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S. Chandrasekhar
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1
Introduction

The term *liquid crystal* signifies a state of aggregation that is intermediate between the crystalline solid and the amorphous liquid. As a rule, a substance in this state is strongly anisotropic in some of its properties and yet exhibits a certain degree of fluidity, which in some cases may be comparable to that of an ordinary liquid. The first observations of liquid crystalline or *mesomorphic* behaviour were made towards the end of the last century by Reinitzer[1] and Lehmann.[2] Several thousands of organic compounds are known now to form liquid crystals.[3] An essential requirement for mesomorphism to occur is that the molecule must be highly geometrically anisotropic in shape, like a rod or a disc. Depending on the detailed molecular structure, the system may pass through one or more mesophases before it is transformed into the isotropic liquid. Transitions to these intermediate states may be brought about by purely thermal processes (*thermotropic* mesomorphism) or by the influence of solvents (*lyotropic* mesomorphism).

1.1 Thermotropic liquid crystals: structure and classification of the mesophases

1.1.1 Liquid crystals of rod-like molecules

The vast majority of thermotropic liquid crystals are composed of rod-like molecules. Following the nomenclature proposed originally by Friedel,[4] they are classified broadly into three types: *nematic*, *cholesteric* and *smectic*.

The nematic liquid crystal has a high degree of long-range orientational order of the molecules, but no long-range translational order (fig. 1.1.1). Thus it differs from the isotropic liquid in that the molecules are

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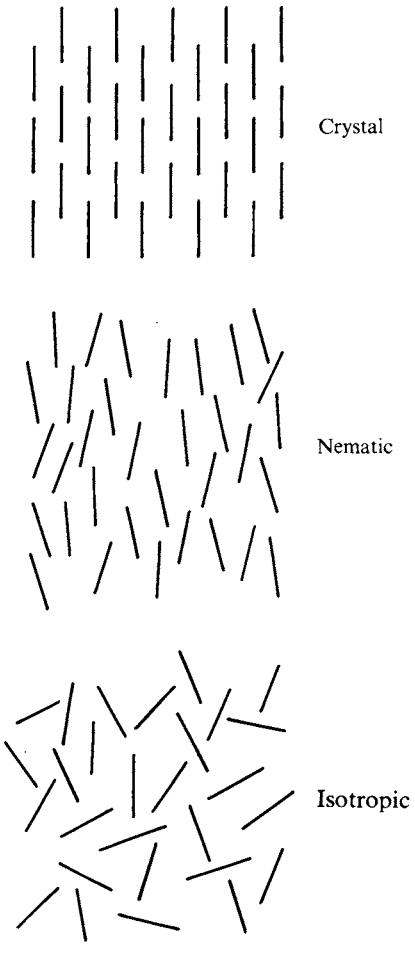

Fig. 1.1.1. Schematic representation of molecular order in the crystalline, nematic and isotropic phases.

spontaneously oriented with their long axes approximately parallel. The preferred direction usually varies from point to point in the medium, but a uniformly aligned specimen is optically uniaxial, positive and strongly birefringent. The mesophase owes its fluidity to the ease with which the molecules slide past one another while still retaining their parallelism. X-ray studies[5,6] indicate that some nematics possess a lamellar type of short-range order, i.e., they consist of clusters of molecules – called *cybotactic* groups[7] – the molecular centres in each cluster arranged in layers. In ordinary nematics the cybotactic groups, if they do exist, are smaller than can be detected by X-ray methods (see figs. 1.1.2 and 1.1.3).

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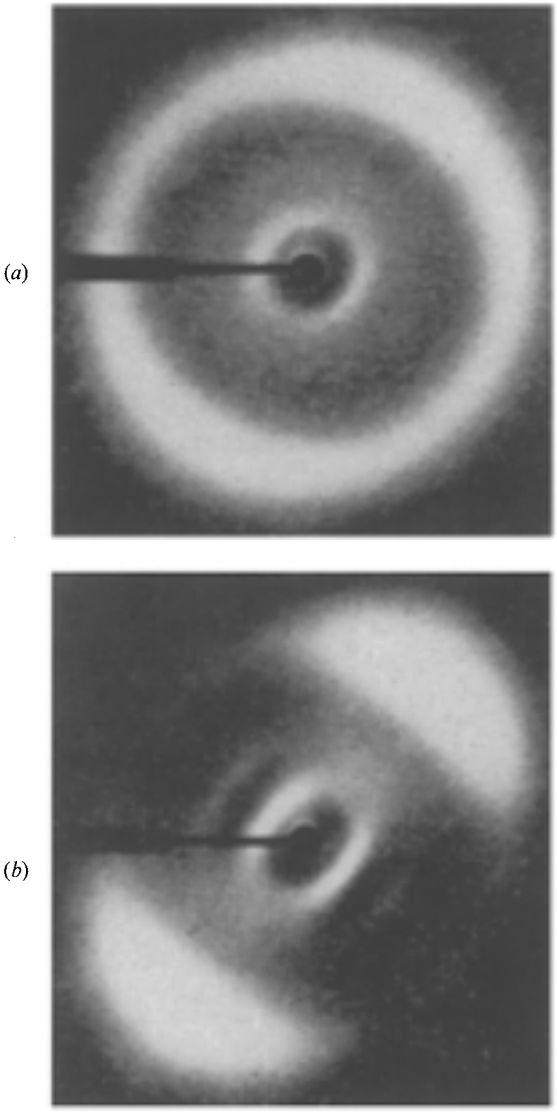

Fig. 1.1.2. X-ray diffraction patterns from an 'ordinary' nematic liquid crystal: 4-n-propyloxy-benzylidene-4′-n-propylaniline: (*a*) an unaligned (though not quite randomly oriented) sample; (*b*) a well aligned sample. (De Vries.[6])

A biaxial modification of the nematic has been discovered recently (see §6.6).

The cholesteric mesophase is also a nematic type of liquid crystal except

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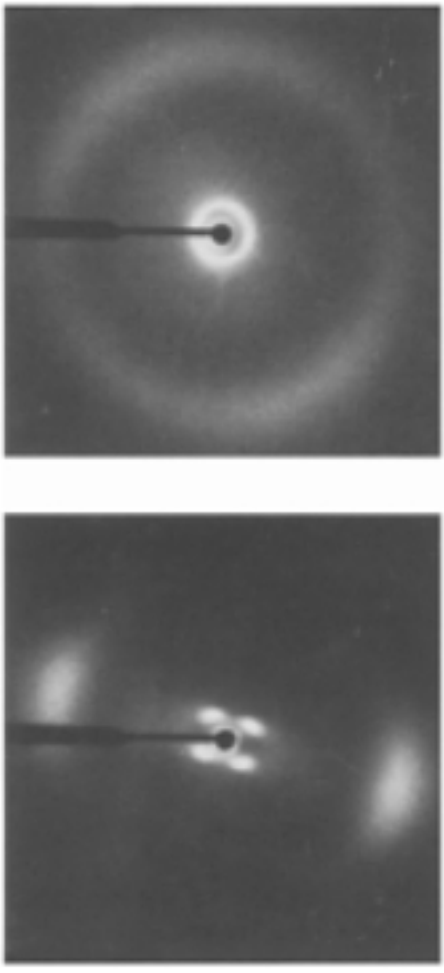

Fig. 1.1.3. X-ray diffraction patterns from a 'cybotactic' nematic: bis-(4′-n-octyloxybenzal)-2-chloro-1,4-phenylenediamine: (*a*) an unaligned (though not quite randomly oriented) sample; (*b*) a well aligned sample. (De Vries.[6])

that it is composed of optically active molecules. As a consequence the structure acquires a spontaneous twist about an axis normal to the preferred molecular directions (fig. 1.1.4). The twist may be right-handed or left-handed depending on the molecular conformation. Optically inactive molecules or racemic mixtures result in a helix of infinite pitch which corresponds to the true nematic. The energy of twist forms only a minute part ($\sim 10^{-5}$) of the total energy associated with the parallel alignment of the molecules,[8] so much so that when a small quantity of a

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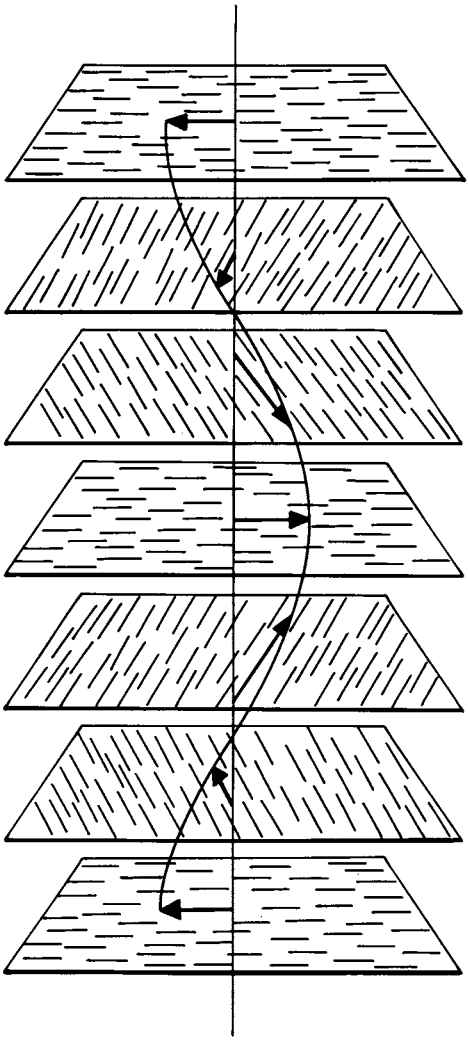

Fig. 1.1.4. The cholesteric liquid crystal: schematic representation of the helical structure.

cholesteric substance,[4] or even a non-mesomorphic optically active substance,[9] is added to a nematic the mixture adopts a helical configuration. The spiral arrangement of the molecules in the cholesteric is responsible for its unique optical properties, viz., selective reflexion of circularly polarized light and a rotatory power about a thousand times greater than that of an ordinary optically active substance. Cholesterics of low pitch, less than about 5000 Å, exhibit what are known as *blue* phases.

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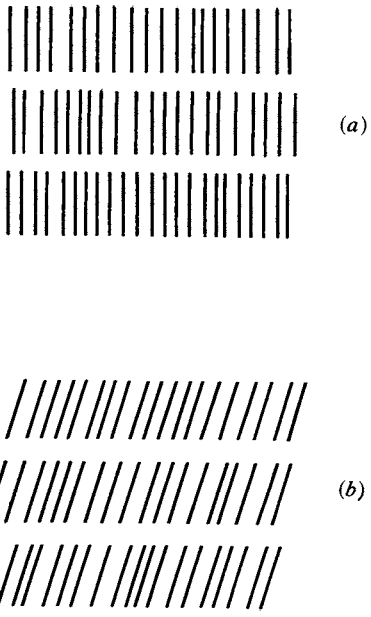

Fig. 1.1.5. Schematic representation of the molecular arrangement in (*a*) smectic A and (*b*) smectic C.

These phases exist over a small temperature range ($\sim$ 1 °C) between the liquid crystal phase and the isotropic liquid. Their structures will be discussed in §4.8.

Smectic liquid crystals have stratified structures but a variety of molecular arrangements are possible within each stratification. In smectic A the molecules are upright in each layer with their centres irregularly spaced in a 'liquid-like' fashion (fig. 1.1.5(*a*)). The interlayer attractions are weak as compared with the lateral forces between molecules and in consequence the layers are able to slide over one another relatively easily. Hence this mesophase has fluid properties, though it is very much more viscous than the nematic. Smectic C is a tilted form of smectic A, i.e., the molecules are inclined with respect to the layer normal (fig. 1.1.5(*b*)). Several polymorphic forms of smectics A and C exist, as we shall see later. Over a dozen other distinct smectic modifications have been identified.[10,11] Some of them (e.g., S_B, S_E, S_G, S_H, S_J and S_K) have three-dimensional long-range positional order as in a crystal, though with weak interlayer forces (and hence energetically weak interlayer ordering), while some others, referred to as *hexatic* phases, have three-dimensional long-range 'bond-orientational' order, but without any long-range positional order.[12] The

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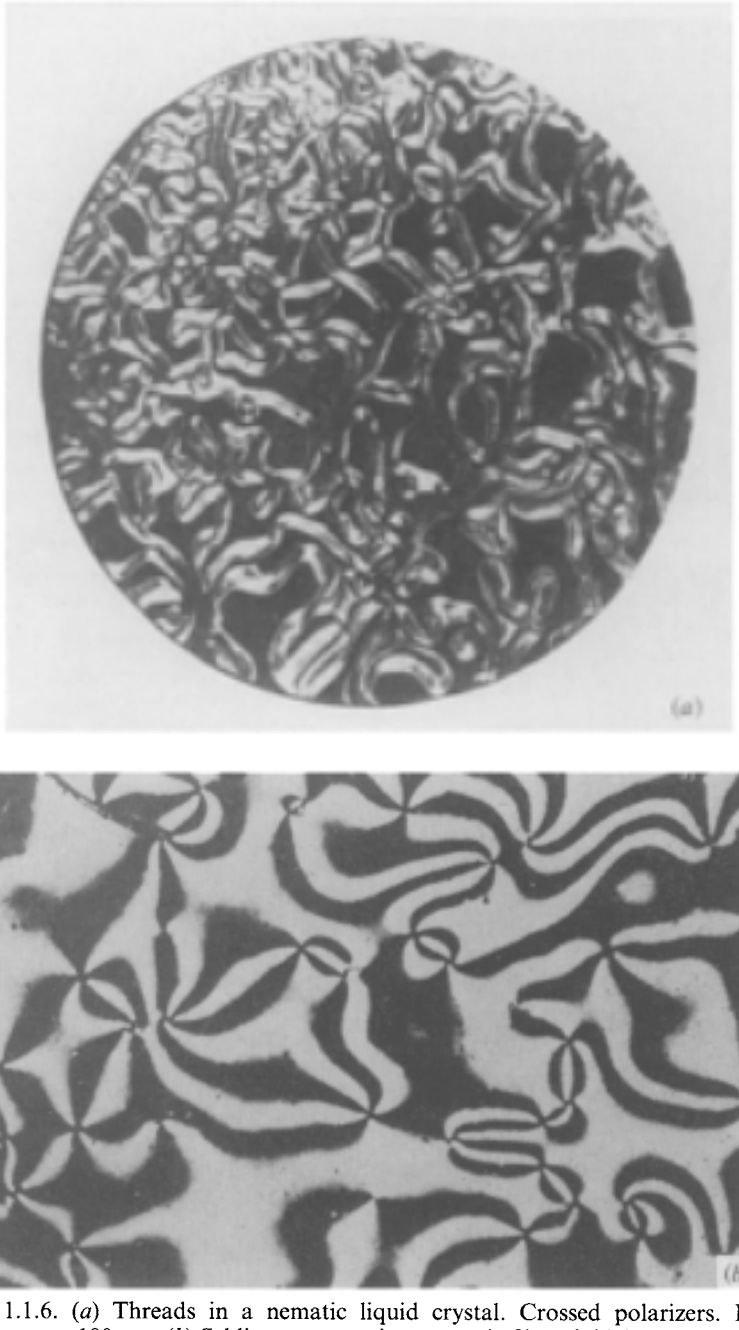

Fig. 1.1.6. (*a*) Threads in a nematic liquid crystal. Crossed polarizers. Film thickness ~ 100 μm. (*b*) Schlieren texture in a nematic film of thickness ~ 10 μm. Crossed polarizers. (Sackmann and Demus.[14])

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D phase has a cubic structure[13] and would appear to be an exception to the rule that smectics have layered structures.

The energy required to deform a liquid crystal is so small that even the slightest perturbation, caused say by a dust particle or a surface inhomogeneity, can distort the structure quite profoundly. Thus when a liquid crystal is taken between glass plates and examined under a polarizing microscope one rarely sees the familiar interference figures expected from the equilibrium structures shown in figs. 1.1.1, 1.1.4 and 1.1.5. Instead, one usually obtains a rather complex optical pattern. For example, a nematic film shows a characteristic threaded texture from which this mesophase derives its name (fig. 1.1.6) and a smectic A film a focal conic texture (fig. 1.1.7). These textures are useful in the optical identification of the mesophases[15,16] and their nature is generally well understood, as we shall see in later chapters. 'Single crystal' films with the molecules aligned perpendicular to the plates (*homeotropic* structure) or parallel to them (*homogeneous* or *planar* structure) can be prepared by suitable prior treatment of the glass surfaces.

From purely geometrical arguments, Herrmann[17] concluded that there should be 18 distinct mesomorphic groups between the perfectly ordered crystalline arrangement and the truly amorphous one. Examples of some of these groups have been found in plant virus preparations[18] and in surfactant–water compositions,[19] but it is not yet clear whether all of them can give rise to energetically feasible configurations. Thus Friedel's nomenclature offers a convenient basis for the classification of thermotropic liquid crystals and is universally adopted at present. The term *calamitic* has come into use in recent years to describe liquid crystals composed of rod-like molecules and to distinguish them from *discotic* systems, which will be discussed in the next section.

1.1.2 Liquid crystals of disc-like molecules

The first liquid crystals of disc-shaped molecules, now generally referred to as discotic liquid crystals, were prepared and identified in 1977.[20] Since then a large number of discotic compounds have been synthesized and a variety of mesophases discovered.[21] Structurally, most of them fall into two distinct categories, the *columnar* and the nematic. The columnar phase in its simplest form consists of discs stacked one on top of the other aperiodically to form liquid-like columns, the different columns constituting a two-dimensional lattice (fig. 1.1.8(*a*)). The structure is somewhat similar to that of the hexagonal phase of soap–water and other lyotropic

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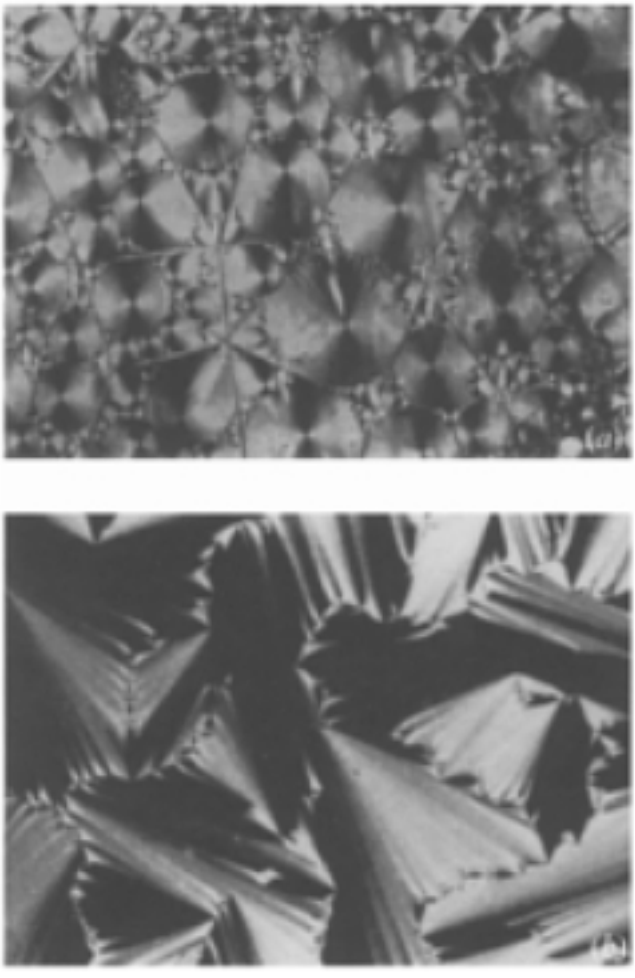

Fig. 1.1.7. Focal conic textures in smectic A. (*a*) The polygonal texture. Crossed polarizers. (Friedel.[4]) (*b*) Simple fan-shaped texture. Crossed polarizers. (Sackmann and Demus.[14])

systems (see fig. 1.2.2), but a number of variants of this structure have been identified: hexagonal, rectangular, tilted, etc. The nematic phase has an orientationally ordered arrangement of the discs without any long-range translational order (fig. 1.1.8(*b*)). Unlike the classical nematic of rod-like molecules, this phase is optically negative. A cholesteric (or twisted nematic) phase has also been identified. A smectic-like lamellar phase has been reported[22] but the disposition of the molecules in the layers has not yet been resolved.

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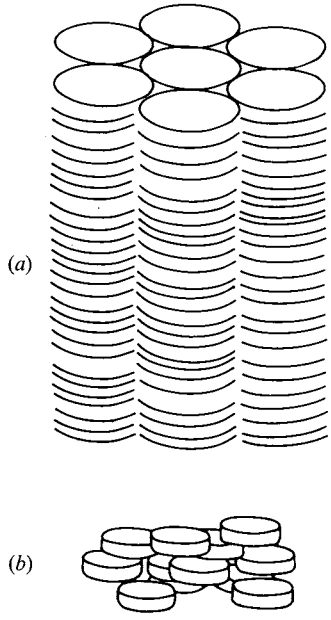

Fig. 1.1.8. The structure of (*a*) the columnar phase and (*b*) the nematic phase of disc-like molecules.

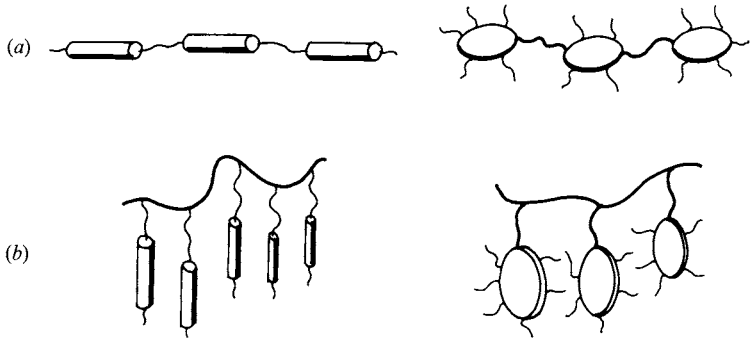

Fig. 1.1.9. Polymers that exhibit liquid crystalline phases. The basic monomer units are low molar mass rod-like or disc-like mesogens which may form part of the main chain (*a*) or attached as side groups (*b*).

1.1.3 Polymer liquid crystals

The structures of polymers that form liquid crystals are illustrated schematically in fig. 1.1.9. The basic monomer units are low molar mass mesogens, rod-like or disc-like, which are attached to the polymer backbone in the main chain itself (fig. 1.1.9(*a*)), or as side groups (fig. 1.1.9(*b*)). The nature of the mesophase depends rather sensitively on the

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