of *p*-azoxyanisole in the nematic structure (Carr and Spence (50)). $H_\perp$ = magnetic field of 2000 gauss; H = no magnetic field; $H_\parallel$ = magnetic field of 2000 gauss.

FIG. 36. Field dependence of the imaginary part of the complex dielectric constant for *p*-azoxyanisole at a temperature of 124°C. (Carr and Spence (50)).

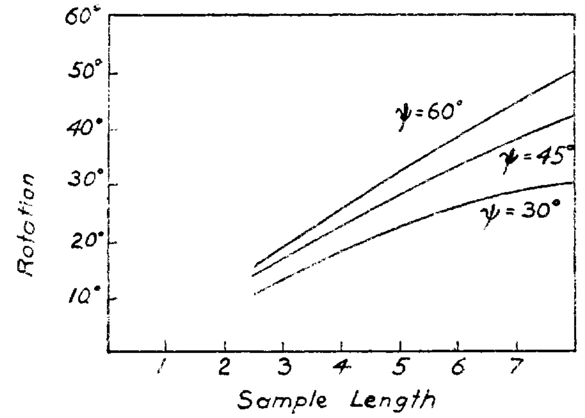


FIG. 37. Rotation (ψ) of the plane of polarization of *p*-azoxyanisole as a function of the length of sample (Carr and Spence (50)). ψ_0 is the angle between the magnetic field and the electric vector of the microwave field. Data taken at 129°C. in a field of 1300 gauss and at a frequency of 9400 Mc.

structure of *p*-azoxyanisole at different angles with respect to the magnetic field. The experimentally measured rotation of the plane of polarization as a function of the length of the sample is shown in figure 37.

IX. X-RAY STUDIES OF THE MESOMORPHIC STATE

Hückel (172) and de Broglie and Friedel (43, 44) were the first to examine liquid crystals by means of x-rays. Hückel concluded that the x-ray diffraction patterns of the nematic structure are similar to those of the liquid. de Broglie and Friedel showed that the molecules in the smectic structure are in equidistant parallel strata.

Whether or not the x-ray diffraction patterns of a nematic structure and of the liquid state are the same was a question of concern for many researchers in the field. Using copper K_α radiation, Hückel (172), Kast (193, 194), and Katz (199) all reached the conclusion that the x-ray patterns of the two systems are the same. However, Kast's (194) plot of intensity versus diffraction angle shows some displacement of the curve of the nematic structure relative to the isotropic liquid. Glamann, Herrmann, and Krummacher (138) reported that there was a small difference in the x-ray patterns in nematic and liquid structures. Using molybdenum K_α radiation, Stewart (371, 372, 374) found that the diffraction-intensity curves are practically the same but that the intensity at the principal maximum is 5 to 15 per cent greater for the nematic structure than for the liquid structure. The greater sharpness of the peak and the sharper inner slope with the nematic structure show more regularity of structure in that phase.

Scattered through the literature are a few other references on the x-ray patterns of the mesomorphic state or structures supposedly related to this state. Glamann, Herrmann, and Krummacher (138) took x-ray patterns by the Debye–Scherrer method of ethyl *p*-azoxybenzoate, allyl phenylethylazoxybenzoate, methyl *p*-(*p*-ethoxybenzalamino)cinnamate, ethyl *p*-(*p*-phenylbenzalamino)cin-

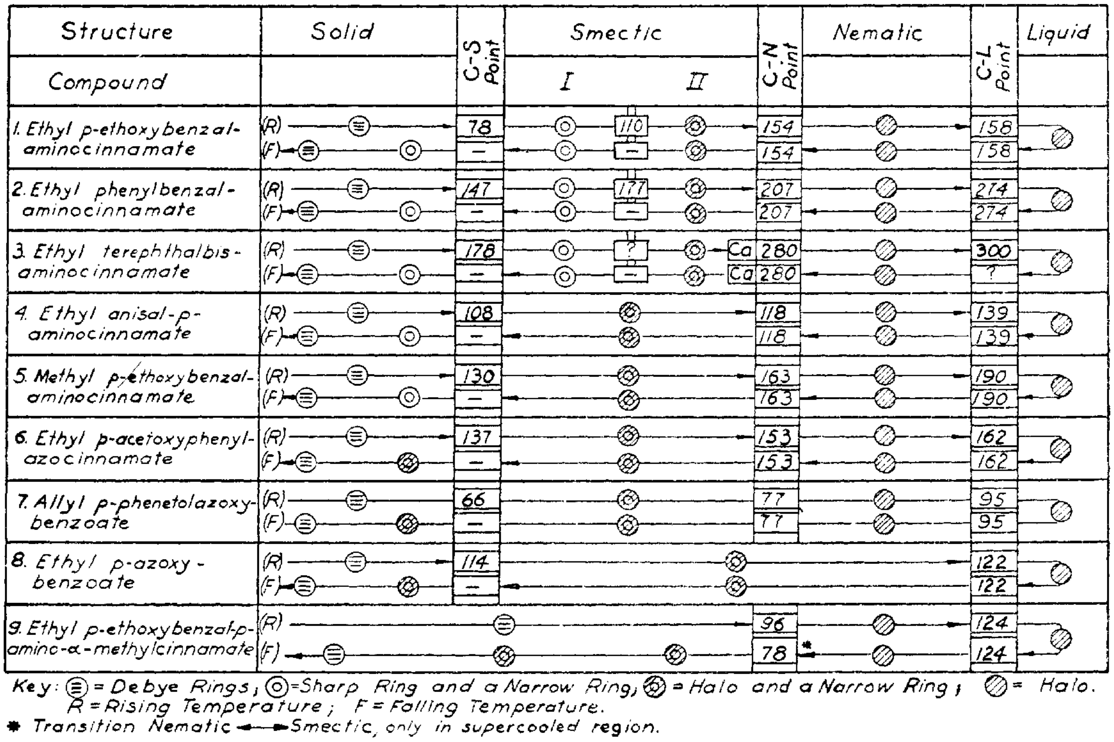


FIG. 38. Change in x-ray diffraction patterns of different mesomorphic compounds with change in temperature (Herrmann (158)).

namate, and ethyl terephthalbisaminocinnamate in the different structures which each exhibits.

Herrmann (158) made an extensive and thorough investigation of the x-ray patterns of the mesomorphic state. He constructed an apparatus for the simultaneous optical and x-ray examination of the structures at controlled temperatures. Seven esters of cinnamic acid and two of benzoic acid were followed through heating and cooling cycles and x-ray photographs were taken of the different phases. The results of Herrmann's work are summarized in figure 38. Classification of the x-ray patterns was made without the aid of microphotometer traces of the x-ray films. According to Herrmann, the first three compounds in figure 38 exhibit a new kind of interference, with rising temperature immediately above the C-S point, whose origin is ascribed to hexagonal cylindrical packing of the molecules within the smectic planes.

Nordsieck, Rosevear, and Ferguson (299) carried out an x-ray study of the stepwise melting of anhydrous sodium palmitate. Between the crystal and the isotropic state two basic mesomorphic state structures ("waxy" and "neat") exist, structures that are crystalline in the direction of long spacing and liquidlike laterally. Between the lower temperature "waxy" structure which includes the previously known subwaxy, waxy, and superwaxy phases and the higher "neat" structure which includes the subneat and neat, there is a pronounced break in the curve of long spacing versus temperature. The three waxy structures exhibit two diffuse short-spacing rings, whereas the neat phases exhibit only one. X-ray data indicate that transitions among the waxy phases and between the neat phases are accompanied by a continuous variation in x-ray pattern; therefore the x-ray method cannot be used to determine the transition temperatures. There is a difference in the results obtained by Nordsieck, Rosevear, and Ferguson (299) and those obtained by De Bretteville and McBain (71) on anhydrous sodium stearate. De Bretteville and McBain did not find the differences in short spacing between the waxy phases and the neat phases which were observed by Nordsieck, Rosevear, and Ferguson. They concluded that the subwaxy and waxy phases were crystalline and that the superwaxy phase more nearly resembled the neat phases. The two research groups agree on the long-spacing breaks at 117°C. (crystal to subwaxy) and 170°C. and 270°C. (waxy to neat regions, respectively). The lack of agreement on the short spacing may be accounted for by the lack of complete conversion of the samples from one phase to another in the case of the work of De Bretteville and McBain and to differences between sodium palmitate and sodium stearate. Nordsieck, Rosevear, and Ferguson found that it took several hours for complete conversion of a phase to the next higher phase (higher used with reference to higher temperature).

Herrmann (157) was the first to present information on the angle made by the intersection of the molecules with the smectic planes. He measured the interplanar spacings for thallium stearate and thallium oleate. At 140°C. a value of 36 A. was found for the interplanar spacing for thallium stearate; the calculated length of the molecule is 27 A. Herrmann postulated double molecules placed end to end at an angle of 42° with the smectic planes. In the solid state the angle of molecular arrangement is smaller and equal to 37°. For thallium oleate the angle between the double molecules and the smectic planes was found to be 53°.

The crystalline state of some of the substances that form the mesomorphic state has been studied by x-rays. Kast (188) took x-ray photographs of single crystals of *p*-azoxyanisole; Glamann, Herrmann, and Krummacher (138) took x-ray patterns of powder samples of a number of different compounds; and Bernal and Crowfoot (17) studied a number of compounds by the use of oscillation and Weissenberg photographs. Müller (290) investigated the normal paraffins near their C-M point, and Herrmann (157) made a study of a number of powder samples and samples prepared by supercooling of the smectic structure. One of the most informative of these articles cited on the x-ray analysis of solids is that of Bernal and Crowfoot (17). A number of projection diagrams are given of the crystalline state of substances that show the nematic, cholesteric, and smectic structures when heated.

The orientation effect of the magnetic and electrical fields on the swarms in the nematic structure is fairly similar and has been studied by the use of x-rays by a number of investigators. In general, using copper K_α radiation, it has been found that the diffraction rings of the nematic structure become crescent-shaped perpendicular to the electrical or magnetic field. Herrmann and Krummacher (161) exposed anisaldazine, *p*-azoxyanisole, allyl *p*-(*p*-phenylethyl)-azoxybenzoate, and methyl *p*-(*p*-ethoxybenzal)aminocinnamate to a field of 5000 volts per centimeter and studied the orientation effect with the help of x-rays. X-ray photographs showed crescents, and from the optical properties it was concluded that anisaldazine and *p*-azoxyanisole had the long axes of the molecules point in a direction perpendicular to the electrical field and that with the other two compounds the long axes are parallel to the electrical field. By x-ray methods Kast studied the critical frequency of the electrical field for which the orientation of the swarms disappears. The relaxation time of the swarms evaluated by this method was found to be 10^{-5} sec., as against 10^{-11} sec. for ordinary molecules. Kast (192) found that *p*-azoxyanisole prepared by different methods gave different results, and the discrepancy in results was attributed to differences in the amount and kind of impurities in the sample. Zocher (465) pointed out that the alignment of swarms in an electrical field is dependent upon the structure of the molecules. Molecules with dissimilar ends should line up with their long axes parallel with the field, while with the same end groups, the axes should be positioned transverse to the field direction. Kast (187, 189, 190) held this view, and Herrmann and Krummacher (161) adhered to this position after finding that x-ray photographs that they had taken of *p*-azoxyanisole and anisaldazine had given anomalous results because of heat flow and not because of structural differences.

Kast (188) made the first study, by the use of x-rays, of the nematic structure oriented by the magnetic field. He found two diffuse interference maxima perpendicular to the field. The x-ray pattern was explained on the basis that the long axes of the molecules were oriented parallel to the applied field. Solidification of the melt under the influence of the field showed a complete orientation of the molecules in the solid. An extensive study of the influence of a magnetic field on *p*-azoxyanisole was carried out by Glamann, Herrmann, and Krummacher (138). Two diffraction rings were found with copper K_α radiation, while three diffraction rings were obtained with molybdenum K_α radiation. In a magnetic field the two diffraction rings obtained using the copper radiation split into crescents, because the long axes of the molecules are oriented parallel to the direction of the magnetic field.

Herrmann and Krummacher (159) took x-ray patterns of allyl phenetoleazoxybenzoate at different temperatures and in the absence and in the presence of a magnetic field. Table 21 represents the results. The d_{Bragg} gives the distance between the molecular axes which is in agreement with the knowledge of the dimensions of the molecule.

Photographs (159) of crystals which had solidified under the action of a magnetic field show the same orientation but not quite so marked as the mesomorphic structure. Herrmann and Krummacher (160) studied the x-ray diffraction patterns of anisal-1,5-diaminonaphthalene in the mesomorphic state while under a magnetic field of 8600 gauss. These authors proposed to interpret the x-ray patterns so as to distinguish between intermolecular and intramolecular interferences. Good photographs of x-ray patterns may be found in a number of references (138, 159, 160) on the mesomorphic state.

Stewart (370) carried out an x-ray study of the magnetic character of liquid-

TABLE 21

X-ray data on allyl phenetoleazoxybenzoate

Herrmann and Krummacher (159)

Temperature	Structure*	Diameter of Outer Ring	$\frac{\theta}{2}$	d_{Bragg}
		Radiation: Cu Kα		
°C.				
100	Liquid, n. m.	32	8°47′	5.0
88	Nematic, w. m.	34	9°18′	4.8
79.5	Nematic, w. m.	34	9°18′	4.8
75.5	Smectic, w. m.	35	9°33′	4.6
72	Smectic, w. m.	35	9°33′	4.6
		Radiation: Mo Kα		
94	Nematic, w. m.	34.4	9°26′	2.16
82	Nematic, w. m.	36.5	9°56′	2.04
70	Smectic, w. m.	38	10°19′	1.96

* n. m. = no magnetic field; w. m. = magnetic field.

crystalline *p*-azoxyanisole and compared these x-ray patterns with those of the liquid. His results are analogous to those cited by the other workers and discussed in the preceding paragraphs. Falgueirettes (91a) has made a recent study of the scattering of x-rays by the nematic structure. This study emphasized the orienting effect of the container and the magnetic field.

C. Hermann (156) discusses symmetry groups of amorphous and mesomorphic phases. The symmetry properties of a crystal are easy to define. In a crystal the symmetry properties are described by space groups and the crystal class or point group. Description of the symmetry of an amorphous system is more difficult to comprehend. In an amorphous material the translation group is statistical in three dimensions; in a crystal there are simultaneously three linearly independent direct (and as many reciprocal) translations, a triplet of either requiring a triplet of the other.

Hermann describes the translatory movements of the mesomorphic phase as "statistical translations," S; "direct translations," D; "pseudo translations," P; and "reciprocal translations," R. These four translation types may be combined in various ways. Hermann gave an amorphous material the translation symbol SSS (general statistical translation in all three dimensions of space) and a crystal the symbol (RD)(RD)(RD) (in each of three linearly independent directions both a direct and reciprocal translation). Between these two extremes there are eighteen mesomorphic translation types. In table 22 Hermann's twenty translation types are arranged so that each succeeding triplet represents a higher order than the preceding; also included is the x-ray diffraction pattern proposed by Hermann for each type. This arrangement does not appear in the original article by Hermann.

Secondly, the paper by Hermann deals with statistical symmetry operations. The latter include noncrystallographic symmetry groups and claims that all possible geometrical intermediate states between the regular molecule structures

TABLE 22*

Hermann's twenty translation types arranged so that each succeeding triplet represents a higher order than the preceding

Hermann's Number	Triple Symbol	Remarks on		
		Statistical translations	Sets of planes	X-ray diffraction patterns
1 (amorphous)	SSS	Three	None	No sharp rings
3a	SSP_2	Two	None	No sharp rings
3b	SSP_1	Two	None	No sharp rings
3c	SSP_0	Two	None	No sharp rings
3	SSD	Two	None	No sharp rings
2	SSR	Two	One	One set of sharp rings
4a	$SS(RP_1)$	Two	One	One set of sharp rings
4b	$SS(RP_0)$	Two	One	One set of sharp rings
4	SS(RD)	Two	One	One set of sharp rings
5a	SP_1R	One	One	One set of sharp rings
5b	SP_0R	One	One	One set of sharp rings
5	SDR	One	One	One set of sharp rings
7b	P_1P_0R	None	One	One set of sharp rings
7c	P_0P_0R	None	One	One set of sharp rings
7a	P_0DR	None	One	One set of sharp rings
7	DDR	None	One	One set of sharp rings
6	DRR	None	Two	At least two sets of sharp rings
8a	$DR(RP_0)$	None	Two	At least two sets of sharp rings
8	DR(RD)	None	Two	At least two sets of sharp rings
9 (crystalline)	(RD)(RD)(RD)	None	Many	Many sharp rings

* The authors are indebted to research workers at the Miami Valley Laboratories of The Procter and Gamble Company for the preparation of table 22 in connection with their study of Hermann's article (156).

and the Schoenflies–Fedorov crystal lattice are discussed, the x-rays proving a discriminant between the various configurations.

X-ray studies have been made on the mesomorphic state formed by the action of a polar molecule on certain molecules. McBain and his coworkers have studied soap and detergent solutions. McBain and Marsden (261) found that for a 36.5 per cent (by weight) solution of dodecylsulfonic acid in water, x-ray photographs indicate a two-dimensional hexagonal arrangement of particles and that a "superneat" phase (96.0 per cent dodecylsulfonic acid) gives an x-ray pattern indicating that the particles are oriented parallel to the long axis of the capillary. Other x-ray diffraction investigations (260, 262, 344) on aqueous anisotropic phases show that 23–70 per cent laurylsulfonic acid solutions give structures that appear to be elongated ellipsoids lying parallel to one another in a hexagonal arrangement. The thickness of the ellipsoids seems to be in the neighborhood of the double length of the molecule. Tilted lamellar structures were reported by Marsden and McBain (274) for the anisotropic phase of nonionic detergent in water. Other references to x-ray observations of the mesomorphic state formed by water and other molecules are cited in Section XII.

A little work has been done on the small-angle region of x-ray scattering; most has been done on aqueous systems. Marsden and McBain (262, 274) did some work on nonionic detergents, and Bernal and Fankuchen (19) carried out small-angle work on aqueous systems of tobacco mosaic virus.

In the realm of natural products (19) tobacco mosaic virus in water systems has been studied. It was found that a system containing 8 to 34 per cent virus and also higher concentrates prepared by centrifugation are spontaneously doubly refractive and consist of particles arranged in a parallel manner. X-ray patterns show the particles to be equidistant and that the system is liquid-crystalline with a hexagonal arrangement in the cross-section. The distance between the particles is dependent upon the concentration, indicating homogeneity of their distribution.

The concept of the "ideal paracrystal" and the theory of its diffraction has been proposed (166–168). This theory uses the convolution of Fourier transformation. In Hosemann's "ideal paracrystal" an average distance between particles is introduced to interpret the presence of a maximum in the x-ray patterns. The centers of the particles are arranged on a more or less distorted face-centered cubic lattice. In such a model each molecule is surrounded by twelve neighbors which are closer than all other molecules, but the distance from the original molecule to each of its twelve neighbors fluctuates around a mean distance, $\bar{d}$. The cell edge of a cubic paracrystal is equal to $\bar{d}\sqrt{2}$. In the (111) plane the scattering angle 2θ for the first maximum of the interparticle interference function is determined by Bragg's law to be $2\bar{d} \sin \theta_2 = 1.22\ \lambda$; at other angles of θ_2 and θ_3, the scattering angles 2θ are $2\bar{d} \sin \theta_2 = 1.41\ \lambda$ and $2\bar{d} \sin \theta_3 = 2.00\ \lambda$, respectively. These maxima are broader and weaker, the higher the corresponding index and the more distorted the lattice; thus it is possible that only the first two or three can be observed.

The model proposed by Hosemann imposes a certain relationship between $\sin \theta_1$ and the volume concentration, C (ratio of the volume of particles to the total volume of the system); the maximum value for this volume concentration for spherical particles can be shown to be 0.74. It can then be written that

$$\frac{C}{0.74} = \left(\frac{d_0}{\bar{d}}\right)^3$$

where d_0 = the diameter of the sphere. This relation can be transformed as

$$d_0 = \bar{d}c^{\frac{1}{3}}(0.74)^{\frac{1}{3}}$$

The equation $2\bar{d} \sin \theta_1 = 1.22\ \lambda$ then becomes

$$\frac{1.22\lambda}{2 \sin \theta}\, C^{\frac{1}{3}}(0.74)^{\frac{1}{3}} = d_0 = \text{constant}$$

It is seen that $\sin \theta_i$ is proportional to $C^{\frac{1}{3}}$; systems following this proportion are rare (319). The value of $\sin \theta_i$ for each maximum in the function $a(h)$ varies in proportion to the one-third power of the volume concentration.

An analogous discussion for a cylindrically symmetrical system could be given. In the cylindrical system $\sin \theta_i$ would be proportional to $C^{\frac{1}{2}}$. This is the experimental relationship found for tobacco mosaic virus systems.

The x-ray patterns of tobacco mosaic virus (19) are a good illustration of Hosemann's model of liquid crystallinity. The model has also been used to establish the diameter of the hemoglobin molecule in concentrated solutions. The diameter of the molecule was found to be 55 A. (333). Bateman, Hsu, Knudsen, and Yudowitch (8) also used the paracrystalline model in their small-angle x-ray study of hemoglobin. X-ray studies show that α-keratin displays the paracrystalline structure as a kind of nematic structure, while collagen is a kind of smectic, close-range order (168).

Photographs of the optical diffraction patterns in green mercury light of lattice models (two-dimensional gratings) are made by photographic size reduction of regular patterns of holes. These patterns (170) simulate the x-ray diffraction patterns of crystals with imperfections such as thermal motion, distortion, or slow wandering from periodicity in one dimension or two. Comparisons are drawn between some of the patterns and the observed x-ray patterns of polyurethan, collagen, α-keratin, and smectic and nematic structures; fair agreement is obtained.

X. Other Observations

A. PREPARATION

The two most productive researchers in the field of the preparation of liquid crystals were Vorländer and Weygand. No attempt will be made in this review to summarize the methods of preparation for the hundreds of compounds they prepared. Both investigators used classical methods which were, in many cases, considerably improved by them. Weygand (445) has summarized Vorländer's contributions to the mesomorphic state in a tribute to him. A bibliography at the end of Weygand's article lists all of Vorländer's publications. Vorländer is reported to have prepared over 250 liquid-crystalline compounds. The contributions of Weygand (443) are summarized in his own book, which was published a few years before his death. Many of the other references in the bibliography of the present review contain information concerning the syntheses of many liquid-crystalline compounds.

Hundreds of organic compounds (about 0.4 per cent of all organic compounds known) exhibit the property of mesomorphism on heating. There is no one reference which gives the preparation and properties of all these compounds. However, a table listing over 250 compounds, with their transition points, has been compiled in *International Critical Tables* (96). References accompanying this compilation will furnish the reader with a wealth of information on methods of synthesis. Landolt-Börnstein (210) gives a listing of transition points on a large number of mesomorphic compounds as well as tables of values of refractive index and viscosity (209, 211).

Most of the transition temperatures reported in the literature have been taken by microscopic observations on the hot stage or by capillary-tube method and bath. Some studies have been made on the transition temperatures by obtaining heating and cooling curves. Hartshorne and Roberts (154) describe a hot stage that permits interference figures of the heated specimen to be obtained. The most recent development of the hot-stage variety is the heating instrument developed by Gray (148). The heating element is designed for use on the rotating stage of a polarizing microscope and different types of phase changes are easily observed.

B. LIGHT SCATTERING

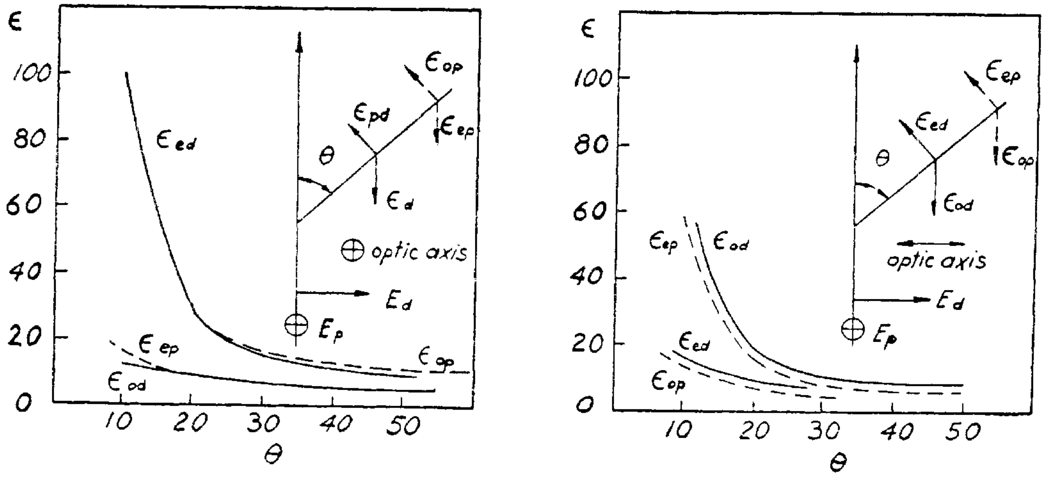
The scattering of light by the nematic structure has been the subject of a study by a number of investigators. A series of careful studies by Chatelain (60, 64) are of the most recent origin and will be outlined here. The articles by Chatelain give references to earlier work in this area of study of the nematic structure. Chatelain found that the intensity of the light scattered by *p*-azoxyanisole in the nematic structure between the angles of 10° and 50° decreased as the angle of scattering increased. It was also found that the most intense vibration of the scattered light was perpendicular to the incident vibration. Falgueirettes (91) obtained the same general results in his study of *p*-butoxybenzoic acid.

Chatelain (63) found that the intensity of the scattered transmitted light can be expressed as

$$\mathcal{E} = \frac{K}{(\sin \phi)^{1.6}}$$

where $\mathcal{E}$ = scattered intensity, K = constant, and ϕ = scattering angle.

At 125°C. *p*-azoxyanisole behaves like a uniaxial crystal and has values of $n_e = 1.85$ and $n_0 = 1.56$. Chatelain (61) studied scattering for ordinary and extraordinary rays as a function of the angle of scattering, θ, for four cases. The study concerned the optic axis (*a*) parallel and (*b*) perpendicular to the angle of scattering, and vibration of the incident radiation (*a*) parallel and (*b*) perpendicular to the plane of scattering. In each case the direction of the incident ray was perpendicular to the optic axis. The results of Chatelain's findings are summarized in figure 39. The more intense scattered ray has its electric vector



(a) (b)

FIG. 39. Light scattering by the mesomorphic state: (a) optic axis perpendicular to the plane of diffusion; (b) optic axis in the plane of diffusion. ϵ = intensity of scattered light; E_d = illuminating vibration in plane of diffusion; ϵ_{ed} = extraordinary vibration perpendicular to the plane of diffusion; ϵ_{od} = ordinary vibration in the plane of diffusion; E_{op} = illuminating vibration perpendicular to the plane of diffusion; ϵ_{op} = diffusion of ordinary ray; ϵ_{ep} = diffusion of extraordinary ray; θ = angle of measurement. From Chatelain (61).

TABLE 23

Diffusion of light by p-azoxyanisole in the nematic structure

Chatelain (62)

Backward diffusion	Angle	180°–8°	180°–11°	180°–16°	180°–20°
	Relative intensity	3.5	4.1	4.1	5
Scattered transmitted light	Angle	8°	11°	16°	20°
	Relative intensity	123	80	46	29

perpendicular to that of the incident ray. The intensity of scattering falls off approximately as $(\sin \theta)^{-2}$.

Chatelain (62) compared light diffused backward with the scattered light that was transmitted. The intensity of the light diffused backward increased slowly with the acuteness of the angle that it made with the incident beam. Illustrative results are given in table 23. The diffusion pattern was ascribed to particles 0.2–0.3 micron in their largest dimensions.

A theoretical study has been made of the scattering of light by a liquid composed of anisotropic particles which show fluctuations in orientation and are so distributed that the medium possesses a unique isotropic axis. Chatelain (65) considered two cases: (*1*) discrete anisotropic molecules and (*2*) large groups of parallel anisotropic molecules dispersed among isolated molecules. In both cases the theory leads to depolarization factors greatly in excess of unity. Spherical groups of radius of 0.1 micron and containing 10^6 molecules of *p*-azoxyanisole are considered as arranged parallel and inclined at an angle less than 36° to the isotropic axis and single molecules inclined at an angle greater than 36° to the isotropic axis. The theoretical results based on these assumptions are in agreement with experimental data. It was concluded that in the nematic structure light scattering is due to fluctuations in the orientation of the molecules around the isotropic axis and that the fluctuations in two molecules can be treated as independent only if their separation exceeds 0.1 micron.

C. SURFACE TENSION

When in contact with a surface, the arrangement of the axis of the components in the mesomorphic state in a parallel or vertical manner to this surface depends upon the variations of the interfacial surface tension. If mesomorphic *p*-azoxyanisole or other nematic compounds are placed against ordinary glass which has been treated with acid, a vertical instead of a parallel arrangement is noted. According to Berstein and Zocher (20) the orientation is reversed if the glass is treated with alkali.

A two-dimensional equation of state has been applied to the structure of surface boundary layers for isotropic liquids. It depends upon the supposition that the surface tension can be treated as the sum of static cohesion in conjunction with temperature-dependent and temperature-independent intermolecular forces

(389). Although applicable to many liquids, including certain fatty acids, it produces anomalous results for all anisotropic liquids. Perhaps with careful extension it could be developed as a means of determining the presence of anisotropic liquids. Through utilization of the data obtained, the dipole moments of *p*-azoxyanisole and *p*-azoxyphenetole could be calculated.

In general, the surface tension of liquids decreases with increasing temperature. The first recent detailed study of the surface tension of the mesomorphic state led to the conclusion that the surface tension in the mesomorphic state increases with temperature (92). Since the results obtained were unexpected, the experiments were repeated many times to verify the upward branches of the surface tension–temperature curves. The method made use of a capillary tube of not greater than 1 mm. bore and involved the forcing of a thread of liquid along this horizontal capillary tube. Although the method has been proven reliable for isotropic liquids, serious limitations may be involved when using associative substances in the mesomorphic state which are seriously affected by the wall effects and orientation of flow. It should be pointed out, however, that metals, such as cadmium, copper, and iron, have also been noted to exhibit abnormal trends in surface tension with increasing temperature.

Taking into consideration the orientation problem in nematic substances, several more recent experiments have been performed on surface tension (296, 359). The structure in which the optical axes of the liquid molecules are mutually parallel, but at the same time perpendicular to the surface walls, was found to exist only on clean surfaces that will show wetting by water. Random orientation at the surfaces, involving these mutually parallel molecules, was found only on contaminated surfaces. Using the radii of curvature of the surfaces of a drop of nematic *p*-azoxyanisole, the surface tension as a function of the temperature was found to be given by $A = 52.1 - 0.100t$ dynes per centimeter (296), where A is the surface tension. These data agreed well with the surface tension measured by the ring method of a duNöuy tensiometer for *p*-azoxyanisole, *p*-azoxyphenetole, and ethyl *p*-azoxybenzoate (359). The first two substances showed a decrease in surface tension of about 0.1 dyne per degree rise in temperature for both the anisotropic and the isotropic phases. In the immediate neighborhood of the anisotropic-isotropic transition the surface tension remained constant. An increase in surface tension with increasing temperature was found, however, for ethyl *p*-azoxybenzoate in the liquid up to 160°C. At this temperature a maximum in surface tension was obtained, and the surface tension then gradually decreased as the temperature was raised. The mesomorphic state exhibited the normal behavior.

D. CALORIMETRIC MEASUREMENTS

Very little thermal data in the form of heat capacities and heats of fusion have been obtained for the mesomorphic state of single compounds. In a few instances the thermal properties of these substances and their transitions have been shown by time–temperature curves.

Using a radiation calorimeter (392), the heat effects for the three stages of ethyl *p*-azoxybenzoate have been investigated over the temperature range of 30° to 150°C. (366), and have been plotted as both time versus temperature and time versus specific heat curves. The heats of fusion for the transitions from the solid to the mesomorphic state at 113.7°C., and from the anisotropic to the isotropic liquid at 122.5°C. are 14.3 cal. per gram and 3.8 cal. per gram, respectively. Only a single value for the specific heat was calculated in the small mesomorphic range and it was probably high. The results are of the same order of magnitude as values calculated from cryoscopic data and other direct measurements on mesomorphic compounds (174, 354, 355).

Elaborate apparatus and careful experimentation have been reported on the calorimetric measurements of *p*-azoxyanisole and related compounds (206, 207); the temperature versus time curves are in general agreement with previously published data, but the heats of transformation are several-fold different from indirectly determined values (355). For the compound *p*-azoxyanisole two values have been reported for the heat of transformation of the N-L point of 1.6 cal. per gram (410 cal. per mole) (207) and 1.79 ± 0.04 cal. per gram (206), while the corresponding transition for *p*-azoxyphenetole is reported as approximately 2.9 cal. per gram (830 cal. per mole) (207) and 3.16 ± 0.07 cal. per gram (206). The differences of C_p values for *p*-azoxyanisole is 0.037 cal. per gram and of C_v values is 0.016 cal. per gram; for *p*-azoxyphenetole a corresponding difference in C_p of 0.11 cal. per gram has been reported, with the isotropic phase having a smaller specific heat than the anisotropic (207).

The heats of transition for all phases of sodium laurate, sodium myristate, sodium palmitate, sodium stearate, and sodium oleate were measured by use of a differential calorimeter (416). Although duplicate results for heats of transition fluctuated much more widely than did those for the calibration compounds, the results are precise enough to allow comparisons of the heat effect at the different transitions. The transitions of curd phase to waxy soap and of subwaxy to waxy soap gave large heat effects which varied with the chain length, while in transitions at the higher temperature the heat effects were small and almost independent of the chain length. The heat effects for successive transitions of sodium myristate, sodium palmitate, and sodium stearate were found to be quite similar.

E. REFRACTIVE INDEX

A property which the parallel molecules of the mesomorphic state exhibit is an orientation in which the optic axes are perpendicular to a glass surface, e.g., the glass prism of a refractometer. This permits the measurement of two indices of refraction, the normal or ordinary index and the extraordinary index. Owing to birefringence and random distribution of swarms, it has been postulated that gradients of refractive index occur in anisotropic liquids and give rise to a scattering coefficient (302) proportional to the square of the difference between the ordinary and the extraordinary indices, $(n_0 - n_e)^2$. For anisotropic liquids (378, 408) this difference between the indices decreases as a function of the temperature up to the anisotropic-isotropic transition (N-L point), at which point a discontinuity of index occurs.

Several theoretical methods have been derived for determining the refractive index of anisotropic liquids. A carefully worked out method has been published for determining the principal indices of refraction involving the determination of retardation of oblique parallel light in thin plates (217). Another approach, using the dipole character of the anisotropic liquids, has attempted to calculate the temperature coefficient of the index of refraction perpendicular to the optic axis from the data available (29, 30).

The values of the refractive index of *p*-azoxyphenetole in the mesomorphic state have been measured by means of Newton's rings at various temperatures and wavelengths (54). Variations in refractive index with temperature and wavelength were obtained and these were found to be in agreement with the data obtained from studies of magnetic birefringence (408). Data on *p*-azoxyanisole are more complete, and the figures obtained for all values of refractive indices at several wavelengths and temperatures were found to satisfy the expression,

$$\frac{1}{3d}\,[(n_e^2 - 1)/(n_e^2 + 2) + 2(n_0 - 1)/(n_0^2 + 2)] = (n^2 - 1)/d'(n^2 + 2) = \text{constant}$$

which can be deduced theoretically from the polarizability and orientation of the molecules (55). This expression represents an expansion over earlier relations (330) which were applicable to the mesomorphic state. The expression has also been checked and explanded in a later paper by Pellet and Chatelain (314).

By comparing and compiling the data obtained from studies of refractive indices of nematic, cholesteric, and several mixtures of mesomorphic compounds (121, 122, 124, 131) various general conclusions were drawn. Some of these conclusions seem improbable in the light of present-day knowledge, but others are still acceptable. For a complete summary, the original literature should be consulted. In general, it would appear that optically negative mesomorphic compounds may usually be mixed in all proportions, and that both optically negative and optically positive properties follow the laws of isomorphous mixtures. The birefringence of the optically negative phases of the ether salts of cholesterol is about double that of quartz and diminishes rapidly with rise in temperature. Measurements of the index of refraction of mixtures of substances having the same optical sign give optical properties intermediate between those of the pure components, but this is not necessarily the case for the refractive index for mixtures of substances having different optical rotation. If the positive components are more refractive than the negative, there is a rise in the refraction, birefraction, and rotatory power; if they are of equal refraction, the properties of the negative component change only very slightly. The difference in the refractive index between the anisotropic and isotropic phases is not always predictable but it is usually significant for compounds exhibiting the nematic structure.

F. SPECTRAL OBSERVATIONS

Some of the early work on the spectra of mesomorphic compounds could determine little if any differences between the mesomorphic and isotropic states

(328). Also, the transition from liquid to mesomorphic state for several esters showed very little change in the absorption spectra as determined by means of a quartz spectroscope (435). The main difference found in the investigation of the Raman spectra of *p*-azoxyanisole in the solid, anisotropic, and isotropic phases (102) was that the spectra of the solid and nematic structures contained a line at 1247 cm.$^{-1}$ but none appeared in the isotropic phase.

A detailed study of the near infrared spectra of isoamyl *p*-(*p*-ethoxybenzalamino)cinnamate (I), anisalamino-α-methyl-propylcinnamic ester (II), and isoamyl *p*-(*p*-ethoxybenzalamino)-α-methylcinnamate (III) was made for the anisotropic and isotropic phases (391), and several small band shifts were noticed on comparison of the spectra for the two phases. The most pronounced difference, however, was a decrease in the background transmission of the anisotropic phase in the region between 1 μ and 6 μ. Isochromatic curves for the three compounds were obtained showing per cent transmission as a function of temperature. The normal, practically constant transmission in the solid and isotropic liquid phases was observed, but distinct arrests in transmission occurred in the anisotropic phase in the heating curves for compounds I and II, and sharp maxima and minima occurred in the ones for compound III. Significant changes in transmission also appeared at the C-M and N-L points, especially at the shorter wavelengths. A possible explanation for the arrests and minima in the isochromatic curves may be based on the possibility of polymesomorphism (74), while an increase in transmission with temperature was attributed to scattering based on both the change and gradients of refractive index (302) and the decrease in the birefringence. At long wavelengths, however, approximately the same transmissions for the solid and mesomorphic phases were obtained and the increase in transmission occurred at the N-L point. The overall small change in the transmission is explained by means of a decreasing birefringence factor $(n_0 - n_e)^2$ with increasing wavelength. The same general type of change has also been reported in the visible region (378, 408).

Very recently, Maier and Soupe (256) have investigated the spectra of *p*-azoxyanisole in the wavelength range of 2300–4000 A. Plane-polarized light was used both parallel and horizontal to the major axes of the molecules. Although slight shifts in absorption with wavelength were observed for various temperatures in the nematic structure and in comparison of the the nematic structure with the liquid, the authors concluded that the ultraviolet spectra would be of little help in indicating novel intermolecular interactions of the nematic structure.

G. ORIENTATION EFFECTS

In a series of papers by Fredericks and Zolina (100, 101) it was pointed out that the orienting effect on a thin surface layer of the nematic structure of *p*-azoxyphenetole and anisaldazine at the walls of the container is unaffected by the magnetic field. If the total liquid between two plates exceeds a certain critical thickness, depending upon whether the field is parallel or perpendicular, the remainder of the liquid will be affected by both an electrical and a magnetic field. The main body of the nematic structure of ethyl *p*-ethoxybenzalaminocinnamate appeared to be in a state of oscillation under the influence of the field. This oscillation could be increased and sustained by means of a vibrating tuning fork pressed to the microscope on which the observations were being made. Zolina (475) has confirmed these data and noted in addition that the vibration of the tuning fork shifted the optical axes of the molecules away from the direction parallel to the beam of polarized light.

Calculations of two elastic constants for *p*-azoxyanisole have been made by Fredericks and Tsvetkov (99) for both parallel and perpendicular magnetic fields, using the fact that the orientation of the molecules within certain limits can be determined by the observation of the limit of total reflection of the extraordinary ray, if the ordinary and extraordinary refractive indices are known.

The molecules of the nematic structure are assumed to have the ability within the swarms of orienting themselves in a parallel arrangement. Naggiar (294) has pointed out that the threads appearing in a nematic structure under the influence of an electrical field are a secondary effect produced by convection currents due to nonuniform heating. The threads are apparent in a direct field of 200–300 volts per centimeter and in an alternating field of the same strength and with a frequency not greater than 50 cycles per second.

The temperature dependence of both the nematic and smectic structures has been discussed by Oseen (308), whose paper presents a mathematical discussion of the relationship. More recently Holland and Stewart (165) have performed experiments where temperature differentials were applied to nematic structures and the effects were determined by use of x-ray diffraction photographs. With a higher temperature at the bottom of a container, convection currents caused a distribution favoring a vertical swarm axes orientation, while with the opposite temperature gradients, a horizonal orientation of swarm axes was indicated. After several more experiments, Stewart (373) reviewed the heat flow phenomenon and transverse orientations and stated that the cause of the phenomena were not to be found in differential temperature expansion, the momentum of high-frequency acoustic waves, the anisotropic heat conduction, and/or unavoidable convection currents.

Lehmann (235, 237) has discussed the influence of rotary motion and twisting on mesomorphic *p*-azoxyanisole as well as nematic structures in general. The hydrodynamic flow lines obtained are the same for both mesomorphic and isotropic liquids, unless the orientation is determined by axes of symmetry or of convergence. If isotropic *p*-azoxyanisole is allowed to solidify between two parallel glass plates and then rewarmed to the mesomorphic state, the molecules are not homogeneous but are oriented. The molecules adjacent to the glass have a fixed orientation, and other molecules near the center of the liquid are also strongly influenced regardless of whether the liquid is at rest or in movement. If the two glass plates are twisted in opposite directions, in the same planes as before, a spiral twisting of the liquid is obtained. The optical properties are now similar to a helical twisting and may be vividly shown by the use of various dyes.

Using the data for the ordinary and extraordinary refractive indices of nematic compounds, Chatelain (67) was able to calculate an average orientation factor as a function of the temperature. Since the distance between two molecules is less than a fraction of the wavelength and the molecules are essentially parallel, a very small variation was found in the factor using accurate data for the refractive index. The orientation factor is

$$\phi(t) = 1 - (3/2) \sin^2 \theta$$

where $\sin^2 \theta$ can be calculated from either refractive index.

The orientation of anisotropic liquids on the surface of crystals has been reported quite extensively. Grandjean (140–142) found that the property of an anisotropic liquid on a crystal cleavage is not a rectilinear property. Near the M-L transition the direction of orientation of the mesomorphic liquid varies considerably. The orientations seem to fall into three classifications: (*1*) one or more orientations which are temperature independent; (*2*) the orientation for any temperature is fairly definite, but changes sharply with change in temperature; and (*3*) the orientation varies continuously with temperature, when using the cleavage faces of minerals such as muscovite, talc, orpiment, sphalerite, etc. Mauguin (264, 266) reported that mesomorphic *p*-azoxyanisole between two mica sheets separated by cleavage showed regular formations which were closely related to those of the supporting crystal.

Chatelain (57–59) has reported the orientation of liquid crystals on polished or stroked surfaces. When glass, quartz, or mica surfaces are rubbed in a given direction and a nematic structure is placed on them, the molecules are oriented in a plane parallel to the surface and the direction of rubbing. The phenomenon was not observed for the smectic state. These facts lead to the theory that the alignment is due to an electrical field produced by the stroking and oriented in the direction of stroking. If nematic *p*-azoxyanisole is crystallized between two surfaces, the extinction angle of the mesomorphic phase produced by melting the solid changes with the number of times the surfaces are stroked over one another during the crystallization. Pretreatment of the surfaces by nitric acid or chromic acid also influences the orientations. Dreyer (79–81) has shown that strong polarizing films can be prepared by the use of a nematic structure on a stroked glass surface. If a solution of a dye is allowed to evaporate at the proper rate on a rubbed surface, the molecules of the dye are oriented relative to the surface. The liquid film is dried rapidly so as to pass through the nematic structure and, when fully oriented, to solidify suddenly, to facilitate the orientation of the molecules of the dye.

H. POLYMESOMORPHISM

The observation that many substances could exist in more than one mesomorphic form was clearly demonstrated by Vorländer (426, 436), who in 1907 and 1937 summarized the compounds known to show polymesomorphism. A later paper (438) discussed the synthesis and association processes involved in the polymesomorphism of mesomorphic arylidene-*p*-aminocinnamates. Gaubert (128) has reported many instances of polymesomorphism in compounds such as amyl cyanobenzylideneaminocinnamate and anisylideneaminoazotoluene.

Apparent changes in the form of the mesomorphic state have been observed for myelin forms by Lehmann (236) when changes in the molecular directing force occurred. These changes of directing force were attributed to polymesomorphic transformations observed in ammonium oleate, ceresin, phrenosin, and protargon. Weygand and Gabler (447) discussed the two or more polymesomorphic phases of azomethine compounds, while Campbell, Henderson, and Taylor (49) have discussed those for azopyridines and azoxybenzenes and also the monotropic mesomorphic compounds. The polyanisotropic phases of the soaps and their aqueous solutions are discussed in detail in Section XII. It will suffice here to say that the work of Vold (416, 421) and his group on the sodium salts of long-chain fatty acids is illustrative of polymesomorphism and shows that as one heats these compounds, they pass through several distinct stable mesomorphic phases before passing to the liquid. The phenomenon is not, of course, limited to the sodium soaps.

I. REACTIONS IN THE MESOMORPHIC STATE

Although most people would not consider using anisotropic liquids as solvent media for studying chemical reactions, experimentation has been reported on such systems by Svedberg (382, 383, 385). The rates of decomposition of picric acid, trinitroresorcinol, and pyrogallol in mesomorphic *p*-azoxyphenetole were studied at 140°C., and it was found that the reaction velocity in all cases was diminished when the system was subjected to a magnetic field. Electrical conductivity was used to follow the reaction. Maleic acid in *p*-azoxyphenetole did not exhibit decomposition when subjected to similar conditions. With a gradual increase in temperature, the reaction between picric acid and *p*-azoxyphenetole gradually changed, until at 165°C. a sudden change in the rate of reaction was indicated as the mesomorphic state became liquid. This change in rate, as determined by the change in conductivity measurements, was attributed to increased rate of diffusion, since the dielectric constant and degree of dissociation remained constant.

A mixed system of *p*-azoxyanisole and *p*-azoxyphenetole was reported by Svedberg as a medium for measurements of the diffusion of *m*-nitrophenol under the influence of magnetic field conditions (386). The rate of diffusion was increased by the use of a field parallel to the direction of flow and decreased when a field was applied transverse to the direction of diffusion.

J. ELECTRICAL CONDUCTANCE

The nematic structure has been used as the solvent for a number of solutes, and the electrical conductance of the resulting solution has been determined. Svedberg (381, 384) carried out a series of these electrical conductance studies in which different solutes were studied in *p*-azoxyanisole and *p*-azoxyphenetole. Figure 40 represents the plot of conductance versus temperature for hydrogen chloride in *p*-azoxyphenetole. As the system is cooled from the liquid state there is a 14 per cent decrease in the conductance on passing through the N-L point into the nematic structure. A comparable plot was obtained with picric acid dissolved in *p*-azoxyphenetole. In passing from the liquid to the nematic structure there is a 20 per cent decrease in the conductance. Too high temperatures cause decomposition of *p*-azoxyphenetole and give conductance values in the liquid state that are abnormal. Voight (412) has discussed the theoretical aspects of the work of Svedberg.

Further study by Svedberg of the electrical conductivity of solutions of pyrogallol and of picric acid in *p*-azoxyphenetole with and without the use of a magnetic field showed a smaller rate of increase of the conductivity with time under the influence of the field than without a field, but the ratio of the rates both with and without the magnetic field was independent of the solute. The ratio was also independent of the strength of the field between 3500 and 9000 gauss, but it shows a greater value for a smaller field in the neighborhood of 500 gauss. This ratio increases with increase in temperature until at the M-L temperature a value of unity is obtained (385).

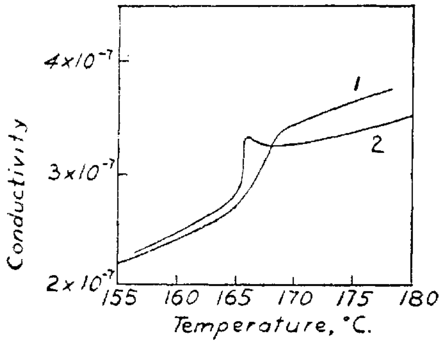


FIG. 40. Conductivity of hydrogen chloride in *p*-azoxyphenetole (Svedberg (381)). The conductivity is in reciprocal ohms. Curve 1, rising temperature; curve 2, falling temperature.

K. PROTON MAGNETIC RESONANCE

Recent studies of proton magnetic resonance have been extended to anisotropic molecules by Spence, Moses, and Jain (367). In the nematic structure, the amplitude of the signal decreases greatly compared to the liquid state and the line splits into three components. The separation between the two satellite peaks is about 3.3 gauss. The splitting of the peak is interpreted by the authors as arising possibly from a very strong hindering of the rotations of the methyl groups or, as an alternate suggestion, the protons in the benzene rings may be magnetically nonequivalent in the nematic structure. The signal for the nematic phase of *p*-azoxyanisole was unlike that found in the solid or isotropic phase of this compound. Extending the measurements to other compounds, it was found that the proton resonance line for the isotropic phase of *p*-azoxyanisole, *p*-azoxyphenetole, and anisaldazine is narrow, while in the mesomorphic state the line splits into three components. The separation between the satellite lines increases as the temperature is decreased in the phase. The central (main) component remains the predominant line in mesomorphic *p*-azoxyanisole and anisaldazine as the temperature is lowered, but this central component gradually shrinks down to the level of the satellites in the case of the temperature-dependent *p*-azoxyphenetole. The calculations and data indicate that the extent of orientation is greatest for *p*-azoxyphenetole. For all the compounds mentioned the sharp structural characteristics of the lines disappear in the solid state, while the resonance lines of cholesteryl benzoate, sodium oleate, and sodium stearate show no structure in the mesomorphic state, according to Jain, Moses, Lee, and Spence (179). The work of Jain, Lee, and Spence (178) showed that 4,4′-dimethoxy-d_3-azoxybenzene consists of a strong doublet and weak central component in the mesomorphic state and that the signal is fairly independent of temperature.

Ethyl anisal-*p*-aminocinnamate exhibits three mesomorphic phases, while ethyl phenylbenzylaminocinnamate exhibits four. Attempts have been made by Ewing and Lee (90) to relate these phases to differences in line shape of the proton magnetic resonance. A triplet signal similar to those found for *p*-azoxyanisole and anisaldazine was found in the highest temperature mesomorphic phaes of ethyl anisal-*p*-aminocinnamate. For this compound, a radical change in line shape was observed with decreasing temperature until only a single narrow line on a broad plateau resulted. The changes for ethyl phenylbenzylaminocinnamate were not nearly as radical. The limited available data on the signals from smectic phases by Moses (289) indicate that in general a single structureless line is obtained which is intermediate in width between that of the liquid and the crystalline phases. The transition temperatures of anhydrous sodium stearate were determined by nuclear magnetic resonance (147), and found to check favorably with the temperatures obtained by conventional methods.

L. STREAMING POTENTIAL

Although normal anisotropy and anisotropy of flow have been mentioned many times, it was only recently that the actual streaming potential for the nematic structure was determined by Bulygin and Ostroumov (46). The streaming potential, *E*, of mesomorphic *p*-azoxyanisole was measured using glass capillaries of 10.3 cm. length and radius of 170 microns, with overpressures, *P*, of 30–200 g. per square centimeter. The glass wall of the capillary contained a negative charge when the mesomorphic state was used, in contrast to the positive charge obtained when distilled water was used in the same apparatus. When holding *P* constant, the value of *E* as well as the slope, E/P, decreased with increase in temperature between 122° and 144°C. A significant discontinuous drop occurred in E/P at 135°C. (the M-L point). From E/P data and the Helmholtz formula, electrokinetic potentials, ζ, were calculated and irregularities were found above the C-M point, probably due to the uncertainty of the values used for the dielectric constant, the viscosity, and the electrical conductivity.

M. POLARIMETRY

The optical rotation of substances in the mesomorphic state generally is quite large compared to liquids and solutions. A layer of a mesomorphic substance that is 1 mm. thick may give rotations of 10^4 to 10^5 degrees (104, 129, 377, 378). Lehmann (222, 224) first described a simple and very ingenious method for measuring the rotatory power of the mesomorphic state by means of a polarizing microscope. If a drop of an optically active mesomorphic material is placed on a glass slide, it will spread to a circular wedge if a planoconvex lens is set into it. The circular wedge is free from optical distortions provided the refractive indices of the lens and of the mesomorphic substance are very similar. Between crossed nicols using monochromatic radiation, the circular wedge exhibits the circular analog to the fringes observed on a thick quartz wedge cut perpendicular to the optic axis. Each of the circular fringes represents the geometrical locus of a phase difference of $n \times 180°$, n being 1 for the intermost fringe, 2 for the second, etc. The center of the circular fringe pattern should be a dark spot if the glass slide and the center of the lens are in optical contact. Absence of such a dark spot in experimental observations indicates that there is a film of mesomorphic substance between the center of the lens and the glass slide. It is observed that because of the curvature of the lens, the fringes are narrower the larger their diameter. The optical rotation can be obtained by this method of measurement from the known curvature of the lens and the distance between the centers of two adjacent fringes. Also, the dispersion can be obtained by carrying out the measurements successively at different wavelengths.

If a diaphragm is used to restrict the passage of light to a rectangular section of the drop between the glass plate and the lens, spectral resolution will lead to a Hussel–Nutting pattern comparable to that obtained when white light is passed through a thick quartz wedge (175, 300). In the pattern of the mesophase, the pairs of symmetrical fringes represent equal rotations of equal sign, while they represent equal rotations of opposite sign in the Hussel-Nutting pattern. Figure 41 is a typical photographic pattern obtained for the mesomorphic state of cyanobenzylideneaminocinnamate in which Stumpf (377) modified the method pro-

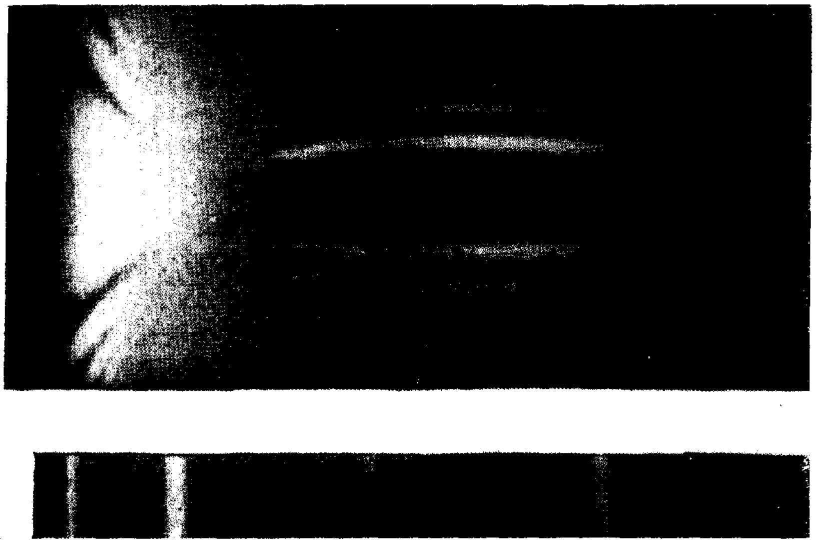


FIG. 41. Photographic record of the rotatory dispersion of the mesomorphic state of cyanobenzylideneaminocinnamate as obtained by Stumpf (377). A reference spectrum of helium is immediately below. The line on the extreme left in the helium spectrum is at 668 mμ, while the one on the extreme right is at 447 mμ.

TABLE 24

Rotation of cyanobenzylideneaminocinnamate in a 1-mm. layer at different wavelengths and for different temperatures

Stumpf (378)

Temperature = 75°C.		Temperature = 80°C.	
Wavelength, λ	Rotation in degrees, α	Wavelength, λ	Rotation in degrees, α
658	5300	642	6000
626	8000	636	8300
610	16300	522	33000
516	37700	508	25900
498	28500	492	22600
468	26400	473	21900
452	27650	460	22500
440	32000	446	25100

posed by Lehmann (222) by using a continuous spectrum. There is an anomalous dispersion of rotatory power in the visible range. Data on rotation versus wavelength (378) are given in table 24. Also, the dispersion of the rotatory power is obtained in a single exposure. A plot of the data in table 24 would give a graph in which the maximum in rotations would appear between 560 and 580 mμ. The narrow spectral region of excessive values of $d\alpha/d\lambda$ is not clear in the photographic pattern. The error of evaluation of the rotation was given as ±25°. This method of study of the rotatory dispersion of liquid crystals affords a quick and easy method for the measurement of the rotatory power of the mesomorphic state and certainly deserves more investigation than it has thus far received.

N. MISCELLANEOUS OBSERVATIONS

The nematic structure of dibenzylidenebenzidine and *p*-azoxyanisole was studied by Beneschevich (12) to see if a strong magnetic field caused a change in the volume of the system. The volume was found to remain constant in magnetic fields from 3000 to 17,000 gauss under conditions in which the accuracy of dV/V was 3×10^{-7}.

Vieth (410) reported that the rate of growth of the first mesomorphic phase of ethyl *p*-ethoxybenzalamino-α-methylcinnamate and the analogous ethylcinnamate increases under the influence of a magnetic field of 14,000 gauss.

Moll and Ornstein (288) reported that there was a change in temperature, keeping all other factors constant, in the nematic structure when a magnetic field was applied perpendicular to the plates holding the system. They explained the result as due to the change in position of the particles in the structure.

With a magnetic field parallel to the direction of observation, a sparking phenomenon was observed in the microscopic study of the nematic structure of *p*-acetoxybenzalazine. Tropper (397) regarded the scintillation phenomenon as a result of the thermal rotational fluctuations of the swarms.

The light extinction of the nematic structure in a magnetic field has been studied by several investigators, with the paper by Björnstähl (24) being representative of the work done as well as summarizing the work that preceded it. Björnstähl found that the light extinction for a system of a given thickness and under the influence of a magnetic field transverse to the field of observation is not clearly fixed by the temperature and that fluctuations in measurements are due to striae. If fluctuations are allowed for the striae, the extinction appears to be unchanged in transverse field. In the longitudinal magnetic field, the light extinction decreases with the intensity of the field at a wavelength of 560 mμ.

The orienting influence of the magnetic field has been studied in relation to a number of properties of the nematic structure, e.g., viscosity and dielectric constant. Optical properties of the nematic structure are affected by the magnetic field. Van Wyk (408) found that for each wavelength and each temperature a series of magnetic field strengths were found at which, using crossed nicols, the nematic structure of *p*-azoxyanisole in convergent linearly polarized light gave a figure similar to that due to a positive crystal cut perpendicular to its axis. For lower magnetic field strengths the figure became faint and unsymmetrical and finally vanished. These observations were made in a container that had been treated before use with sodium hydroxide solution. If the container was previously treated with sulfuric acid the polarization figure did not vanish as the magnetic field was decreased in strength. This difference in figures was explained as due to the influence of the washing solution on the container, thus changing the orienting effects of the walls on the molecules.

Naggiar (295) used a 0.1 mm. film of *p*-azoxyanisole stretched across a hole to study the effects of a magnetic field parallel and perpendicular to the surface of the film. In the magnetic field parallel to the surface, extinction is found between crossed nicols when one of the nicols has its direction parallel to the magnetic field. From a corresponding observation in the absence of a field, it follows that in the parallel magnetic field the optic axes of the swarms are all parallel to the free surface of the drop. If the magnetic field is perpendicular to the surface of the film, the birefringence rings disappear at a particular value of magnetic field strength and new rings appear which are at the outer circumference of the film, but rings do not appear at the center of the drop. Naggiar suggested that this phenomenon was due to a readjustment of the nematic structure within the system but not near the free surface.

Mixtures of *p*-azoxyanisole and methoxycinnamic acid, as well as other mixtures, between glass plates were subjected to a parallel and a perpendicular magnetic field (398). Molecular layers near the surface were oriented perpendicular to the surface, although the pure components form molecular layers parallel to the glass surfaces. The constant that characterizes the deformation properties of the mixture is determined by the transformation temperature of the mixture rather than the percentage composition. In an electrical field the dielectric anisotropy of the mixture reverses sign at a definite temperature determined by the concentration of the components.

The appearance of oriented, soft, twinned crystals in drops of anisotropic *p*-azoxyanisole on muscovite has been explained as due to impurities which are soluble in liquid *p*-azoxyanisole but separate on cooling (134).

The parachors (329) of *p*-azoxyanisole, *p*-azoxyphenetole, and *p*-methoxybenzalazine at different temperatures were calculated on the assumption that the azoxy compounds contain the grouping $O \leftarrow N = N$. The parachor of the nematic structure decreases to a minimum value and then increases abruptly a few degrees before the C-N point to attain a value 12–14 units higher at the N-L point. The abrupt rise is explained by Ray (329) on the assumption that the molecules in the nematic structure are associated in swarms of seven or eight individual molecules.

Ultrasonic absorption and diffusion have been discussed by Gierer and Wirtz (137) in terms of the structure of the mesomorphic state on the basis of a relaxation effect of the structure. It appears that the ultrasonic absorption affects the fluidity of the liquid. The adiabatic compressibility and molecular sound velocity were calculated by Gabrielli and Verdini (115) for *p*-azoxyanisole and cholesteryl benzoate throughout their mesomorphic state ranges and into the liquid region. This involved obtaining the velocity of propagation and coefficient of absorption of ultrasonic waves. Cholesteryl benzoate showed no unusual effects, but an anomalous variation of ultrasonic velocity, absorption, and molecular sound velocity with temperature was obtained with *p*-azoxyanisole with a maximum of compressibility and of absorption coefficient at the N-L point. Hoyer (171) used a pulse-reflecting technique and obtained maximum compressibility and maximum absorption of ultrasonic waves by cholesteryl benzoate very close to the N-L point.

Mesomorphic substances were shown by Mann and Spence (257) to be able to produce a rotation of the plane of polarization in a circular wave guide placed in a transverse magnetic field. The rotation most likely results from the differences of absorption coefficients and of phase shifts along and transverse to the direction of the magnetic field, with the former predominating as indicated by a strongly polarized emergent wave. Although the rotation per wavelength was found to be quite large even at small values of the magnetic field, the possible rotation is limited by certain saturation effects.

Anisotropic absorption of mesomorphic biaxial molecules in a constant magnetic field has been reported by Kikuchi (200). Since the molecules of liquid crystals have two axes, the electric and the magnetic, the constant magnetic field tends to freeze the motion of the magnetic axis, while the electric axis will attempt to follow the electrical field. In addition, the molecular axes will show rotational Brownian motion. These developments can be constituted into a diffusion equation, similar to ones published by Gans (116) and by Perrin (315).

Studies (287) of the influence of a magnetic field on the heating and cooling curves have been made, but the results were not conclusive.

Hulett (173) made a study of the pressure–temperature curves for a number of substances that exhibit mesomorphism. In general he found a linear relationship between increase in temperature and increase in pressure. Lyons and Rideal (250) related their findings of pressure versus area per molecule on a unimolecular film of sodium palmitate with those of Hulett and concluded that the liquid-condensed types of films corresponded to the smectic structure of liquid crystals.

The influence of pressure on the C-N and N-L points of *p*-azoxyanisole was determined by Pushin and Grebenshchikov (326). The variation with pressure, *p*, of the N-L point (135.9°C.) and the C-N point (117.3°C.) is given by the equations $t_p = 135.9 + 0.03949p$ and $t_p = 117.3 + 0.0256p$, respectively, using pressures up to 1088 and 2645 kg. per square centimeter. Piezometric research on many liquid crystals has been performed by Robberecht (339), using pressures up to 950 kg. per square centimeter. The C-M transition temperature showed less increase with pressure than the M-L transition temperature. The former transition had a value of dt/dp which differed with each compound, while the latter dt/dp ratio appeared to have a value approaching 0.05 for most compounds tested.

Herz (162) attempted to relate the C-M point (T_c) of mesomorphic substances to the M-L point (T_k). Taking values from Landolt-Börnstein (209) an average value of T_c/T_k was found to be 0.94.

A small change in volume was associated with the N-L transition temperature for *p*-azoxyphenetole, according to Bauer and Bernamont (9). The measured maximum cubic coefficient of expansion is 0.00146 at 166.2°C. (the N-L temperature).

From the C-N and N-L points for homologous ethers of azoxyphenol, azophenol, and azomethinephenol a thermal persistence order was derived by Weygand and Gabler (446). The observed persistence order of the mesomorphic phases of the azoxy compared to the azo and the azomethine series is both qualitatively and quantitatively related to the molecular weights of the three groups of compounds. Although the data appear to support this contention for comparison of these three groups, most other systems cannot be readily fitted into the order.

Measurement of thin films on surfaces can be observed and measured by phase contrast (98). This contrast difference, measured photometrically, enables the thickness to be deduced within 2 A. Layers of stearic acid of unimolecular thickness on glass were found to have a thickness of 24 A.

Lehmann (233) suggested that liquid crystals possess the power of self-purification. For example, finely powdered particles of an impurity added to a solution of *p*-azoxyanisole in bromonaphthalene will be forced out of the spherical drops of liquid-crystalline *p*-azoxyanisole as they are formed and the drops will be perfectly clear.

Very recently two interesting types of compounds have been found that exhibit mesomorphism. Diisobutylsilanediol exists as a mesophase between 89.5°C. and 101.5°C. (86). The mesophase is optically negative and cannot be classified unequivocally as smectic, nematic, or cholesteric as these structures have been defined by Friedel (104). The diisobutyl compound is the only one of the dialkylsilanediols that has been reported as giving the mesomorphic state. Fürst and Dietz (113) have shown that *N*-methyl(3-*n*-alkoxypyridinium)methosulfate and *N*-methyl-(*n*-alkyl-3-pyridylsulfide)-*p*-toluolsulfonate and related compounds exhibit long mesomorphic ranges.

Attempts have been made to attribute some properties of metals and alloys to the mesomorphic state (94, 297).

XI. Mixed Liquid Crystals

Few systematic studies have been made on binary systems of substances that exhibit the mesomorphic state. A number of investigators made studies which were important to the general field of mixed liquid crystals and these will be considered briefly. After this background on the general contributions, additional details will be given on the more recent papers in the field.

The modifying action of a foreign substance on mesomorphic structure has been discussed in general terms (135), while various samples of *p*-azoxyanisole containing different amounts of impurities were shown (192) to give different values for the critical frequency of the applied electrical field at which the orientation of the mesomorphic phase disappeared. It has been reported that the anisotropy of *p*-azoxyanisole decreased with the addition of foreign substances (380).

The addition of minute quantities of a circularly polarizing compound to an optically inactive nematic structure can transform it into a strongly active and pleochroic one; the rotatory power of such a system is proportional to the amount of asymmetric substance present (105). Several differences, especially dextrorotatory versus levorotatory property and the heating and cooling transitions, were noted and described when phlorizin, cholesterol, its benzoate, propionate, or isovalerate, ergosterol, or other optically active substances were added to *p*-azoxyanisole (136). Collective liquid crystallization can often be brought about rapidly and uniformly when cholesteryl chloride is added to other mesomorphic compounds.

The addition of a substance that showed a large tendency to set uniaxially, e.g., *p*-ethoxybenzalamino-α-methylcinnamic acid, brings randomly arranged mesomorphic compounds into a uniaxial arrangement. The structure of the planes noted in amyl cyanobenzalaminocinnamate may be observed in mixed cholesteryl salts and mixtures of cholesteryl salts with liquids such as *p*-azoxyphenetole (109, 110). The C-N point and N-L point curves of mixtures of *p*-azoxyphenetole with *p*-azophenetole, of *p*-azoxyanisole with *p*-azoanisole, and of *p*-azoanisole with *p*-azophenetole have been investigated (26). The azoxyphenetole and azophenetole system is isomorphous and forms a continuous series of mixed compounds.

Mesomorphic compounds were obtained by melting cholesterol in turn with succinimide, the tartaric acids, malic, maleic, lactic, malonic, succinic, cinnamic, and anisic acids (123, 125); by melting ergosterol propionate, acetate, and butyrate with glycolic acid, glycerol, and orcin (119); and by melting compounds of cholesterol and ergosterol with urea (120).

Tammann (390) prepared mixtures, in different ratios, of two compounds that exhibit liquid crystallinity when by themselves and observed them under a microscope; he observed that many of the mixtures were mesomorphic. Gaubert (126) mixed cholesteryl propionate (optically negative) and ethyl anisalaminocinnamate (optically positive) and determined the refractive indices at different concentrations. The double refraction of the mixtures using sodium light was found to increase from $n_0 - n_e = 0.0177$ to 0.1009. This effect occurs in spite of the fact that the two substances have different optical character.

Lehmann (225) made measurements of transformation temperatures on mixtures of two substances that exhibit mesomorphism as well as mixtures of two substances one of which does not exhibit mesomorphism. Vorländer and Ost (437) made a detailed qualitative study of the C-M point lowering caused by mixing several pairs of mesomorphic substances. In some cases the C-M point of the hybrid was calculated empirically and compared with the observed value. Smits (365) deduced a theoretical P–T–X (pressure–temperature–composition) diagram for two components which are miscible in all proportions in the mesomorphic state. From this diagram he pointed out that the relations of special cases of mixtures may be obtained by making sections.

Mlodzeevskiĭ (285, 286) studied cholesterol and cetyl alcohol systems as well as cholesterol and glycerol systems. It was found that mixtures of cholesterol and cetyl alcohol form mesomorphic systems yielding two solid phases at the lower transformation temperature and a liquid and a solid phase at the upper transformation temperature. Cholesterol and glycerol mixtures yield a solid and a liquid phase at the lower transformation temperature and two liquid phases at the upper temperature. Using thermodynamic principles, Mlodzeevskiĭ constructed phase diagrams corresponding to these phenomena.

Kravchenko and Pastukhova (202–204) have made a series of studies of the mesomorphic systems formed by two-ring components such as indene, isoquinoline, and naphthalene with each other and with coumarone. They found that indene and naphthalene form an uninterrupted series of solid solutions which exhibit the mesomorphic state over temperature ranges of 7° to 10°C. Other combinations of compounds gave interesting results, some with smaller, others with larger ranges of mesomorphism. Phase diagrams are given for the different systems.

Bogojawlensky and Winogradow (27) and later Walter (441) pointed out that the boundary separating the mesomorphic state and the liquid regions in the phase diagrams is linear. This implies that a perfectly mixed mesomorphic system of two components is being formed analogous to a similar series of solid solutions. They deduced that in cases where only one component appears to exhibit mesomorphism, the other must have a potential or latent mesomorphic property. These substances that do not exhibit mesomorphism but potentially possess it evade observation because the transition to the liquid lies below the normal melting point. Bogojawlensky and Winogradow, and also Walter, deduced the transition temperature for a number of substances by extrapolation; they even found it possible to obtain the mesomorphic state for pairs of substances whose individual components showed no nematic structure. The melting points of the mixtures were so depressed as to allow the mesomorphism of the mixtures to be observed.

Several rather extensive studies have been made on binary systems of substances in the mesomorphic state; these studies will be summarized in some detail. De Kock (201) and Prins (324) studied binary systems in which one or both components showed mesomorphism and discussed the results in terms of

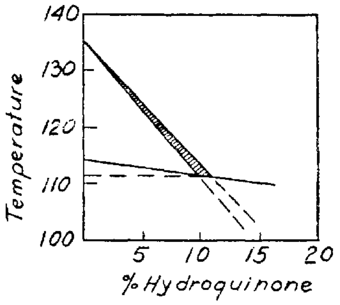


FIG. 42.

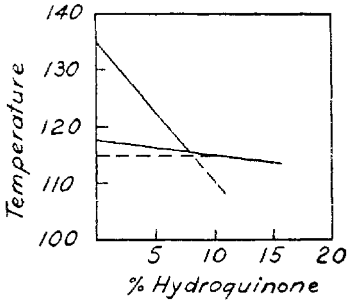


FIG. 43.

FIG. 42. Phase diagram for the system *p*-azoxyanisole–hydroquinone (after de Kock (201)).

FIG. 43. Phase diagram for the system *p*-azoxyanisole–hydroquinone (after Dave and Dewar (70)).

the phase rule. They concluded that the M-L transition temperature should not occur sharply in two-component systems but that, as a rule, there should be a range of temperatures over which the two mesomorphic phases of different composition could coexist. Figure 42 shows the phase diagram of the system *p*-azoxyanisole–hydroquinone as interpreted by de Kock. Hydroquinone alone does not exhibit the mesomorphic state, while *p*-azoxyanisole does. De Kock interpreted the shaded area as a region in which two distinct liquids coexist, one isotropic, the other anisotropic. The experimental evidence on which de Kock based his results is scanty. The transitions were followed mainly by observing the change in the liquid from cloudy to clear without careful temperature control and without stirring. Dave and Dewar (69) repeated the experiment with the system *p*-azoxyanisole–hydroquinone with great care and obtained the phase diagram shown in figure 43. The phase diagram in figure 43 does not show any indication of the two-phase liquid system observed by de Kock.

Dave and Dewar concluded that mixtures of anisotropic liquids are in all cases homogeneous one-phase mixed mesomorphic systems. Using a variety of "solute" molecules in *p*-azoxyanisole, it was found that the main qualitative difference in the phase diagrams lies in the slopes of the anisotropic liquid-liquid transition lines. These slopes are steeper the more the "solute" molecules depart from the phenomenon of mesomorphism.

Dave and Dewar (70) extended their study of the effect of structure on the transition temperatures of mixed liquid crystals. It seems reasonable that any substance with anisotropic molecules would form a liquid crystal if it could be obtained in liquid form at a sufficiently low temperature. If the molecules are asymmetric, or if the form fields around them are asymmetric, the internal energy of the liquid would be less if the molecules were all oriented parallel to one another in an appropriate mutual relationship. In other words, a nematic form of the substance must have a lower energy than the true liquid, and this in turn implies that the true liquid will undergo transition to a nematic structure if it is cooled sufficiently. Whether this nematic form can be observed in practice will depend on the C-N point; in most cases the transformation will be virtual, since it will be below the C-N point.

In the case of a mixture of two different substances both with asymmetric

TABLE 25

Transition-line slopes for compounds of the type p-y—C_6H_4—x—C_6H_4—z-p mixed with p-azoxyanisole

Dave and Dewar (70)

Slope in °C. per 10 per cent change in molar composition

	y	x	z	Slope		y	x	z	Slope
1.	H	CH=N	H	29.5	12.	CH_3O	CH=N	Br	11.0
2.	H	N=N	H	28.0	13.	Cl	N=NO	Cl	10.0
3.	CH_3	CH=N	H	26.0	14.	CH_3O	CH=N	Cl	9.5
4.	H	N=NO	H	25.0	15.	Cl	CH=N	OCH_3	9.0
5.	H	CH=N	$N(CH_3)_2$	23.0	16.	CH_3	CH=N	OCH_3	9.0
6.	H	CH=N	OCH_3	22.0	17.	CH_3O	CH=N	CH_3	8.5
7.	CH_3	CH=N	Br	16.0	18.	NO_2	CH=N	CH_3	8.0
8.	CH_3	CH=N	CH_3	14.5	19.	CH_3O	CH=N	$N(CH_3)_2$	7.5
9.	Cl	CH=N	Cl	14.5	20.	CH_3O	CH=N	OCH_3	4.0
10.	Cl	CH=N	CH_3	14.5	21.	NO_2	CH=N	OCH_3	2.5
11.	CH_3	CH=N	$N(CH_3)_2$	13.0					

molecules, two factors will influence the ease of formation of liquid crystals: (*1*) the ability of the molecules to pack into a single liquid-crystalline "lattice" and (*2*) the decrease in energy on the orientation of the liquid. If the two components are of similar size and shape, the steric factors will be uniform for mixtures of all compositions. If the molecules of the two components differ in size and shape, there will be more difficulty in packing them together. The transition temperature should be less than that predicted for the "ideal" behavior considered previously. The transition line in the phase diagram should then be concave upward; when the components differ markedly the concavity should show a minimum. Such a behavior was found by Dave and Dewar (69) with mixtures of *p*-azoxyanisole and *p*-anisic acid. Mixtures of compounds that have extremely little tendency to form liquid crystals and a substance such as *p*-azoxyanisole should yield a phase diagram in which the slope of the transition line is very steep. Table 25 from Dave and Dewar (70) shows the slopes of the transition lines of mixtures of *p*-azoxyanisole and molecules of similar shape. The lower the slope, the greater is the tendency for the second component to form a mesomorphic system with *p*-azoxyanisole.

Several conclusions may be drawn from table 25. First, isomeric pairs have similar slopes (e.g., Nos. 14 and 15 in table 25). Secondly, the presence of two polar groups in the molecule is necessary for a low value of the slope. Thirdly, the effects of terminal groups are approximately additive, the order of group efficiency in mesomorphic formation being $NO_2 > OCH_3 > (CH_3)_2N > CH_3 > Cl > Br > H$. Fourthly, the effects of Cl and CH_3 are quite similar. Lastly, the large effect of the nitro group is surprising, since few liquid-crystalline nitro compounds are known.

It was suggested by de Kock (201) that the depression of the N-L point by solutes might be used as a method of determining molecular weights. This was pursued further by DuPont and Lozac'h (85), using *p*-azoxyanisole as the cryoscopic solvent in the Rast method. Dave and Dewar (70) point out from their study that the use of the N-L point to determine molecular weight would be correct in principle only if the solute were almost insoluble in the mesomorphic substance, the two-component liquid being a mixture of two phases, one containing only the liquid-crystalline component and the other being a normal liquid containing both components. Dave and Dewar (69) showed that birefringent two-component liquids are composed of single liquid-crystalline phases. Reproducible molecular weights could not be obtained by using the method of depression of the N-L point (70).

Dreyer (82) has made commercial applications of mixed liquid crystals.

XII. Lyotropic Mesomorphism

A. GENERAL

Those systems that exhibit lyotropic mesomorphism are not discussed in the literature as extensively as those mesomorphic systems prepared by the thermal process. There is, however, no doubt that these lyotropic systems possess properties comparable to those prepared by heating certain pure compounds. The studies of the properties of lyotropic mesomorphic systems have not, in most cases, been as thorough or as extensive as those of the thermally prepared systems.

The relationships between the mesomorphic phase and colloidal systems have been reviewed by Ostwald (311). A few years later, Lawrence (214) discussed three subclassifications of mesomorphism: (*1*) crystalloidal mesoforms of soaps, (*2*) colloidal mesoforms of soaps, and (*3*) structure in mesomorphic crystalloidal solutions in general. The swelling and molecular organization of colloidal electrolytes have been discussed by Dervichian (72). He showed that by mixing two long-chain substances, one soluble and the other insoluble in water, different types of equilibria could be formed such as myelinic figures, anisotropic droplets, and coacervates. A general theory was formulated to explain the limited amount of water that can enter some systems, e.g., a mixture of cholesterol and sodium lauryl sulfate. Booij (28) has presented a very interesting discussion of association in soap solutions.

When substances like bromophenanthrenesulfonic acid are mixed with water, they form mesomorphic phases which appear similar to those of pure anisotropic melts and to soap solutions. Sandquist (346–348) prepared a series of aqueous systems of 10-bromo- and 10-chlorophenanthrene-3(or 6)-sulfonic acids which on cooling showed mesomorphic states as shown by optical properties and the existence of a critical point. The colloidal nature of the solutions varies considerably with the concentration, the temperature, and the presence of foreign substances. There seems to be no change in viscosity at the N-L transition. According to Lehmann (238), 10-bromophenanthrene-3(or 6)-sulfonic acid forms two mesomorphic hydrates with water, which appear to form mixed crystals to a limited extent. Mesomorphic forms also exist for the alkali salts of the higher homologs of 3-methylcyclopentylcarboxylic acids.

Balaban and King (6) have described the mesomorphic phases of the substituted naphthylaminedisulfonic acids and related compounds. Structurally these compounds are far removed from the fatty acid type and belong more with the organic dyes or 10-bromo- and 10-chlorophenanthrene-3(or 6)-sulfonic acids. These derivatives of naphthylaminedisulfonic acids are soluble in hot water, and upon cooling give highly hydrated products which may vary greatly in consistency. They have been reported to exist in such forms as waxy state, limpid fluids which exhibit a sheen, clear gels, or wormlike growths but in almost all cases strongly birefringent. Alcoholic solutions generally do not exhibit these forms and a high degree of hydration seems essential. The mesomorphic character of aqueous systems of a large number of alkali metal and ammonium salts of a number of fatty acids, sulfonates, etc., has been described (473).

Trapeznikov (394, 395) has considered the temperature dependence of monolayer pressure as a method of studying the hydrates of higher aliphatic compounds and their mesomorphic phases. The hydrates of higher alcohols have been studied especially with reference to the latent heats and temperatures of phase transformations in the monolayer and in bulk amounts of the hydrates. Crystals of palmitic acid, when dissolved in hydrochloric acid, were found by Trapeznikov (396) to form hydrates with liquid-crystalline properties. Gaubert (130) has reported a mesomorphic phase of calcium phosphate formed by the reaction of phosphoric acid and calcite, while Paul (313) has reported one for a mixture of rosin, alcohol, and soda solution. Gaubert (127) found that evaporation of solutions of anisal-*p*-aminoazotoluene in organic solvents such as diethyl ether, chloroform, and carbon disulfide gave a liquid-crystalline system which proved to be unstable. A number of nonionic wetting agents such as polyethylene glycol oleate show the nematic structure when mixed with controlled amounts of water (83).

B. SOAPS

1. Lyotropic soap systems

Lehmann (221) was the first to recognize the mesomorphic state of ammonium oleate in aqueous solution. Later, soap solutions and myelin forms were mentioned by Adami and Aschoff (1) and by Friedel (104). An insight into the scope and breadth of the field and the start of experimentation into the equilibria involved were provided by Maclennan (251) and by McBain and Langdon (272).

The review by McBain (268) on typical colloidal solutions embracing soap and soap solutions discusses the forms known up to that time. Only the neat and middle soap mesomorphic phases had been distinguished and these are discussed. The anisotropic anhydrous neat phase can be admixed with water and even salt in various proportions without losing its homogeneity, and in this paper the anhydrous neat phase is continuous with the neat phase of the soap kettle. Middle soap exists between the neat and the isotropic phases, and the range of concentration in which it can exist is quite wide. Addition of salt to form a soap–salt–water system involves no new features except the change in limits of concentration for different phases. The salt favors the formation of isotropic solutions with a corresponding decrease in the middle soap.

McBain and Elford (270) and Dervichian (72) pointed out that the aqueous neat and middle phases are both smectic structures—systems of variable water content which may or may not contain other dissolved components such as electrolytes. Vold (414) pointed out that these are of importance in both soaps and synthetic detergents such as the sulfonates.

According to Lawrence (214) the action of the water (or other "solvent") and heat are not dissimilar in regard to the effect of breaking the bonds holding the molecules in their crystalline orientations in one or possibly two directions. In solution, this permits the entrance of "solvent" molecules into the lattice, with a corresponding swelling of the structure. Time is often an important factor, for equilibrium is reached in some cases only after long periods of time. The phase rule has been applied to the soap systems by many workers and shows how narrow are some of the limits of the mesomorphic phases. The narrowness of the phase ranges helps to explain contradictory statements concerning these phases. A number of phase studies have been made on soap systems. For example, Vold (415) has reported phase equilibria studies on sodium oleate; Vold and Vold (424) on sodium laurate; Vold and Ferguson (418) on sodium palmitate; McBain, Vold, and Frick (277) on sodium stearate; Vold, Reivere, and McBain (422) on sodium myristate; and Gonick and McBain (139) on hexanolamine oleate. These papers show solubility measurements as well as dilatometric measurements. The vapor pressure–concentration curves for aqueous sodium palmitate and sodium laurate exhibit flats at 90°C. which have been interpreted as indicating the possible coexistence of two phases in equilibrium.

Vold and Vold (424) found that the ratio of activity to mole fraction of the soap, a_2/N_2, decreased uniformly for both waxy soap and the curd fiber phase as the amount of soap was increased. The net change in the ratio for the middle soap and neat soap is slight and qualitatively different from those for waxy soap. The activity–concentration curves are discussed in terms of possible structures for these mesomorphic phases.

The anisotropic liquid phases of systems containing the exceptionally soluble colloidal electrolyte hexanolamine oleate and water have been discussed by Gonick and McBain (139) and Ross and McBain (344). They found a minor decrease in electrical conductivity in passage from the isotropic solution of the colloidal electrolyte to the anisotropic phase. The colloidal particles are micelles existing in both phases but oriented in a parallel manner in the anisotropic phase. These lamellar micelles consist of alternate layers of soap and water. The soap molecules are packed side by side, and thus give rise to the side spacings observed in the x-ray data. The long spacings obtained are attributed to alternate layers of soap and water, and the spacings increased approximately linearly over the range of concentration studied.

McBain (268, 269) has shown that in systems where only liquid or mesomorphic phases are involved, a mixture of soaps with water and salt is similar in behavior to that of a single soap. McBain, Lazarus, and Pitter (273) have shown that the system potassium oleate–potassium laurate–water presents the same phases as found in either soap alone. McBain, Vold, and Jameson (278) presented a phase rule study of the mixed soap system sodium palmitate–sodium laurate–sodium chloride–water at 90°C. From their data a curve was constructed which would permit fairly accurate prediction of a phase diagram for any mixture of the two soaps. Smith (363) showed that the system sodium oleate–sodium chloride–water has one more degree of freedom than is allowed by the phase rule at 25°C. because the solubility of the curd fibers varies with their diameter. Smith has also discussed the solvent properties of soap solutions in general, while considering three- and four-component systems. The many phases exhibited by systems such as sodium oleate, ethyl acetate, and water and these three plus sodium chloride have been examined in terms of middle, neat, and curd soap composition. It is found that the quaternary system (use of sodium chloride) introduces no new phase and retains all phases found in three-component systems.

Vold and Heldman (419), using electrical conductivity measurements, came to the conclusion that the anhydrous neat and subneat soap phases of sodium palmitate and sodium stearate could incorporate no more than 3–4 per cent of water without transformation to another phase. Conductivity values for the neat soap phase resembled those for ordinary salts. Changes in slope of the plot of the specific resistance versus temperature curves could be attributed to phase changes occurring in the sample. Calculations of the energies and entropies of activation for conductivity in subneat and neat soap were made, and are correlated with the discrepancies between the calorimetric and dilatometric results for the transition temperature between subneat and neat soaps reported by Vold (417).

Recently Rosevear (343) has reported microscopy studies of the mesomorphic neat and middle phases of soaps and synthetic detergents. Certain nongeometric textures are exhibited by middle soap but not by neat soap, while certain planar textures exhibited by neat soap are not found in the middle phase, and thus the identification of phase mixtures is often possible. The findings also apply to certain dyes and wetting agents. This article contains very beautiful photomicrographs of different aspects of the mesomorphic state.

2. Soaps in organic liquids

McBain and Field (271) and McBain and Stewart (276) have studied the phase equilibria for acid soaps using visual, microscopic, and dilatometric methods. They discuss the amounts of corresponding fatty acid that can dissolve in mesomorphic soap phases and still obtain a homogeneous conic anisotropic phase. In the phase diagram, an isotropic phase in equilibrium with the two components in different structures (mesomorphic or solid) are found in one area, while a heterogeneous region consisting of mixtures of two immiscible phases is found in the other area. Lawrence (216) has reported a systematic examination of soaps in Nujol, while Vold, Leggett, and McBain (420) have studied sodium palmitate in organic liquids such as glycerol, diethylene glycol, isopropyl alcohol, palmitic acid, and many others. At sufficiently high temperature the soap is completely miscible in all proportions with these solvents and forms isotropic liquids, but at lower temperatures anisotropic gels, mesomorphic phases, wax-like phases, and crystalline phases are observed. It is concluded that there may be a dependence of solubility on polarity which may be related to secondary valence forces. These forces would involve nonstoichiometric complex formation between polar solvent molecules and the dipole of the soaps.

Soap–oil solutions have been investigated by Doscher and Vold (76–78) as well as by Smith and McBain (364). Very small amounts of water have pronounced effects on the physical behavior. Conductance, viscosity, and optical properties of the anhydrous sodium stearate–cetane systems indicate the existence of large mesomorphic aggregates above 117°C. Dielectric absorption curves by Doscher and Davis (75) indicate that the role played by water in stabilizing these sodium stearate–cetane systems is related to the peptization of the mesomorphic aggregates above 117°C. and conversion to crystals of soap when the systems are taken below this temperature.

Hyde, Langbridge, and Lawrence (176) have discussed ternary systems of the type soap–water–amphiphile. The soap may be carboxylate, sodium alkyl sulfate, alkyltrimethylammonium bromide, alkylpyridinium bromide, or nonionic. The usual amphiphilic solubilizate would be fatty acid, alcohol, phenol, or amine. Branched-chain or aromatic substituents have been studied for both components. A general phase equilibrium pattern was found to apply to all soaps and to all amphiphilic additives containing a straight chain of at least five carbon atoms. Certain minimum amounts of amphiphile have to be added to soap solutions before a mesomorphic form is obtainable. The physical properties are dependent upon the concentration of the soap and upon the nature of the polar groups and the hydrocarbon chain length for both additive and soap. These authors further state that the formation of the smectic structure is a true transition from spherical micelle to layer lattice due to greater order of the system because of closer packing of the solute. The smectic region is considered an analog of a solid solution. Such physical properties as electrical conductivity, viscosity, surface tension, and refractive index were also used to study the system of a branched-chain sodium alkyl sulfate (Teepol) in water plus amphiphiles such as phenols and amines. Hyde, Langbridge, and Lawrence (176) raise a serious question about the validity of data on phase equilibria of this type taken by other research workers; the concern is whether equilibrium was really attained in the systems under observation.

C. IONIC AND NONIONIC DETERGENTS

Broome, Hoerr, and Harwood (45) have discussed the binary systems of water with dodecylammonium chloride and its *N*-methyl derivatives. Several mesomorphic phases are found to exist which are similar to those reported by Vold, Reivere, and McBain (422) for soap diagrams. Although these cationic colloidal electrolyte systems have regions corresponding to the "middle," "neat," and "curd-fiber" phases of the soap–water systems, they do not display the numerous changes referred to as "waxy" and its variations. Except for one transition found in dodecylammonium chloride at 57.5°C., no phase changes were observed in any of the other anhydrous amine salts.

Marsden and McBain (262) have studied the aqueous systems of nonionic detergents by the use of x-ray diffraction and have given a discussion of the smectic phases. Bury and Browning (48) have compared the nonionic and ionic detergents using *n*-octyl glucoside and *n*-octylpyridinium bromide as typical examples, but the mesomorphic phases are discussed only briefly. Marsden and McBain (262) used x-ray data to show that many detergent–water systems show a change in long spacing of the mesomorphic structure with changes in concentration.

The phase equilibrium data and behavior of solutions containing water, water-soluble organic solvent, water-insoluble organic solvent, and amphiphilic salt have been reported in detail by Winsor (458, 460–462). At high concentrations of amphiphilic salts, and in certain multicomponent systems, smectic phases are produced. They are most often gelatinous and appear to contain one form of micelle. Aqueous solutions of sodium 3-undecyl sulfate are isotropic but form mesomorphic phases when aqueous solutions of cyclohexylamine and hydrochloric acid are added. An anisotropic phase (gel) of this system which was not normally turbid was subjected to an electrical potential of the order of 30 volts per centimeter until maximum turbidity was obtained (approximately 30 sec.). The turbidity decreased on removal of the potential but a residual turbidity was found. This phenomenon occurred only in concentrations of the mesomorphic phase range. Winsor (459) obtained a similar turbidity phenomenon for other mesomorphic solutions containing an amphiphilic salt. Other systems studied were potassium 7-tetradecyl sulfate, aerosol OT, and sodium 8-pentadecyl sulfate. The phenomenon was attributed to the alignment of a randomly oriented anisotropic solution by use of the electrical field. A corresponding change in the refractive index was observed. An alternating current of 50 cycles per second did not produce the effect.

Philippoff and McBain (320) have studied the anisotropic aqueous phases of some detergents and found that all the water added appears to enter an expanded lamellar lattice. In the system aerosol OT (sodium dioctylsulfosuccinate)–water, the mesomorphic phase at 25°C. extends from almost the pure solid crystal to about 16.5 per cent aerosol OT. An equation has been derived which assumes that swelling occurs only in one direction and that the amount of swelling is determined solely by volume increase due to the added water. X-ray long-spacing data at various concentrations and swelling fit the equation for this system as well as for aqueous glyceryl monolaurate and diglycol laurate. Systems which do not follow this behavior have also been reported, and the references for these cases are also given (320). McBain and Marsden (275) reported that many lyotropic mesomorphic systems of detergents and soaps give birefringent smectic or nematic structures. In the smectic structure the small-angle x-ray diffractions are in the order of $1:\frac{1}{2}:\frac{1}{3}$ and correspond to the first, second, and third orders of a repeating distance which has been found to increase inversely as the concentration of the system until a limiting concentration is reached where the structure breaks down and addition of more water gives a new phase. The long spacing at the limiting concentration may lie between 100 and 200 A. In other systems, called the nonexpanding lamellar type (275), the long spacing does not change on dilution.

A comparison of the dodecylsulfonic acid–water system with typical soap solutions was given by Vold (414). The lithium, sodium, and potassium dodecylsulfonates each have only one mesomorphic phase resembling the subneat soap, and the phase rule diagram of these salts with water is similar to those of sodium soaps. Dodecylsulfonic acid itself does not, however, form any mesomorphic phases in the absence of water, in contrast to the soaps, and yet in water at least two mesomorphic phases are obtained which correspond closely to the superneat and middle forms of the soap system (277). The thermal stability of the anisotropic solutions is also similar for both systems, as are the microscopic appearance and consistency.

D. LYOTROPIC MESOMORPHISM OF DYES

Since Zocher and Coper (472) first showed that Methylene Blue and Neutral Red as well as other dyes gave orientation on a rubbed surface, many dyes have been tested for mesomorphic character. Gaubert (127, 132, 133) showed that *p*-aminoazotoluene, tartrazine, and Brilliant Crocein with water gave mesomorphic phases, while Branner (41) showed the same for the potassium salt of Methyl Orange.

Dreyer (80) has discussed the behavior of films from the aqueous solutions of amaranth and Naphthol Yellow S, as well as dyes of other classes which exhibit a mesomorphic phase.

Sheppard's work (362) on 1,1′-diethyl-2,2′-cyanine salts (diethyl-ψ-cyanine) proposes a new type of nematic molecular phase, that of plurimolecular filaments rather than elongated molecules. The structure proposed involves intermolecularly coördinated water molecules between opposite terminal nitrogen atoms along parallel resonance chains. Porphyrins and phthalocyanines could also exist in forms of the proposed structure, although these dyes are assumed to involve intermolecular hydrogen bonding and different conditions for intermolecular resonance. In addition, the effects of aggregation and environment on absorption spectra are also discussed in detail. Both Jelley (180) and Scheibe (350), independently, reported an absorption (and fluorescence) band corresponding to a slight vibration parallel to the axis of the filament.

Jury and Ernst (185) support the idea of Scheibe and Kandler (351) and of Scheibe, Kandler, and Ecker (352) that the orientation, and hence the mesomorphic phase, is due to the association of molecules resulting from secondary valence forces. They base their judgment upon studies of photographic sensitizers as well as of dyes which give mesomorphic solutions.

XIII. BIOLOGICAL SYSTEMS

The one field of research in the mesomorphic state that has been most neglected is that of the biological areas of study. Many brief references or observations have been noted, but only a few investigators have made any effort to apply the knowledge gained about the mesomorphic state to certain aspects of living matter, even though it appears to the authors that much could be gained by such an effort.

The authors of this article have attempted to include those pertinent papers related to biological systems that are found in abstract journals. Since some papers on biological systems make only minor mention of mesomorphism, it would appear that they are not indexed as such in abstract journals. Again it would appear that authors of a number of papers describing properties of certain biological systems are not aware of the mesomorphic state and thus do not consider it in their discussions. In addition to the papers cited in this section, some others may be found in Section IX.

It would be extremely difficult, if not impossible, to interpret all of the literature on biological systems that makes any mention of properties showing resemblance to properties characteristic of the mesomorphic state. Some of the literature mentions such properties as birefringence and turbidity but, as may be learned from the previous sections of this review, these properties alone are not sufficient to prove the presence of the mesomorphic state.

Of recent years the literature pertaining to biological systems has been introducing the idea of mesomorphism. A perusal of journals such as *Discussions of the Faraday Society* and *Biochemica et Biophysica Acta* and of the annual issues of *Progress in Biophysics and Biophysical Chemistry* will result in the location of the description of a number of biological systems that show mesomorphism and are thus discussed in this light. In a recent paper, Kacser (186) pointed out that there is good evidence that native protein and nucleic acid in genetic material are paracrystalline. Feughelman (93) gives experimental evidence to this effect.

It may be pointed out that the mesomorphic state is singularly well fitted to provide complex forms in which organization and lability can be combined to a unique degree. Compounds can be found in the biological systems whose molecular structure and orientation represent every intermediate degree of orientation, plasticity, and viscosity between crystalline substances on the one hand and mesomorphism or even isotropic substances on the other. A quotation along this general line of thought will be given from Bernal,[3] who said:

> The biologically important liquid crystals are plainly systems of two or more components. At least one must be a substance tending to paracrystallinity and another will in general be water. This variable permeability of liquid crystals enables them to be as effective for chemical reactions as true liquids or gels, as against the relative impenetrability of solid crystals. On the other hand, liquid crystals possess internal structure lacking in liquids, and directional properties not found in gels. These two properties have far-reaching consequences. In the first place, a liquid crystal in a cell, through its own structure, becomes a proto-organ for mechanical or electrical activity, and when associated in specialized cells (with others) in higher animals gives rise to true organs, such as muscle and nerve. Secondly, and perhaps more fundamentally, the oriented molecules in liquid crystals furnish an ideal medium for catalytic action, particularly of the complex type needed to account for growth and reproduction. Lastly, a liquid crystal has the possibility of its own structure, singular lines, rods and cones, etc. Such structures belong to the liquid crystal as a unit and not to its molecules, which may be replaced by others without destroying them, and they persist in spite of the complete fluidity of the substance. They are just the properties to be required for a degree of organization between that of the continuous substances, liquid or crystalline solid, and even the simplest living cell.

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[3] Quoted from J. D. Bernal (16) by permission of the Faraday Society.

Wald (440) has pointed out that very little of a living cell is highly fluid. Most of the cell consists of molecules which have varying degrees of orientation to one another, i.e., most of the cell represents various degrees of approach to crystallinity. Wald points out that much of the dynamic plastic quality of cellular structure, the capacity for constant change of shape and interchange of material, derives from the property of liquid crystallinity.

The first observation of a mesomorphic state in biological systems, although not reporting it as such, seems to be the mention of myelin forms in 1854 (411). A few years later minute fatty globules from the juice of the suprarenal gland were found to exhibit double refraction under polarized light and to exhibit a small black cross in each drop when observed between crossed nicol prisms (279). Since these earliest reports, many substances and organs have been reported as exhibiting myelin forms or anisotropic systems under physiological or pathological conditions, and a score or so known by 1906 have been reviewed (2, 226).

An important feature of these myelin bodies, as well as of the acid esters of cholesterol—cholesteryl oleate, benzoate, propionate, stearate, palmitate, butyrate—and ammonium stearate and palmitate as well as others, seems to be the power of dissolving other substances while maintaining their mesomorphic character. In contrast to many ordinary crystalline substances that can only dissolve isomorphous components, these compounds can dissolve other mesomorphic type substances in large proportions and can even dissolve substances of entirely different molecular character. Undoubtedly myelin bodies play important roles in certain microbiological reactions where this dissolving power is of high significance. Diffused myelin, or myelins of lecithinlike nature, probably are essential constituents of the cells of most tissue. Indeed, the lecithin present in significant amounts in the red corpuscles probably fits these bodies "to be the common carriers of the organism" (2).

Many living tissues such as the muscles, tendons, nerves, organs, and bones show the optical property of double refraction (291). The magnitude, character, and conditions under which the double refraction exists are very different for each group and do not necessarily signify that the substance is in a mesomorphic condition. Muscle globulin solutions have been shown to possess a mesomorphic phase with a constant angle of isocline between 76° and 78°, whereas in pure liquids, where the viscosity is normal throughout, the angle of isocline is found to be 45°. If the muscle globulin solutions are practically salt-free, a clear gel can be formed by slow evaporation of excess water; if this thixotropic gel is studied under certain conditions, two crosses of isocline are observed with a black isotropic ring separating them when viewed between crossed nicol prisms (291). At a different concentration, the muscle globulin preparations have been found to give a colorless, viscous fluid when not in motion which appears dark when observed through a nicol prism in plane-polarized light. When the solution is set in motion, double refraction of flow is observed and the field of vision becomes bright. Typical denaturing agents destroy this double refraction of flow which has been associated with the orientation of anisotropic protein, probably myosin, which is responsible for the double refraction in the intact living muscle fiber (292, 293).

The diffuse double refraction often obtained in laboratory preparations from biological extracts has been attributed to gels or sols composed of anisotropic colloid particles (471). Aqueous commercial lecithin shows a smectic phase, but the pure synthetic form does not. When biologically isolated lecithin is added to water it swells and forms myelinic figures especially on the periphery, and soon cylindrical excrescences are observed. Lysolecithin, associated with cholesterol, behaves in much the same manner by swelling and producing myelinic figures; the insoluble cholesteryl molecular portion undoubtedly hinders the true solubility of the lysolecithin molecule. The myelins of the nerve sheath or of an alcoholic extract of the brain also behave much like lecithin. In contrast, cephalin is dispersed completely when similarly added to water (72). It has been found by Rinne (338) that merely moistening sphingomyelin, kerasin, and lecithin preparations with water or aqueous glycerol and heating causes the formation of a smectic phase. Phrenosin and kerasin were separated from galactosides of the brain by use of cold pyridine and mesomorphic forms were obtained (341, 342). Cerebron and nervon, in addition to the other compounds mentioned above, have also been reported as exhibiting a typical nematic structure on gentle heating (337).

Upon saponification of certain fats, myelin forms of fatty acids, lecithins, and cholesterols are produced which are mesomorphic compounds. Under other circumstances, substances may show myelin forms and not be able to exhibit a mesomorphic phase and vice versa. Since this is the case, many early reports on myelin formations in biological systems should be reëxamined before one can apply a blanket statement as to which systems of those reported only in terms of myelin formation really contain a mesomorphic phase. A concentrated solution of lecithin in water or a water–alcohol mixture exhibits a mesomorphic phase very similar to that produced by oleates (230, 369), but if too much water is added myelin forms appear (230). Addition of water to cholesterol or to cholesteryl oleate is not sufficient to produce a myelin mesomorphic phase; the former requires the presence of a fatty acid and possibly a small amount of alkali (369), while the latter requires an alcoholic medium.

The inability of duplicating some of the earlier experiments in developing a mesomorphic phase has been discussed by Adami and Aschoff (2). It was found that a slight excess of one or another constituent or change in the relative amounts of the solvent seriously influences the appearance and development of the mesomorphic phase in certain cases.

The mesomorphic (in some cases possibly only myelin) state was identified with mainly the pathogenic tissues in much of the earlier reported works (338), undoubtedly because of its appearance in areas where large lipid deposits had formed. Later it appeared that under nonpathological conditions cholesterol was probably being taken up by the normal fatty globules which then became anisotropic; that lecithin could be anisotropic under normal as well as adverse conditions; that choline readily combined with oleic acid to form a mesomorphic (also myelin) phase (2). Although these phases were seemingly similar to those obtained from aqueous soap solutions, evidence was found which pointed to several types of myelin (and mesomorphic) forms. Water, hydrogen peroxide, and chromates were shown by Diamare (73) to differentiate between oleate and soap mesomorphic forms on the one hand and lipoid forms on the other.

It has been demonstrated that the gray matter of the brain contains a large proportion of a mesomorphic phase when existing in the neurokeratogenic colloid, as does the telencephalon in the earliest stage and the embryo while still in the blastemic stage (73). Massive deposits of mesomorphic compounds are found in the kidneys, liver, spleen marrow, and aorta walls, through the utilization of cholesterol compounds. This can best be shown by feeding rabbits pure cholesterol or foods containing it (52). The body heat of vertebrate animals is said to cause "lipoid drops" to appear in the mesomorphic state (338).

Mesomorphic forms are not restricted to the lipoids, but find suitable environment in the fibrous, stringlike, or braided formations of the muscles or nerves. The necessary softness and suppleness are found in the smooth muscle fibers which exhibit positive uniaxial double refraction (discussed above), their longitudinal direction corresponding to their axis of isotropy. Upon contraction of the fibers the double refraction is reduced, owing to partial compensation (optical) of the randomly distributed and deformed micelles. The optical anisotropy is increased again upon the stretching of the fibers, owing to the alignment of the units of the fibers (338). In these systems forms are observed which may be considered to be a mesomorphic phase coupled with micelles and crystalline "threads." The bundle network observed with some gel-like fine structure provides the necessary utility for the physiological expansion and contraction, often involving swelling and subsequent constriction. The external sheaths of some nerve systems are also optically anisotropic. The lecithin–myelin slough boundaries show strong double refraction, while the interior of the nerve appears to be only very weakly optically active (337).

Living sperms, composed in part of protein, nucleoproteins, and albumins, have been shown to possess a mesomorphic phase (335, 357). The one most carefully studied, that of *Sepia officinalis*, exhibits the same double refraction both when living and when preserved in alcohol (334). The anisotropy occurring quite commonly in the sperms is exhibited in the extended form of the sperm head. This double refraction can be destroyed by the artificial swelling of the sperm heads. The morphology, x-ray data, optical and thermal properties of the sperms of *Sepia officinalis* have been compared to organic compounds exhibiting a mesomorphic phase (336). A recent discussion of the structure of chromosomes is given by Ambrose (3).

The possibility that the mesomorphic phase may be an important factor in the activity and growth rate of meristematic cells has been proposed (53). Intracellular granules were observed to be in the mesomorphic state in the unstained portions in the growing tips of the squash root. The granules were smaller and more numerous in the area near the tips and fewer and larger in more remote areas.

Aqueous solutions of tobacco mosaic virus (18, 37, 39, 213) as well as cucumber virus (38) have been shown to possess a mesomorphic state. After standing for several days, a 2 per cent solution of tobacco mosaic virus will separate into two layers. The top layer is isotropic but shows double refraction of flow of the rods, while the more concentrated lower layer is a strongly double-refracting thixotropic gel. The rod-shaped virus protein in the lower phase has been shown (18, 37) by x-ray analysis to be arranged in a hexagonal close-packed array of parallel cylinders. As the concentration of the virus increases in the solution, the distance between adjacent molecules continuously decreases in the order of 500 A. to about 125 A. When the molecules show the arrangement of the smectic structure, the layers are perhaps a thousand molecules thick (19).

A theoretical explanation for the anisotropic phase occurring in solutions of tobacco mosaic virus in the order of 1–4 per cent has been put forth in terms of the repulsive forces and thermal agitation (177, 301). By this theory, the relation between the critical concentration and the molecular shape of the coacervations of the prolate spheroid or circularly cylindrical tobacco mosaic virus can be expressed, and it gives the required condition for the appearance of a mesomorphic phase. The excess attractive force of the coulombic attraction between the micelles and oppositely charged species in the solution is balanced by the dispersive action of thermal agitation and another repulsive force (212). The mutual covolume of two swarms is approximately proportional to the sine of the angle between their orientation and larger than the volume of the molecules by a factor proportional to the asymmetry (301). The osmotic pressure of the anisotropic phase predicted by this theory is nearly proportional to the concentration and only slightly greater than $3cRT/V$.

Structural studies of collagen have been reported (358) in which the properties described, although not so specified by the author, resemble the mesomorphic state. X-ray diffraction (10) studies of collagen indicate a pseudo-hexagonal packing. Trypsin (111) under certain conditions of preparation contains coiled threads, a representative property of the nematic structure.

Perutz, Liquori, and Eirich (316) found on microscopic observation that the hemoglobin of sickle cell anemia gives a liquid-crystalline pattern. When this reduced hemoglobin was sheared between slide and cover glass it became optically negative with respect to the direction of the shear, a result which suggests that the heme groups are normal to this direction.

Birefringent solutions of poly-γ-benzyl-L-glutamate in several solvents have been studied (340). These systems show parallel equidistant lines which are visible even in natural light. The periodicity of these lines, which is dependent upon concentration, may exceed 100,000 A. The structure is also associated with very high optical rotatory power and is therefore like the cholesteric structure, but there are some features, including the appearance of visible spirals and radial lines of dislocation, which have not been observed in the cholesteric structure. A model of the structure is proposed.

The mesomorphic state is probably one form exhibited by fibrinogen during the clotting of blood (4). The myelin forms of lecithinlike nature which exhibit the great dissolving power mentioned above probably play an important role in the equilibrium of many cells and tissues.

It seems probable that the mesomorphic modifications are of important biological significance, for slight changes in composition and in physical and chemical properties can materially affect the formation, continuation, or cessation of the mesomorphic state, a delicate balance characteristic also of many biological processes. Catalytic processes in biological systems could readily find a favorable environment in the structure of the mesomorphic state. The extended molecules, with fairly strong dipoles and easily polarized groups so characteristic of biological fluids, are comparable to those molecules of inanimate nature exhibiting the mesomorphic state. Further work is needed to unravel the mysteries of the functions of the mesomorphic state in biological systems.

The authors wish to express their appreciation to Professor Jacob H. Sarver of the University of Cincinnati for drawing figures 6, 7, 8, 10, 11, 12, and 13. Acknowledgment is made of the aid received from Mr. John F. Dreyer of Polacoat Incorporated, and also from Dr. F. B. Rosevear and Dr. O. T. Quimby of The Procter and Gamble Company, who read the manuscript and made suggestions for its improvement.

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