

INTRODUCTION TO LIQUID CRYSTALS

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***INTRODUCTION TO
LIQUID CRYSTALS***

Preface

The existence of liquid crystals has been known for nearly a century; yet it is only in the last ten years that their unique optical, electrical, electro-optic, and thermal properties have been exploited to any significant extent in such technological applications as digital displays and thermography. Digital watches equipped with liquid-crystal displays (LCD's) have recently made their debut in the electronic watch market, and the large-scale use of LCD's in a variety of other applications requiring reliable, low-power digital displays is imminent. There is good reason to believe that liquid crystals will be the first electro-optic materials to find widespread commercial use. Apart from applications, liquid crystals are unique among the phases of matter. Lurking beneath their garish display of color and texture is a great complexity of physical and chemical interaction that is only now beginning to unfold in the face of a decade-old resurgence in all aspects of liquid-crystal research. RCA Laboratories has participated in this resurgence from its beginning in the early 1960's and at present maintains active liquid-crystal programs both in basic research and in device engineering.

In view of the widespread interest in liquid crystals at RCA Laboratories, an in-house weekly seminar devoted to the subject of liquid crystals was organized in the fall of 1973. The resulting lectures were subsequently published in three issues of the *RCA Review* and, with the incorporation of much additional material, eventually grew into the present volume.

The book is intended as a tutorial introduction to the science and technology of liquid crystals. We believe it will serve as a useful primer for those interested in the physics of liquid crystals and those using or contemplating the use of liquid crystals in practical devices. The book is not meant to be a review of the entire field of liquid crys-

tals, and no attempt has been made to include exhaustive compilations of literature references. Emphasis has been given to areas generally ignored in other texts; specific topics emphasized include the statistical mechanics of the molecular theory and various aspects of device fabrication.

The eighteen chapters in the present volume can be divided into four groups. Chapters 1 and 2 give a brief introduction to the structural and chemical properties of liquid crystals. The next eight chapters develop both the microscopic statistical theories (Chapters 3–7) and the macroscopic continuum theories (Chapters 8–10) of liquid crystals. Chapters 11 through 17 treat various aspects of device applications and related considerations, including packaging; optical, electro-optic, and electro-chemical effects; addressing techniques; and the use of liquid crystals in optical waveguides. The final chapter presents an overview of lyotropic liquid crystals with particular emphasis on the crucial role of the hydrophobic effect in their stability.

Important contributions to the success of this venture were made by several individuals. We wish to express our sincere appreciation for their kind efforts. Roger W. Cohen made the initial suggestion for the seminar series and has given continued encouragement and support during the preparation of the book. George D. Cody was most instrumental in arranging for the publication of the lectures in the *RCA Review* and had the foresight to suggest that they be incorporated in the present volume. Ralph F. Ciafone provided outstanding editorial support during publication of the lectures in the *RCA Review* and also assumed substantial editorial responsibility for many of the tasks involved in putting the lectures together as a book. Mrs. Dorothy C. Beres was especially helpful in typing the manuscripts for the majority of the chapters. Thanks are also due each lecturer-author whose contributions were invaluable in making the seminar series and this resulting volume complete.

E. B. Priestley
Peter J. Wojtowicz
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Liquid Crystal Mesophases

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1. Mesophases

Everyday experience has led to universal familiarity with substances that undergo a single transition from the solid to the isotropic liquid phase. The melting of ice at 0°C to form liquid water is perhaps the most common such phase transition. There are, however, many organic materials that exhibit more than a single transition in passing from solid to liquid, thereby necessitating the existence of one or more intermediate phases. It is not surprising that the molecular ordering in these intermediate phases, known as "mesophases", lies between that of a solid and that of an isotropic liquid. The partial ordering of the molecules in a given mesophase may be either translational or rotational, or both. Clearly, translational order can be realized regardless of molecular shape, whereas rotational order has

meaning only when the constituent molecules are nonspherical (elongated). Thus, there is good reason to expect molecular structure to be an important factor in determining the kind and extent of ordering in any particular mesophase.

Two basically different types of mesophases have been observed. First, there are those that retain a 3-dimensional crystal lattice, but are characterized by substantial rotational disorder (i.e., disordered crystal mesophases), and second, there are those with no lattice, which are therefore fluid, but nevertheless exhibit considerable rotational order (i.e., ordered fluid mesophases). Molecular structure is in fact important and, generally speaking, molecules comprising one of these two types of mesophase are distinctly different in shape from molecules comprising the other. Indeed, with the possible exception of some polymorphous smectic materials, there are no known substances that show both disordered crystal and ordered fluid mesophases.

1.1 Disordered Crystal Mesophases

Disordered crystal mesophases are known as "plastic crystals".¹ In most cases plastic crystals are composed of "globular" (i.e. essentially spherical) molecules, for which the barriers to rotation are small relative to the lattice energy. As the temperature of such a material is raised, a point is reached at which the molecules become energetic enough to overcome these rotational energy barriers, but not sufficiently energetic to break up the lattice. The result is a phase in which the molecules are translationally well ordered but rotationally disordered, i.e., a disordered, or plastic crystal. Further increase in the temperature will result eventually in the molecules becoming energetic enough to destroy the lattice, at which point a transition to the isotropic liquid occurs. Perhaps the most striking property of plastic crystal mesophases is the ease with which they may be deformed under stress. It is this softness or "plasticity" that gives these mesophases their name.

A detailed discussion of plastic crystals is outside the scope of this chapter. However, those interested in pursuing the subject further are directed to Ref. [1] which provides an excellent elementary review of the properties of plastic crystals.

1.2 Ordered Fluid Mesophases

Ordered fluid mesophases are commonly called "liquid crystals"²⁻⁶ and are most often composed of elongated molecules. In these mesophases, the molecules show some degree of rotational order (and in some cases

partial translational order as well) even though the crystal lattice has been destroyed. Lack of a lattice requires that these mesophases be fluid; they are, however, *ordered* fluid phases. It is this simultaneous possession of liquid-like (fluidity) and solid-like (molecular order) character in a single phase that makes liquid crystals unique and gives rise to so many interesting properties.

In what follows, the various ordered fluid mesophases are described, with particular attention being given to the nature of the molecular ordering in each case. Also, some of the consequences of simultaneous liquid-like and solid-like behavior in a single phase are discussed qualitatively. Later chapters will deal at length with many subjects we can consider only briefly here.

2. Types of Liquid Crystals

Two types of liquid crystal mesophases must be differentiated, viz. thermotropic and lyotropic. Thermotropic liquid crystals are of interest both from the standpoint of basic research and also for applications in electro-optic displays, temperature and pressure sensors, etc. Lyotropic liquid crystals, on the other hand, are of great interest biologically and appear to play an important role in living systems.

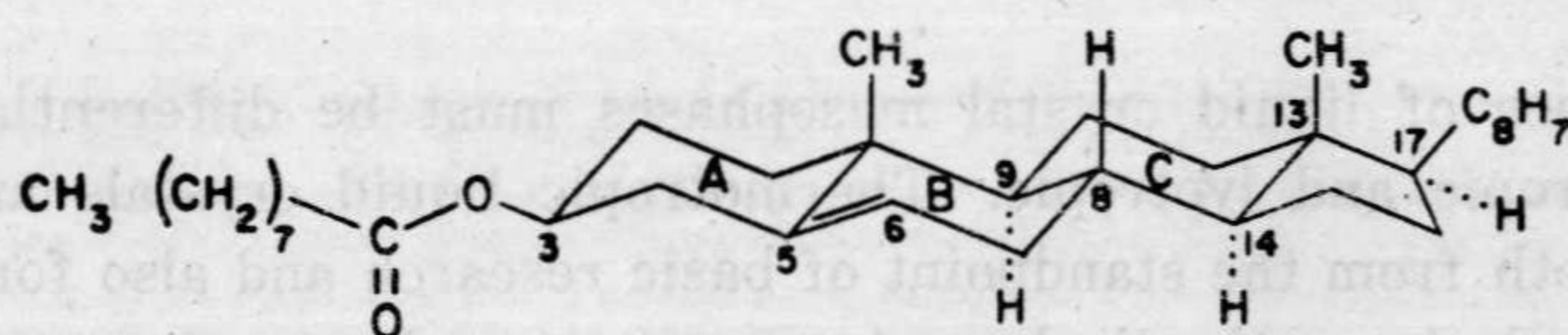
2.1 Thermotropic Liquid Crystals

The term "thermotropic" arises because transitions involving these mesophases are most naturally effected by changing temperature. Materials showing thermotropic liquid crystal phases are usually organic substances with molecular structures typified by those of cholesteryl nonanoate and N-(p-methoxybenzylidene)-p'-n-butylaniline (MBBA) shown in Fig. 1. Axial ratios of 4-8 and molecular weights of 200-500 gm/mol are typical for thermotropic liquid crystal mesogens. In this type of liquid crystal, every molecule participates on an equal basis in the long range ordering.

2.2 Lyotropic Liquid Crystals

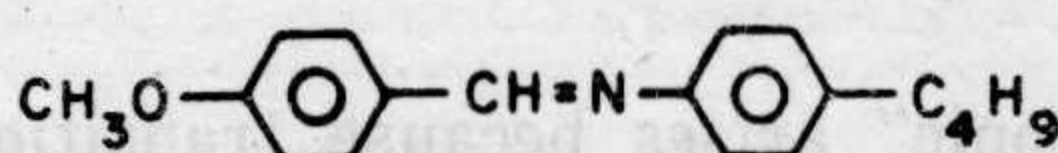
Solutions of rod-like entities in a normally isotropic solvent often form liquid-crystal phases for sufficiently high solute concentration. These anisotropic solution mesophases are called "lyotropic liquid crystals".⁷⁻⁹ Although the rod-like entities are usually quite large compared with typical thermotropic liquid-crystal mesogens, their axial ratios are seldom greater than ~ 15 . Deoxyribonucleic acid (DNA), certain viruses (e.g., tobacco mosaic virus (TMV)), and many synthetic poly-

peptides all form lyotropic mesophases when dissolved in an appropriate solvent (usually water) in suitable concentration. The conformation of most of these materials is quite temperature sensitive, i.e. the rods themselves are rather unstable with respect to temperature changes. This essentially eliminates the possibility of thermally inducing phase transitions involving lyotropic mesophases. A more natural parameter which can be varied to produce such transitions is the solute concentration. The principal interaction producing long range order in lyotropic liquid crystals is the solute-solvent interaction; solute-solute interactions are of secondary importance. To a good approximation, then, only the rod-like entities (solute) participate in the long range ordering.



CHOLESTERYL NONANOATE

(a)



N-(P-METHOXY BENZYLIDENE)-P'-BUTYLANILINE (MBBA)

(b)

Fig. 1—Examples of molecular structures that give rise to thermotropic mesophases.

3. Classification According to Molecular Order

With the distinction between thermotropic and lyotropic mesophases in mind, we proceed to the classification of these mesophases using a scheme based primarily upon their symmetry. This scheme, first proposed by Friedel in 1922,¹⁰ distinguishes three major classes—the nematic, the cholesteric, and the smectic.

3.1 Nematic Order

The molecular order characteristic of nematic liquid crystals is shown

schematically in Fig. 2. Two features are immediately apparent from the figure:

- (1) There is long range orientational order, i.e., the molecules tend to align parallel to each other.
- (2) The nematic phase is fluid, i.e., there is no long range correlation of the molecular center of mass positions.

In the state of thermal equilibrium the nematic phase has symmetry ∞/mm and is therefore uniaxial. The direction of the principal axis \hat{n} (the director) is arbitrary in space.

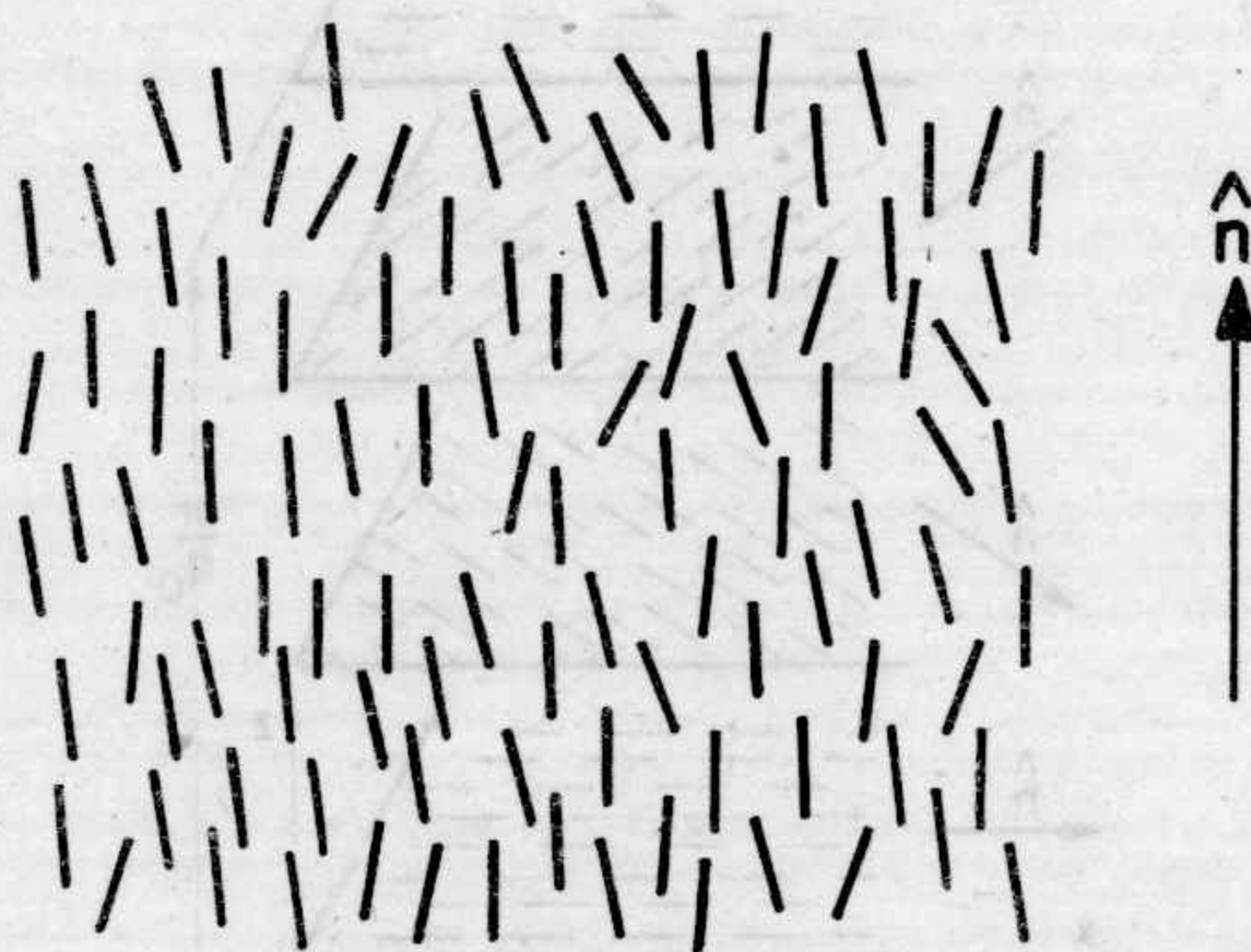


Fig. 2—Schematic representation of nematic order.

3.2 Cholesteric Order

Fig. 3 shows the equilibrium structure of the cholesteric phase. As in the nematic phase, lack of long range translational order imparts fluidity to the cholesteric phase. On a local scale, it is evident that cholesteric and nematic ordering are very similar. However, on a larger scale the cholesteric director \hat{n} follows a helix of the form

$$n_x = \cos(q_0 z + \varphi)$$

$$n_y = \sin(q_0 z + \varphi)$$

$$n_z = 0$$

where both the direction of the helix axis z in space and the magnitude of the phase angle ϕ are arbitrary. Thus the structure of a cholesteric liquid crystal is periodic with a spatial period given by

$$L = \frac{\pi}{|q_0|}.$$

The sign of q_0 distinguishes between left and right helicies and its magnitude determines the spatial period. When L is comparable to optical wavelengths, the periodicity results in strong Bragg scattering of light. If the wavelength of the scattered light happens to be in the visible region of the spectrum, the cholesteric phase will appear brightly colored.

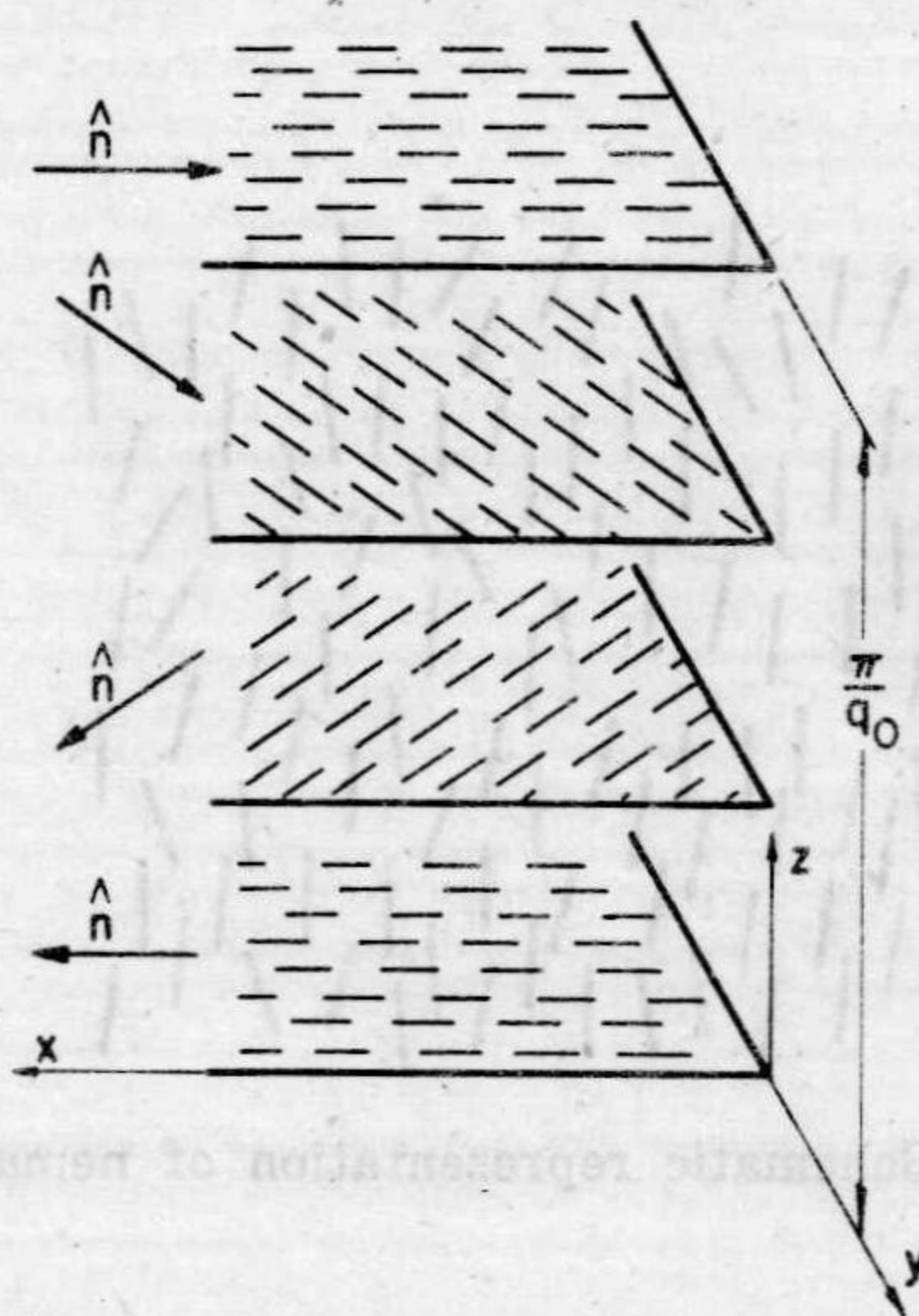


Fig. 3—Schematic representation of cholesteric order.

It is interesting to note that a nematic liquid crystal is really nothing more than a cholesteric with $q_0 = 0$ (infinite pitch). In fact, the two are subclasses of the same family, the distinction being whether the equilibrium value of q_0 is identically zero, or finite. If the constituent molecules are *optically inactive*, i.e., are superimposable on their mirror image, then the mesophase will be nematic. If, on the other hand, the constituent molecules are *optically active*, i.e., are not superimposable on their mirror image, then the mesophase will be cholesteric (except if the molecule and its mirror image are present in precisely equal amounts, i.e. a “racemic” mixture, in which case the mesophase will again be nematic).

Finally, a comment on nomenclature is in order. Cholesteric liquid