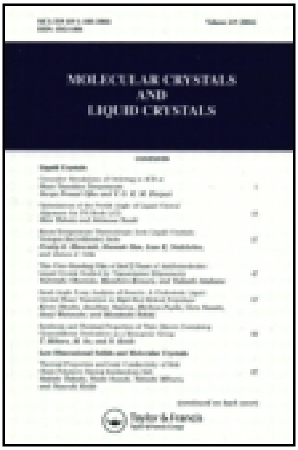

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

X-Ray Diffraction by Liquid Crystals

Leonid V. Azároff [a] [b]

[a] Physics Department and Institute of Materials Science, University of Connecticut, Storrs, Connecticut, 06268, USA

[b] Polymer Science and Engineering Department, University of Massachusetts, Amherst, 01003

Version of record first published: 20 Apr 2011.

To cite this article: Leonid V. Azároff (1980): X-Ray Diffraction by Liquid Crystals, Molecular Crystals and Liquid Crystals, 60:1-2, 73-97

To link to this article: http://dx.doi.org/10.1080/00268948008072426

Mol. Cryst. Liq. Cryst., 1980, Vol. 60, pp. 73–98
0026-8941/80/6001-0073$04.50/0

Printed in the U.S.A.

X-Ray Diffraction by Liquid Crystals

LEONID V. AZÁROFF†

Physics Department and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268, USA

(*Received July 31, 1979; in final form November 1, 1979*)

Following a very brief historical review, x-ray diffraction by nematic and smectic liquid crystals is critically examined in terms of the data available and the structural models and molecular theories that have been proposed to explain it. Studies of TBBA are used to illustrate some of the principal mesophases that have been distinguished. Other types of liquid crystals and their phase transitions are also briefly reviewed.

This analysis shows that careful experimental work is still needed to decide the kinds of models that best describe the various types of mesophases that have been shown to exist.

INTRODUCTION

As is well known, X-ray diffraction provides a powerful tool for the structural characterization of most materials. For atomic or molecular arrays having three-dimensional periodicity it is possible, in principle, to determine an exact and usually unique structure whereas for liquids, in which the constituent atoms are in constant motion, only a time-averaged or statistical distribution can be established. For intermediate kinds of arrays, such as are encountered in liquid crystals (mesophases), it is possible to deduce structural information in proportion to the degree of correlation that exists along specific directions in the array. When proposing structural models to account for observed diffraction patterns, therefore, it is important to address the question: "What kind of molecular array produced the observed intensity distribution?" rather than the more usual procedure of demonstrating an agreement between an X-ray photograph and the proposed model.[1] This is so because it is not generally possible to derive a unique

---

† Work performed while on sabbatic leave in Polymer Science and Engineering Department, University of Massachusetts, Amherst, 01003.

molecular array directly from an analysis of the observed intensity distribution in the case of partially ordered systems.

Following the discovery of liquids that exhibit crystal-like (anisotropic) optical properties almost a century ago,[2,3] it was established that liquid crystals can be formed by heating certain crystalline solids above their melting points (*thermotropic*) or by dissolving certain compounds in polar solvents (*lyotropic*). One of the first to use X-ray diffraction to characterize these "liquid crystals," G. Friedel classified them as *smectic* (soap-like) and *nematic* (thread-like)[4] and argued that the term *mesomorphs* be used to describe them[5] since the substances are neither true crystals nor true liquids. This early history, as well as subsequent developments through 1956 (including the third class of mesomorphs called *cholesteric*) have been reviewed very thoroughly by Brown and Shaw.[6] Subsequent X-ray studies have been reviewed by Falgueirettes and Delord[7] and by de Vries.[8] Like these, the present review will be limited to a discussion of thermotropic mesophases with special focus on the molecular arrays that can give rise to the observed diffraction patterns.

To the present day, most publications citing X-ray studies base their interpretations on normal-beam photographs of unaligned mesomorphic phases, typically recorded with filtered Cu $K\alpha$ radiation directed at right angles to a stationary specimen and flat film. Such photographs are then used like fingerprints to classify the substances as nematic or smectic (see further discussion below) depending on the relative intensity and diffuseness of the recorded Debye-Scherer rings. (Usually only two rings are recorded.) Although such photographs are adequate to distinguish the mesophases from each other and from the isotropic liquid phase, they provide little information about the molecular arrays present other than estimates of molecular lengths and intermolecular (side-to-side) separations. This is despite the fact that, as early as 1931, it was noted that the molecules can be aligned in an electric (or magnetic) field to yield fiber-like diffraction patterns.[9,10] (Because such aligned liquid crystals contain molecules more nearly parallel to each other in a single domain, they are much more useful for discovering what the various possible arrays encountered in nature actually are.) This practice has tended to direct attention in the past on how the isotropic liquid orders rather than on the ways in which the ordered (crystalline) phase disorders.

In an analysis of the symmetry that partially-aligned assemblies of linear molecules can have in spatial arrays, Herrmann[11] considered "statistical", "direct," "pseudo," and "reciprocal" translations and concluded that eighteen mesomorphic translation groups can be distinguished. Like a later analysis of the possible cylindrical symmetries that linear molecular arrays can exhibit,[12] such descriptions may be useful for classification purposes but provide limited assistance in interpreting observed diffraction phenomena. Similarly, the paracrystalline model,[13] which is based on a distorted three-dimensional order, has found limited utility in the study of liquid crystals.[14] Nevertheless, it is these kinds of approaches that are most likely to provide new insights into the structural characteristics of mesophases in the future.

By analogy to X-ray diffraction studies of liquids, it has been suggested that the intensity distributions recorded for aligned mesophases along the equatorial and the meridional diameters in reciprocal space can be used to determine radial distribution functions along the two corresponding directions in real space (Ref. (12), Chapter 4). Since such functions display the projections of the entire molecular array onto a single line, they are usually difficult to interpret except for purposes of following possible changes produced by altering the molecular arrays or their composition.[15] Moreover, as pointed out by de Vries,[16] the conditions of statistical molecular randomness assumed in deriving such radial distribution functions usually are not met in the case of aligned mesomorphs so that an unambiguous interpretation is difficult.

By analogy to X-ray diffraction studies of natural and synthetic polymers, Vainshtein and his collaborators[17] and Hosemann and his collaborators[18] have advocated the use of optical transforms to compare proposed two-dimensional arrays with their Fourier transforms (reciprocal-space patterns). This is possible because the molecular arrays in liquid crystals typically are believed to have cylindrical symmetry. A cross section containing the cylinder axis, therefore, is representative of the entire array and its optical transform is fairly easy to obtain.[17] A corresponding cross section containing the origin in reciprocal space, however, displays the intensity distribution for scattering by the entire liquid crystal array projected onto its cross-sectional plane. It is necessary, therefore, to check how such a projection may alter the optical transform obtained.[19] These procedures, nevertheless, remain very useful in the interpretation of diffraction by polymer fibers since they enable relatively rapid examination of the effect that possible molecular structures, as well as their array in space, have on the transform. In the case of liquid crystals, however, the detailed molecular structure usually is "lost" because the molecules have rotational freedom about their long axes whereas their spatial disposition may be difficult to portray in a cross-sectional representation only.†

---

† Vainshtein and Chistyakov (last citation in Ref. 17) note that "using two-dimensional models, we cannot describe directly the distortions in three dimensions." They suggest, however, that indirect methods can be used to take them into account.

NEMATIC MESOPHASES

Nematic mesophases (N) can be formed when a *nematogenic* crystal, comprised of rigid-rod-like organic molecules, is heated above its melting point.[20] The constituent molecules typically have a planar moiety with partly flexible end chains with overall lengths of the order of 20–30 Å. In the nematogenic crystal, the molecules are arrayed periodically whereas, in the nematic mesophase, they assume no periodicity except, possibly, along their axial directions. As illustrated in Figure 1, the molecular centers of gravity (dots in Figure 1*a*) form a lattice array in a crystal and the molecules have fixed orientations about the lattice point. In the nematic mesophase, the constituent molecules are relatively free to assume any orientation about their long axes and form, statistically, true "rigid rods" of cylindrical symmetry whose centers of gravity may constitute very nearly periodic arrays along one direction (Figure 1*b*) or aperiodic but more or less linear arrays (Figure 1*c*). Upon heating above the liquidus temperature, the arrays (and molecular orientations) become completely random (Figure 1*d*). In the nematic mesophase, the molecules may tilt about their centers of gravity (dots in Figure 1), although space constraints tend to limit such tilts so that it is generally assumed that groups of molecules tend to be parallel to a single direction called the *director* of that group. When placed in an external electric or magnetic field, all the molecules tend to become parallel to a single director so that alignments like those depicted in Figures 1*b* and *c* give rise to characteristic diffraction patterns that can be distinguished from those produced by a true liquid (Figure 1*d*).

Early investigators of unaligned nematic mesophases found their X-ray diffraction patterns hard to distinguish from those of the liquid phases[21–24]

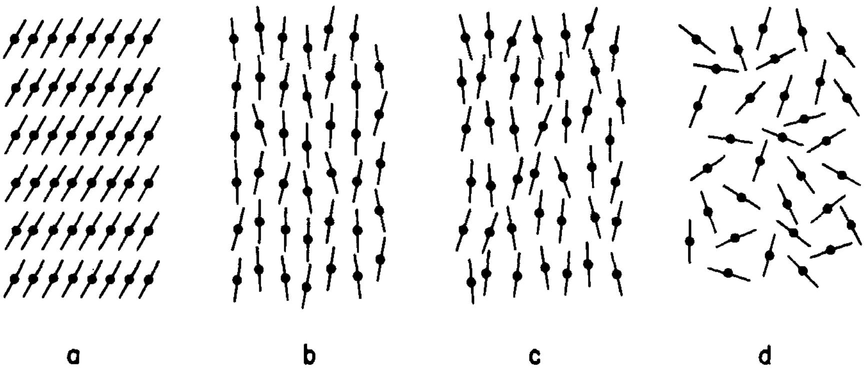

FIGURE 1 Molecular arrays in nematic mesophases. (Dots mark molecular centers of gravity). *a*. Nematogenic (periodic) array. *b*. Aligned nematic array, centers in vertical alignment. *c*. Random nematic array, i.e., no vertical alignment. *d*. Liquid (random) array.

FIGURE 2 Tracings of normal-beam x-ray photographs of nematic phases. (After Kast.[27]). *a*. p-azoxyanisole without a field. (Arcing is attributed to orientational effect of capillary walls). *b*. p-azoxyanisole aligned in an electric field (direction indicated by arrow).

although Kast noted that slight line shifts occurred in the nematic phase.[24] Using Mo $K\alpha$ and direct ionization counters, Stewart found that one of the Debye–Scherrer rings became sharper and relatively more intense in the nematic phase.[25] Previously, he had postulated that "a type of molecular arrangement wherein there is combined mobility of the component molecules and yet a recognizable space array" exists in certain liquids.[26] He called these arrays *cybotactic* groups and suggested that they may play a role in the formation of nematic phases.[27] Using an alternating electric field to align the nematic mesophase of *p*-azoxyanisole, Kast observed that the molecules tended to line up in the field, causing the Debye–Scherrer ring to split into pronounced crescents or arcs.[28] Figures 2*a* and *b* show schematic reproductions of two of the photographs that he published in his Figure 1 for an unaligned nematic (no external field) and one aligned by a field of 500 V/cm, respectively. Regrettably, the central portions of his photographs are blacked out by the direct X-ray beam but, as indicated in Figure 2*b* by the dashed lines, the tips of the crescents are joined by less intense but very nearly straight lines. In fact, it is now generally accepted[7] that an aligned nematic mesophase produces a diffraction pattern consisting of two or more intense and broad maxima along an equatorial direction (normal to the director) and several periodically spaced lines along the meridian in reciprocal space (parallel to the director) that are straight or slightly fanned.

As has been demonstrated by James,[29] periodic molecular chains that are parallel to each other but are randomly displaced along their long axes give rise to periodically spaced planes of diffracted intensity oriented at right angles to the chain axes. Finite bundles of such randomly displaced, periodic chains produce limited parallel disks normal to, say, the meridian[30] whereas bundles of (vertical) parallel continuous cylinders give rise to equatorial intensity distributions whose maxima depend on the number of cylinders in a bundle and their separation.[31] If one examines bundles of randomly displaced parallel and periodic chains, as is the case, for example, in nematic fibers of polybenzothiazole,[32] then the diffraction pattern consists of a combination of meridional disks and equatorial maxima (Figure 3). This suggests the following model for possible molecular arrays in nematic

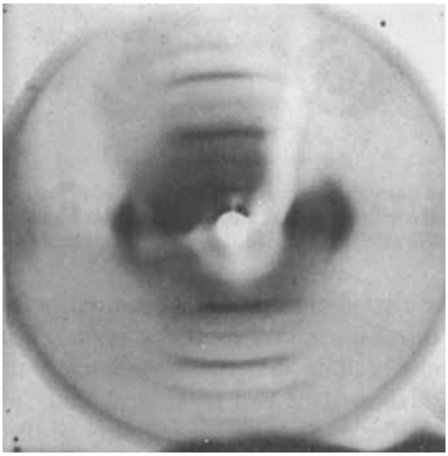

FIGURE 3 X-ray photograph of nematic fiber of polybenzothiazole.[32] This is a zero-level precision photograph containing the meridional diameter (vertical) and equatorial diameter (horizontal) in reciprocal space.

mesophases: The rod-like molecules tend to form linear arrays or "strings" that may be periodic (Figure 1*b*) or aperiodic (Figure 1*c*). The formation of periodic strings, that align themselves parallel to each other in an external field, produces disks along the meridian (meridional diameter) in reciprocal space (Figure 3). Since the periodic disks are separated by $c^* = 1/c$, where c is the periodic repetition along the string, the spacing of the meridional intensities can be used to calculate molecular lengths while their breadths, measured along the meridian, can be used to calculate the average length of the strings by means of the familiar Scherrer equation.[33] Whenever such disks are observed (linear meridional intensities) then the equatorial intensities can be used to determine inter-string separations by calculating intensity distributions on the assumption of specific parallel arrays.[32] In this case, it is *not* appropriate to use the breadths of the equatorial maxima to calculate the cross-sectional dimensions of a bundle either by means of the Scherrer equation nor by means of the paracrystalline model.[34]

The relative weakness of the intensity of meridional disks attests to the fact that not all the molecules in a nematic phase form periodic strings whereas the arcing of equatorial maxima signifies that the rod-like molecules tend to deviate (tilt) from strict parallelism. Deviations from parallelism by entire strings also causes an arcing in the equatorial maxima but it must be accompanied by a corresponding "fanning" of the equatorial disks.[32] (See also Ref. (29), pp. 577 and 584.) Since not all the published X-ray photographs of oriented nematic phases feature meridional disks, it is probable that they

FIGURE 4 Tracings of aligned normal-beam photographs of nematic phases. (After Leadbetter, Richardson and Colling.[36]) *a*. MBBA at 18°C. *b*. EBBA at 25°C.

contain aperiodic strings of molecules. In this case, the arced meridional reflections still can be used to determine molecular lengths and the equatorial ones to determine intermolecular (side-to-side) separations. As already pointed out,[35] in the latter case, it is not appropriate to use the Bragg equation for this purpose since it is based on diffraction by parallel planes rather than by parallel cylinders.

More recently published photographs[36] of nematic liquid crystals aligned in a magnetic field support the above model (Figure 4). In addition to a pronounced equatorial crescent, the photographs contain two or more parallel disks of intensity periodically arrayed along the meridian. As already pointed out by Guinier,[37] if the periodicity in a one-dimensionally periodic array is perturbed by local displacements, they can be expressed by their moments of inertia Δ_3^2 along the long direction and Δ_1^2 transverse to it, respectively. The diffraction maxima then take on the shape of an ellipse given by $\xi^2\Delta_1^2 + \delta^2\Delta_3^2 = A^2/S^2$ where $\boldsymbol{\xi}$ and $\boldsymbol{\delta}$ are the components (direction cosines) of the diffraction vector $\mathbf{S}$ ($|\mathbf{S}| = 2 \sin \theta$) along the equator and meridian of reciprocal space, respectively. Leadbetter, *et al.*[36] applied this relation to deducing the degree of ordering (misalignment) in MBBA and EBBA as a function of temperature and concluded that they had simple structures without strong correlations in local order. In a parallel study of MBCA and two biphenyls, they concluded that these two nematic liquid crystals had more pronounced local orders.[36] (See Table I for definition of chemical abbreviations.)

A somewhat different array of intensities has been observed in oriented nematic *p*-azoxybenzenes,[38] bis-(4′-*n*-octyloxybenzal)-2-chloro-1,4-phenylenediamine,[35] and in *n*-alkoxyazobenzenes.[39] The meridional reflections, reproduced schematically in Figure 5, are described by Chistyakov and Chaikowsky[38] as "flat disks in reciprocal space." For the longer homologues, the first meridional intensity distribution breaks up into two relatively intense maxima in the form of a dumbbell which "with increase in temperature ... changes first into a disc with uniform thickness" and later becomes arced upon transition to the liquid state.[38] The structural model proposed by de Vries to explain these sharpened intensity maxima[39] consists of a grouping of "smectic *C*-like arrangements" which he named[8] "skewed cybotactic

TABLE I

Chemical terminology of some liquid crystals

Abbreviation	Compound
BBEA	4-*n*-butyloxybenzal-4′-ethylaniline
EPAP	ethyl *p*-azoxybenzoate
EBBA	*p*-ethyoxybenzylidene *p*-*n*-butylaniline
IBPBAC	iso-butyl 4(4′ phenylbenzylidineamino)cinnamate
MBBA	*p*-methoxybenzylidene *p*-*n*-butylaniline
MBCA	*p*-methoxybenzylidene *p*-cyanoaniline
80SF	octyloxybiphenyl-4-carboxylate
PBAPC	*p*-phenyl benzylidene-*p*-amino-*n*-pentylcinnamate
TBBA	terephthal-bis-(4-*n*-butylaniline)
TBPA	terephthalydine-bis-4-*n*-pentylaniline
TLST	thallium stearate

groups." As discussed further in the next section, a smectic *C* mesophase is comprised of parallel layers in which the molecules are tilted with respect to the plane of each layer. de Vries pictures a skewed cybotactic group as one such smectic *C* layer in which the molecules are parallel to the nematic director but the layer boundaries are tilted at an angle corresponding to the location of the four spots in Figure 5.

It should be noted that a single skewed cybotactic layer, such as the one depicted by de Vries,[39] would give rise to a radial intensity distribution in reciprocal space passing through the origin and directed at right angles to the tilted layer.[29,40] A stack of a large number of parallel layers, conversely, would give rise to a periodically spaced set of reciprocal-lattice points along

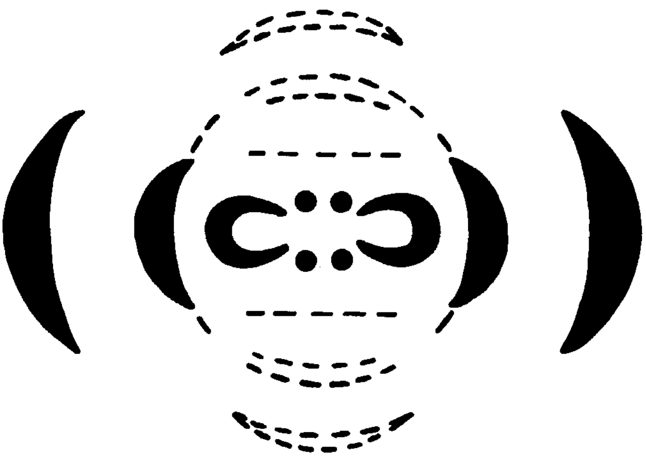

FIGURE 5 Tracing of x-ray intensities in an aligned nematic photograph. (After Chistyakov and Chaikowskii[39]).

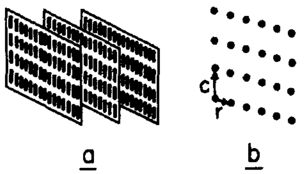

FIGURE 6 *a*. Planar arrays of molecules aligned parallel to a common direction. *b*. Two-dimensional net within a planat array.

this radial direction. Clearly, a smaller stack of such layers, intermediate between the two extreme cases above, would give rise to one or more elongated reciprocal-lattice "spots." Since the actual intensities are observed to have linear extensions normal to the meridian,[38,39] Azároff suggested that the nearly periodic strings of rigid molecules present in an aligned nematic (Figure 1*b*) tend to array themselves into diperiodic sheets as indicated in Figure 6*a*. The linear molecules may be tilted about their centers of gravity (Figure 6*b*), in or out of the sheets, and such tilts account for the arcing of the equatorial intensities. Parallel stacks of such sheets are regularly spaced but the stacks are not periodic along any direction out of the sheets so that they give rise to rod-like intensity distributions in reciprocal space, with the rods constrained to planes normal to the meridian. It can be shown[40] that such finite stacks of parallel sheets account for the observed intensity distribution. Note that the occupation of space in an actual nematic mesophase also requires the presence of uncorrelated periodic molecular strings between such stacks. Upon heating the mesophase, the number and size of the stacks decreases while the number of uncorrelated strings increases accounting thereby for a progressive formation of intensity disks that replace the intensity dumbbells.

As stressed in the concluding section below, careful experimental techniques, not employing the normal-beam arrangement favored in previous investigations, should help develop correct models for the structural arrays in mesophases. Samples aligned in an external field intrinsically give more information about their molecular arrays and any molecular motion[41] than do unaligned ones. It is doubtful that conclusions regarding the possible presence of cybotactic groups can be deduced from unaligned samples as has been suggested in some recent studies.[42,43] Even when neutrons whose scattering cross sections do not fall off with scattering angle as they do for X-rays are used, the only differences that can be observed between the scattering by unaligned nematic and liquid phases is a slight change in the relative intensities of the diffraction maxima.[44] Incidentally, because the incoherent neutron scattering cross section for hydrogen can approach 90% of that of an entire molecule, neutron diffraction experiments should be carried out on fully deuterated samples, which are difficult to prepare.

SMECTIC MESOPHASES

The rigid-rod-like molecules believed to be the building blocks of all liquid crystals can array themselves in parallel layers to form a *smectic* mesophase.[4, 5] The molecules may be normal to the planes of the layers or tilted within them. They may be randomly distributed within the layers or partly ordered or, in some cases, assume very nearly a lattice array. There can exist correlations between the layers but, except in the more ordered ones, there are none; although some evidence exists that there may be correlations forming "strings" of molecules penetrating several neighboring layers.[45] This leads to an almost bewildering number of possible arrays so that it is not surprising that proposals for a single classification scheme can still encounter considerable debate.

Initially, liquid crystals were classified according to their optical anisotropies:[46] Smectic A mesophases ($\mathrm{Sm_A}$) are optically uniaxial because the molecules are assumed to be normal to the layers and randomly distributed within them. The perpendicular rods are believed to be ordered in a hexagonal array within a smectic layer of the smectic B mesophase ($\mathrm{Sm_B}$) with limited correlation between layers so that $\mathrm{Sm_B}$ also is optically uniaxial. With one exception (an isotropic mesophase believed to have an isometric structure), the other smectic phases are optically biaxial. In the smectic C mesophase ($\mathrm{Sm_C}$) the molecules are believed to be tilted and randomly distributed throughout the layers, whereas in the other mesophases ($\mathrm{Sm_D}$, $\mathrm{Sm_E}$, etc.) the molecular arrangements become increasingly more ordered,[47,48] as indicated in Table II and discussed briefly below.

Diele, Brand, and Sackmann[49] describe their X-ray diffraction photographs of unaligned $\mathrm{Sm_A}$, $\mathrm{Sm_B}$, and $\mathrm{Sm_C}$ as containing one or more sharp inner rings (with Cu $K\alpha$, the first-order reflection occurs at $\theta \sim 2°$) and typically, one outer ring ($\theta \sim 10°$) that is quite sharp for $\mathrm{Sm_B}$ but diffuse in the case of $\mathrm{Sm_A}$ and $\mathrm{Sm_C}$. The outer ring is used to calculate a d value that they equate to the intermolecular (side-to-side) separation and attribute its diffuseness in $\mathrm{Sm_A}$ and $\mathrm{Sm_C}$ to the disorder and nonparallelism of the molecules within the layers. The sharp inner ring or rings can be used to calculate the effective layer thickness which, in turn, can be compared to molecular lengths deduced from model calculations.† In Part II of their publication,[49] Diele *et al.* describe an isotropic smectic phase ($\mathrm{Sm_D}$) which gives rise to six inner spots in addition to an outer diffuse ring in a normal-beam photograph, and a more highly ordered SmE which has three sharp

---

† Knowing the length L of the constituent molecules and finding that the inter-layer separation d is considerably less than L, has led several investigators[62] to suggest that the molecules must be tilted, in which case d/L is the cosine of the tilt angle.

TABLE II

Liquid crystal arrays

Symbol	Name	Molecular alignment
N	Nematic	Strong tendency to parallel a single director and, sometimes, to form nearly periodic molecular strings. (Figure 1*b*)
Sm_A	Smectic *A*	Molecular layering in which the molecules within each layer tend to be parallel, but uncorrelated, with long axes normal or nearly normal to plane of layer. (Figure 7*a*)
Sm_B	Smectic B	Molecular ordering within each layer into a regular hexagonal packing.
Sm_C	Smectic *C*	Uncorrelated but nearly parallel molecules that are tilted relative to plane of layer. (Figure 7*b*)
Sm_D	Smectic *D*	Believed to have isotropic (cubic) molecular array
Sm_E Sm_H	Smectic *E* to Smectic $_H$	More highly ordered molecular arrays within parallel layers with molecular correlations within layers and between layers possible.

outer rings. The authors also show X-ray photographs of aligned smectic *A*, *B*, and *C* mesophases. In all thee cases, the outer rings become equatorial arcs (relatively sharp in Sm_B) while the inner ones become periodic spots (small disks?) along the meridian. The innermost meridional intensity distributions contain, in addition the narrow disks (lines) normal to the meridian, short intense lines (reciprocal-lattice rods?) coincident with the meridian. Similar meridional extensions are visible in photographs of smectic mesophases published by Chistyakov *et al.*[50] Whether they are characteristics of the samples or experimental artifacts has not been discussed in the literature.

The classification system proposed by Sackmann and co-workers was expanded by de Vries[51] to include three kinds of nematic, two cholesteric and eight distinguishable smectic phases ranging from *A* to *H*, which are grouped into α, β, and γ classes. The basis for the proposed groupings is structural and relies entirely on the interpretation of unaligned and aligned normal-beam photographs. This publication also contains the only X-ray photograph of an oriented Sm_C mesophase in which the "meridional" intensity distribution appears to be tilted relative to the line joining the

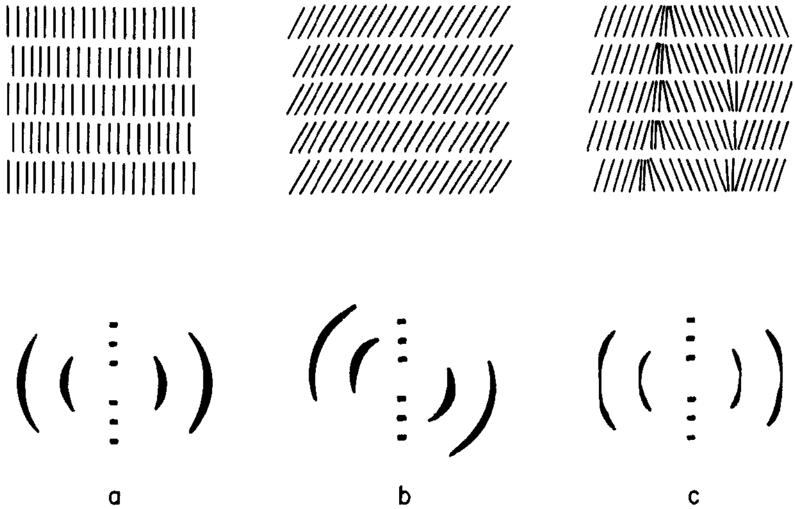

FIGURE 7 Molecular arrays (cross sections of parallel layers) and normal-beam diffraction patterns of smectic mesophases produced when incident beam is parallel to the smectic layers. *a*. Aligned $\mathrm{Sm_A}$. *b*. Aligned $\mathrm{Sm_C}$. *c*. Polydomains in $\mathrm{Sm_C}$.

centers of the equatorial arcs that the present author has encountered during his review of the X-ray literature published prior to 1979.† Only one pair of diffuse inner spots appears (his Figure 6) close to the beam stop as compared to four more distant meridional spots visible in a companion photograph of a $\mathrm{Sm_A}$ mesophase. This is of more than passing interest because McMillan has developed a molecular theory for smectic mesophases[53] from which it follows that the rigid molecules in $\mathrm{Sm_A}$ are free to rotate about their long axes, are normal to the layers, and have no translational order, while in $\mathrm{Sm_C}$ they are frozen in orientations that are tilted relative to the planes of the layers but without translational order. If, in fact, the planes of the molecules in $\mathrm{Sm_C}$ are aligned, then *X*-ray diffraction patterns should show intensity redistributions as discussed next.

In their review paper, Falgueirettes and Delord[7] show how the normal-beam photographs of $\mathrm{Sm_A}$ and $\mathrm{Sm_C}$ may differ. [Their Figure 3.2(*c*) and (*d*) are emulated in Figures 7(*a*) and (*b*).] The meridional intensities appear as sharp spots along the vertical (the smectic planes are assumed parallel and quite regularly spaced) but the equatorial reflections are shown skewed for $\mathrm{Sm_C}$ in order to account for the tilted molecules in the layers. Although this point is not stressed, a photograph like Figure 7(*b*) occurs only if the

---

† A schematic drawing showing such a skewed relation also was published by de Vries.[52] See also discussion of $\mathrm{Sm_C}$ and $\mathrm{Sm_F}$ mesophases below.

irradiated sample forms a single domain in which all the molecules are tilted parallel to a common director (Figure 8). The probable reason for the paucity of published photographs of such an array can be attributed therefore, to the difficulty of obtaining monodomains.† But it is less clear why aligned polydomain photographs based on such an array are not also easily found in the literature. As suggested in Figure 7(*c*), if several domains like the "accepted" model of $\mathrm{Sm_C}$ are irradiated, the meridional spots should lie along a line normal to the line joining the equatorial arcs (the molecular centers of gravity remain parallel to the layers regardless of how the molecules dispose themselves.) While the intensity distribution in the equatorial arcs should reflect the intensity distribution (scattering) in reciprocal space of individual molecules (structure factor, intermolecular correlations, and orientational distribution). Clearly, many more possible arrays can be imagined for $\mathrm{Sm_C}$ mesophases (c.f. Ref. (7)) and it is possible that more determined efforts to discern them will provide a better picture of the actual arrays present.

Diele, Brand and Sackmann recorded normal-beam photographs like Figure 7(*a*) for all but one of the $\mathrm{Sm_A}$, $\mathrm{Sm_B}$, and $\mathrm{Sm_C}$ mesophases that they examined from which they concluded that the molecules must be normal to the layers in all three.[49] As pointed out above, without a careful analysis of the intensity distribution within the meridional and equatorial maxima, an unambiguous conclusion cannot be drawn, and de Vries has reviewed[8] various experimental data (in addition to X-ray diffraction) regarding the tilt in $\mathrm{Sm_C}$ and its dependence on temperature. This has led him to suggest that more than one kind of $\mathrm{Sm_C}$ phase can be distinguished and to consider how this would affect $\mathrm{Sm_C}$ to $\mathrm{Sm_A}$ phase transitions.[55] It is interesting to note in this connection that three different theoretical models for $\mathrm{Sm_C}$ ordering[53,56,57] were examined by de Jeu[58] with the aid of X-ray data from alkyl- and alkoxy-substituted azobenzenes and a qualitative agreement with McMillan's model[53] obtained. On the other hand, Bartolino, Doucet and Durand[59] have compared optical and X-ray data for four compounds forming both $\mathrm{Sm_A}$ and $\mathrm{Sm_C}$ mesophases and concluded that a rigid core of each molecule underwent progressive tilting as the temperature was lowered below the transition point to the $\mathrm{Sm_C}$ phase but the aliphatic end chains remained more nearly normal to the layer boundaries.[60] Aliphatic end chains also appear to play an important role in determining the degree of inter-layer correlations and, hence, the relative stability of the different mesophases.[61]

---

† Monodomains (stepped drops) were used in a diffractometric study of the structure of three $\mathrm{Sm_A}$ mesophases,[54] two of which were shown to have the component molecules (EPAB and TLST) tilted relative to the plane of the layers, but no photographs were published.

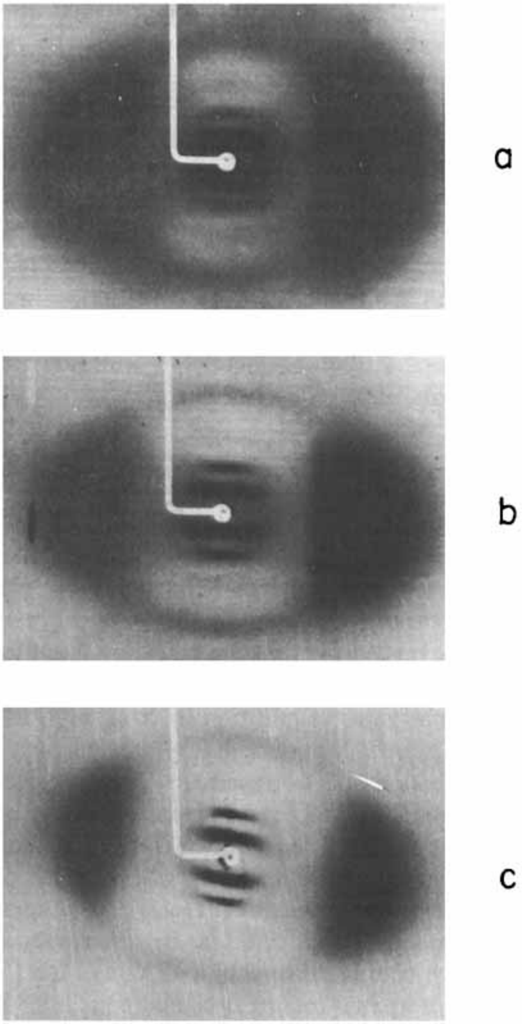

FIGURE 8 Normal-beam photographs of aligned TBBA. (After Leadbetter and Wrighton[108]). *a*. Nematic at 207°C. *b*. Sm_A at 128°C. *c*. Sm_C at 159°C.

More recently, de Vries has suggested that the molecules are tilted in Sm_A as well as Sm_C mesophases since the orientational order parameter (see next section) in Sm_A is less than unity.[62] This is consistent with his structural model for liquid crystals in which their formation is attributed to a slight disorder in the alkyl chains at the ends of the rigid molecules.[63] Expanding this concept, de Vries has shown that it is necessary to distinguish molecular tilt angles from optically measured tilts[64] and suggests that the former agrees better with the temperature dependence of the molecular tilt at the Sm_A to Sm_C transition.

In addition to optical and X-ray data, it has been suggested[46] that the miscibility of two mesophases could serve as a criterion in determining whether they should be classified in a common grouping. In the case of solid crystals, it is well known that two compounds must be isotypic and contain atoms whose radii differ by less than 15% before extensive solid solutions are possible. In the case of smectic mesophases, however, the fluidity of the layers apparently relaxes such criteria and considerable miscibility between two seemingly different end members can occur.[65] Further examples of miscibility criteria involving normal and tilted Sm_B mesophases have been given by Goodby and Gray[66] while Richter, Demus and Sackmann[67] have examined the solubility of TBBA and BBEA with several other mesophases and present classifications for various polymorphic phases of each that appear to remove previous contradictions between miscibility criteria and X-ray structures.

Instead of attempting an evaluation or classification of all the various structures that have been described so far, some illustrative examples have been chosen for discussion here. Probably the most carefully and thoroughly studied mesomorphic system, that of TBBA, is considered first. Terephthal-*bis*-butylaniline can exist in two crystalline polymorphs and in Sm_B (1130, Sm_C (144°), Sm_A (172°) and N (200°) mesomorphs (transition temperatures are shown in degrees Celsius), before becoming an isotropic liquid (236°). Two additional smectic phases have been reported to form (reversibly) between the crystalline and Sm_B mesophase[68] and will be included in the present discussion. Starting with the X-ray photographs of a single crystal and a Sm_B monodomain prepared by Mmes. Levelut and Lambert,[69] the structural features of these two phases have been worked out by Doucet *et al.*[70–73] as follows:

1) The crystalline (room-temperature) phase is monoclinic, space group $C2/c$, with $a = 17.57$, $b = 5.75$, $c = 53.2$ Å, $\beta = 115.47°$.

2) The diffraction by the Sm_B phase can be indexed with a cell that has $a = 10.15$, $b = 5.18$, $c = 28.6$ Å, $\beta = 119°$.

3) The TBBA molecules are parallel to the **a** axes in the crystalline and smectic phases with the Sm_B layers parallel to (001) planes (based on above cell).

4) Strings containing about seven molecules can move parallel to **c** and independently of each other in the mesophase and give rise to diffuse disks in reciprocal space normal to the string direction.

5) In a plane normal to **c** (string director) the molecules have a very nearly hexagonal packing.

6) The lengths of the strings decline to about four molecules at the transition point to Sm_C (disks broaden along meridian) and thermal vibrations increase (causing relative decline of higher-order intensities).

7) In the Sm_B mesophase, the molecules can rotate about their long axes.

This last deduction was confirmed by inelastic neutron scattering experiments[74] which also showed that the molecular reorientations favor six alignments $\pi/3$ apart. As the Sm_B is cooled to about 84°C, domains containing molecules fixed in each of these six alignments grow in size, producing the Sm_E mesophase. Further evidence for the rotational freedoms of TBBA molecules is provided by NMR,[75] quasielastic neutron scattering,[76] NQR,[77] and inelastic neutron scattering.[78]

A neutron diffraction study of the Sm_A modification[79] also indicates that a very weak magnetic field can induce order via cooling through the nematic phase in TBBA with only a few degrees of misorientation of the smectic planes, as calculated from rocking-curve widths. After examining a monodomain of PBAPC, Doucet *et al.*[80] concluded that its Sm_E structure is quite similar to the TBBA mesophase formed upon cooling Sm_B below 84°C. The second TBBA mesophase, formed upon cooling the Sm_E phase below 68°C, is intermediate in structure between Sm_E and the crystal,[68] having $a = 55.24$, $b = 5.27$, $c = 10.17$ Å and $\beta = 122°$. It is interesting to note that, despite the high degree of structural regularity in these phases,† as Sm_E phases are heated, the rotational motion of constituent molecules increases in a fairly regular way.[82] Thus it would seem that the liquid-crystalline state is frequently accompanied by the presence of some degree of rotational freedom for the rod-like molecules.

Citing just a few other recently published X-ray studies of special interest,‡ normal-beam photographs taken along the smectic layers of monodomains of two mesophases of several benzylideneanilines show sharp and diffuse streaks (disks) normal to the meridian and crescents normal to the equator.[83] When the incident beam is directed at right angles to the smectic layers in these monodomains, there appear six broad reflections that are symmetric about the direct beam, suggestive of Sm_B type packing.[83] A reexamination of the isotropic Sm_D modification led Tardieu and Billard to conclude[84] that the body-centered unit cell has $a = 102$ Å because the observed d-value ratios are $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{8}$, $\sqrt{10}$ and $\sqrt{11}$. With this choice of a, the first observed reflection is from (211), followed by (220), etc., a somewhat unusual but not impossible result.

---

† Goodby and Gray have proposed a new classification scheme[81] in which these phases are labelled Sm_E (molecules orthogonal) and Sm_G (molecules tilted).

‡ X-ray studies prior to 1975 have been described in earlier review papers.[6,7,51]

A very careful X-ray characterization of some new smectic phases of TBPA and 80SF have been published by Leadbetter *et al.*[85] (Figure 8). Both compounds form nematic N, Sm_A, Sm_C, Sm_F, Sm_H, and Sm_G phases upon cooling from the isotropic liquid. By means of very careful experimental procedures, including slow cooling in a strong magnetic field, monodomains (or very highly aligned samples) are obtained for X-ray examination. Thus the photographs (their Figures 2(*a*) and 4(*a*) clearly show sharp reflections from the Sm_C planes lying along a line that is tilted relative to the equator joining the diffuse arcs (Figures 7(*b*) and 8(*c*) in the present paper). The reader is referred to the original publications for structural details, but the five smectic phases formed are similar in each compound and differ primarily in the degree of molecular tilt relative to the smectic layer and the degree of ordering within the layers. In this connection, Helfrich[86] has drawn attention to the fact that the possible orders in smectic layers must conform to the tabulated plane-group symmetries.[87] Although there appears to be some confusion (p. C3–111) between the symmetries of molecules and those of the equipoint sets present in each plane group,[87] the speculations regarding the way that the more ordered Sm_B, Sm_E, Sm_F, Sm_G and Sm_H mesophases may be grouped and may transform into each other should prove to be helpful in analyzing such relationships in the future. Thus a classification system based on a herringbone array of linear molecules has been proposed[88] that yields two sets of five orthorhombic and three monoclinic smectric layer structures, for centric and acentric molecules, respectively.

In what will, hopefully, become a model for future X-ray diffraction studies of liquid crystals, Leadbetter *et al.*[89] first present the crystal structure of smectogenic IBPBAC (space group *Cc* with $a = 20.115$, $b = 5.589$, $c = 37.816$ Å, $\beta = 97.53°$) and then compare the diffraction diagrams of Sm_E oriented by cooling in a strong magnetic field to those obtained by melting single crystals that were first oriented so that each of the three crystal axes, respectively, was parallel to the incident beam. In this way, they discover that what is a seemingly simple monolayer pattern appears to be so deceptively because "the patterns are not symmetrical about zero," i.e., the specimen is misaligned relative to the incident beam. Again, the reader should refer to the original paper for structural features of the Sm_B and Sm_E mesophases. It is worth repeating here their admonition, however, that "it should be emphasized that the subtleties of structure discussed above would not generally be observed with a powder or a poorly aligned specimen."

Most recently, Leadbetter *et al.* have examined Sm_A mesophases of a number of cyano derivatives.[90] When the smectic layer spacings (*d*) are compared to the molecular lengths (*L*), an anomalous ratio $d/L \sim 1.4$ is obtained. It is shown that the quantity *d*-*L* is directly related to the lengths of the alkyl or alkoxyl tail of the molecules but not to the lengths of their aromatic cores. This led the authors to postulate the presence of bimolecular layers having overlapping molecular cores at the centers of the layers.[90] Bimolecular groupings also have been postulated for nematic liquid crystals[36] and for double-axis Schiff's bases which provide examples of Sm_C arrays in which the phenyl rings within the molecular cores are enjoined from rotation about the molecular axes by such pairings.[91]

Bilayer stacking sequences also have been observed to occur in Sm_B mesophases.[92] This is the first time that detailed information is presented about the packing of adjacent layers in Sm_B mesophases and that the fine structure manifest in the meridional reflections is correlated to possible structural models. In another publication, Leadbetter *et al.*[93] describe how hexagonal closest-packed layers can form ... *AB* ..., ... *ABC* ..., and random stacking sequences in Sm_B mesophases.

PHASE TRANSITIONS

When speaking of phase transitions in liquid crystals, it is necessary to describe the way that the molecular order changes as a function of temperature. Starting with the theory for nematic ordering of an isotropic liquid developed by Maier and Saupe,[94] other theories have been proposed and refined for nematic mesophases,[95–97] for Sm_A mesophases,[95, 97–101] for Sm_C mesophases,[53, 102] and for the more highly ordered mesophases[102, 104] as well. Basically, Maier and Saupe demonstrated that the angle ϕ between the director and the long axes of a rod-like molecule can be used to calculate an orientational order parameter $\eta = \langle(3\cos^2\phi - 1)/2\rangle$ in a nematic phase. What subsequent theoretical analyses have done is to define the order parameter as the amplitude of a one-dimensional electron-density wave. This, in turn, allows the calculation of the mean squared fluctuations in the alignment parallel to the director, along two mutually orthogonal directions, in terms of elastic constants that relate the splay, twist, and bend (of smectic planes) to these fluctuations.

To test the predictions of these theories by X-ray diffraction it is necessary to measure the intensity distribution along the meridian (parallel to the director and at right angles to it at the position of the l diffraction maximum, as a function of temperature. McMillan has made careful diffractometer measurements on nematic mesophases[97, 105] and near a Sm_A–N phase transition;[106] these agree well with his calculated curves. Litster *et al.* has used light scattering and high-resolution X-ray diffractometry to examine the parameters controlling order fluctuations near the Sm_A–N transition in several mesophases.[107] Light scattering is especially suited to determine the director-mode fluctuations, while X-ray diffraction intensities are sensitive to electron-density fluctuations, so that they complement each other perfectly. Molecular orientational distributions also have been studied in N, $\mathrm{Sm_A}$ and $\mathrm{Sm_C}$ phases photographically, with intensity contours provided by a microdensitometer.[108] Although careful photographic technique is capable of yielding intensities that are quantitatively as good as diffractometer measurements, the latter have obvious advantages of speed when temperature-dependent parameters are being studied. On the other hand, diffractometers do not record intensities in any part of reciprocal space that they are not specifically directed to explore. It is good practice, therefore, to supplement measurements of intensity made with a diffractometer with photographic records of the total intensity distribution being scanned.

Using densitometer tracings of normal-beam photographs of two compounds forming nematic and $\mathrm{Sm_C}$ mesophases and one forming N and $\mathrm{Sm_A}$ mesophases, Leadbetter and Norris[109] have determined the complete distribution functions for the molecular tilts as well as the density waves along the directions of the directors. They obtain reasonable agreements with the simple mean field theory[94] although their values of the order parameter generally differ from this theory. This is the first time that complete distribution functions (as distinct from order parameters) have been reported for nematic and smectic mesophases.

X-ray diffraction also can be used to determine the transition temperature of a phase change by noting, for example, a displacement of the meridional reflection in a $\mathrm{Sm_A}$–$\mathrm{Sm_C}$ or Sm–N transition. It is not as sensitive for this purpose as is either polarized-light microscopy or differential scanning calorimetry. Nevertheless, X-rays can disclose structural changes accompanying transitions, such as, for example, the presence of a mixed-phase region and its composition,[110] changes taking place in the short-range order,[111] and the dependence of the transition temperature on prior thermal history.[112]

OTHER MESOPHASES

X-ray diffraction by cholesteric mesophases has been ignored so far in this review largely because most of the limited number of published studies deal with lyotropic mesophases examined by small-angle X-ray scattering.[113] Based on wide-angle X-ray scattering intensities, Chistyakov compared the radial-distribution functions of a smectic and cholesteric phase,[114] McMillan measured the short-range order fluctuations,[97] and Suresh and Chandrasekhar reported preliminary optical and X-ray results on a couple of compounds that form twisted nematic and twisted $\mathrm{Sm_C}$ mesophases.[115]

Many polymers display physical characteristics and X-ray diffraction patterns similar to those of liquid crystals† (c.f. Ref. (32)) so that it is possible to follow mesomorphic transitions in polyorganophosphazenes,[117] for example. The liquid-crystalline order that can occur in polymers recently has been described in a book edited by Blumstein[118] and includes discussions of lyotropic biological and block copolymers and regular polymers whose side groups can exhibit nematic, cholesteric, and smectic order. This latter group can be studied by wide-angle X-ray scattering and preliminary data on a list of compounds has been recently presented.[119]

A new type of liquid crystal can be formed from planar molecules that tend to array themselves in columns which, in turn, prefer hexagonal closest packing.[120] Since this structural model is based on only three diffuse Debye–Scherrer rings, it is not possible to conclude whether columns or lamellar ordering of the disk-like molecules[121] forms the structure of these mesogens.

CONCLUSION

In looking back to assess what has been firmly established and what needs further exploration, it almost seems that the latter need outweighs the former gain. Are the molecules in mesophases free to rotate? Recent evidence clearly says that they are and that rotational freedom persists.[122, 123] For X-ray diffraction purposes, of course, the molecules do not need to be physically rotating in order to liken them to cylindrically symmetric rods. Since X-rays can only record intensities averaged over the time of measurement (minutes or hours) and irradiated volume (mm^3), it is sufficient that they be allowed to assume statistically random orientations about their long axis.

One can similarly wonder whether the molecules are tilted in some, all, or none of the various smectic mesophases. Contradicting his own previous conclusions, de Vries now seems to believe that the molecules are tilted in all Sm_A phases.[124] Before this or similar questions can be answered definitively, however, considerably more evidence is needed.‡ Thus the presence of correlated strings of molecules in nematic and even smectic mesophases should be investigated by careful studies based on monodomain samples. In their speculation about the apparent success of the Maier–Saupe theory,[94] Luckhurst and Zannoni argue that long-range

---

† Both lyotropic and thermotropic types of polymeric liquid crystals have been reviewed recently by Samulski and DuPré.[116]

‡ Among these needs is that of more carefully measured X-ray data. For example, a recent publication[125] describes a computerized procedure for correcting photographic scans for noncircularity in the recorded Debye-Scherrer ring. Such a procedure can be avoided by assuring that the film is placed exactly normal to the incident X-ray beam.

forces are more important than short-range forces because the latter do not change much at the transition from the liquid state.[126] Whether this kind of model or one based on one-dimensional density waves in what is a three-dimensional, orientationally ordered liquid[107] will turn out to be more useful in explaining mesomorphic properties also still has to be tested. It may prove helpful, in this connection, to redefine the original classification of matter proposed by Friedel.[4] In place of describing the liquid, nematic, smectic, and crystalline phases as having 0-, 1-, 2-, and 3-dimensional order, respectively, it may be helpful to introduce the concept of *directional* order. Thus, a "classic" nematic has only 1-directional order whereas a "cybotactic" nematic and Sm_C have 2-directional order, etc. Since two or more directions can lie in the same plane, the distinction between "direction" and "dimension" is real and may prove helpful. (See also Ref. (88).)

Another experimental detail that has received relatively little attention is the orientating effect that the liquid-crystal container may have on the molecular alignments observed. This is probably so because it is presupposed that the array has cylindrical symmetry so that cylindrical containers should be suitable, even though the orientating effect of container walls is well known from optical studies.† Another probable reason for this neglect is that, typically, only a normal-beam photograph is prepared so that possible departures from cylindrical symmetry are not noted. Almost fifty years ago, however, Kast observed[10] that nematic *p*-azoxyanisole yields regular Debye–Scherrer rings when the crystalline powder is first heated. Following recrystallization in the capillary container and subsequent heating, the nematic mesophase shows considerable molecular alignment (see Figure 2(*a*)) along a direction determined by the container's walls.

In closing, a plea is addressed to future investigators of liquid crystals by X-ray diffraction: Whenever the intensity distribution in reciprocal space contains maxima not limited to the equator and meridian, make use of moving-film methods[127] to record the intensities. Normal-beam, stationary-crystal photographs are Laue pictures which are difficult to interpret even when the symmetry is high (cubic) and the X-ray beam is polychromatic. By comparison, the Buerger precession method yields an undistorted view of any part of reciprocal space and removes any possible ambiguities in its interpretation. Alternatively, an equi-inclination rotating-crystal camera[128] may prove to be more convenient. As is well known, equi-inclination enables exploration of almost the entire accessible reciprocal lattice without the blind spots along the meridian that arise in the normal-beam method.

---

† The effect of container shape was checked recently[92] and found to be insignificant in the case of an aligned Sm_B mesophase.

NOTE ADDED IN PROOF

Three complimentary review articles have just appeared in two books:

A. de Vries, "Structure and classification of thermotropic liquid crystals" in *Liquid Crystals*, Ed. F. D. Saeva (Marcell Dekker, Inc., New York, 1979) pp. 1–72.

A. J. Leadbetter, "Structural studies of nematic, smectic A and smectic C phases" in *The Molecular Physics of Liquids*, Eds. G. R. Luckhurst and G. W. Gray (Academic Press, New York, 1979) pp. 285–316.

J. Doucet, "X-ray studies of ordered smectic phases" in above pp. 317–341.

Acknowledgements

The author wishes to express his thanks to Professors W. J. MacKnight, R. S. Porter and R. S. Stein for their hospitality at the University of Massachusetts and to Professors M. J. Buerger, A. C. Griffin, J. R. Knox, and J. F. Johnson for their helpful critiques of this manuscript. Thanks are also due to Professor Leadbetter for providing prepublication copies of several of his recent contributions and to L. F. McCurdy for preparing the illustrations in their final form.

References

1. C. A. Taylor, *European Polymer J.*, **2**, 279 (1966).
2. F. Reinitzer, *Monatsch. Chem.*, **9**, 421 (1888).
3. O. Lehman, *Z. Physik. Chem.*, **4**, 462 (1889).
4. G. Friedel, *Ann. Phys.*, **18**, 273 (1922).
5. G. Friedel, *Colloid Chemistry*, ed. by J. Alexander (The Chemical Catalog Co., Inc., New York, 1926), Vol. I, p. 102 ff.
6. G. H. Brown and W. G. Shaw, *Chem. Rev.*, **57**, 1049 (1957).
7. J. Falgueirettes and P. Delord, *Liquid Crystals and Plastic Crystals*, ed. by G. W. Gray and P. A. Winsor (Harwood, Sussex, 1974), Vol. 3, p. 62.
8. A. de Vries, *J. de Phys.*, **36**, Cl-1 (1975).
9. K. Herrmann, A. H. Krummacher and K. May, *Z. Phys.*, **73**, 419 (1931).
10. W. Kast, *Z. Phys.*, **71**, 39 (1931); **79**, 146 (1931); **76**, 19 (1932).
11. K. Herrmann, *Z. Krist.*, **79**, 186 (1931).
12. B. K. Vainshtein, *Diffraction of X-Rays by Chain Molecules* (Elsevier Publishing Co., Amsterdam, 1966), Chap. 3.
13. R. Hosemann and S. N. Bagchi, *Direct Analysis of Diffraction by Matter* (North-Holland Publishing Co., Amsterdam, 1962), Chap. 9.
14. R. Hosemann and B. Müller, *Liquid Crystals II*, ed. by G. H. Brown (Gordon and Breach Science Pub., London, 1969), p. 139.
15. K. Vainshtein and I. G. Chistyakov, *Sov. Phys. Dokladi*, **8**, 1044 (1963).
16. A. de Vries, *J. Chem. Phys.*, **56**, 4489 (1972).
17. B. K. Vainshtein, I. G. Chistyakov, E. A. Kosterin, V. M. Chaikowskii, and A. D. Inozemstva, *Sov. Phys. Crystallogr.*, **16**, 624 (1972); *ibid* **17**, 424 (1973); B. K. Vainshtein and I. G. Chistyakov, Pramaña, SI, 79 (1975).
18. R. Hosemann and B. Müller, in *Liquid Crystals II*, ed. by G. H. Brown (Gordon and Breach Science Pub., London, 1969), p. 139.
19. U. Mukhopadhyay and C. A. Taylor, *J. Appl. Cryst.*, **4**, 20 (1971).
20. P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1974), p. 3.
21. E. Hückel, *Physik. Z.*, **22**, 561 (1921).
22. J. R. Katz, *Naturwiss.*, **16**, 758 (1928).

23. W. Kast, *Naturwiss.*, **21**, 737 (1933).
24. W. Kast, *Ann. Phys.*, **19**, 571 (1934).
25. G. W. Stewart, *Trans. Faraday Soc.*, **29**, 982 (1933); *J. Chem. Phys.*, **4**, 231 (1936).
26. G. W. Stewart and R. M. Morrow, *Phys. Rev.*, **30**, 232 (1927).
27. G. W. Stewart, *Phys. Rev.*, **38**, 931 (1931).
28. W. Kast, *Z. Phys.*, **71**, 39 (1931).
29. R. W. James, *The Optical Principles of the Diffraction of X-Rays* (G. Bell and Sons, London, 1948), p. 582.
30. R. S. Bear and O. E. A. Bolduan, *Acta Cryst.*, **3**, 236 (1950).
31. G. Oster and D. P. Riley, *Acta Cryst.*, **5**, 272 (1952).
32. W. W. Adams, L. V. Azároff, and A. K. Kulshreshtha, *Z. Kristallogr.*, in press (1979).
33. c.f. L. V. Azároff, *Elements of X-Ray Crystallography* (McGraw-Hill Book Co., Inc., New York, 1968), p. 551.
34. R. Hosemann, K. Lemm, and W. Wilke, *Liquid Crystals I*, ed. by G. H. Brown (Gordon and Breach Science Pub., London, 1969), p. 449.
35. A. de Vries, *Mol. Cryst. Liq. Cryst.*, **10**, 219 (1970).
36. A. J. Leadbetter, R. M. Richardson, and C. N. Colling, *J. Phys.*, **36**, Cl-37 (1975).
37. A. Guinier, *X-Ray Diffraction* (W. H. Freeman and Co., San Francisco, 1963), p. 304.
38. I. G. Chistyakov and W. M. Chaikowsky, *Mol. Cryst. Liq. Cryst.*, **7**, 269 (1969).
39. I. G. Chistyakov and W. M. Chaikowskii, *Sov. Phys. Crystallogr.*, **18**, 181 (1973).
40. L. V. Azároff, *Proc. Nat. Acad. Sci.*, (to be published in 1980).
41. A. J. Leadbetter, R. M. Richardson, and J. C. Frost, *J. Phys.*, **40**, C3-125 (1979).
42. K. A. Suresh and S. Chandrasekhar, *Mol. Cryst. Liq. Cryst.*, **40**, 133 (1977).
43. A. Blumstein and L. N. Patel, *Mol. Cryst. Liq. Cryst. Letters*, **41**, 195 (1978).
44. N. Niimura, *Mol. Cryst. Liq. Cryst.*, **31**, 123 (1975).
45. J. Doucet, A. M. Levelut, and M. Lambert, *Mol. Cryst. Liq. Cryst.*, **24**, 317 (1973).
46. H. Sackmann and D. Demus, *Mol. Cryst.*, **2**, 81 (1966); *Fortschr. Chem. Forsch.*, **12**, 394 (1969).
47. H. Sackmann and D. Demus, *Mol. Cryst. Liq. Cryst.*, **21**, 239 (1973).
48. D. Demus, *Z. Chem.*, **15**, 1 (1975).
49. S. Diele, P. Brand, and H. Sackmann, *Mol. Cryst. Liq. Cryst.*, **16**, 105 (1972); *ibid* **17**, 163 (1972).
50. I. G. Chistyakov, L. S. Schabischev, R. I. Jarenov, and L. A. Gusakova, *Mol. Cryst. Liq. Cryst.*, **7**, 279 (1969).
51. A. de Vries, *Pramaña, Supp.*, **1**, 93 (1975).
52. A. de Vries, *Acta Cryst.*, **A25**, S135 (1969).
53. W. L. McMillan, *Phys. Rev.*, **8A**, 1921 (1973).
54. W. R. Krigbaum, J. C. Poirier, and M. J. Costello, *Mol. Cryst. Liq. Cryst.*, **20**, 133 (1973).
55. A. de Vries, *Mol. Cryst. Liq. Cryst. Letters*, **41**, 27 (1977).
56. A. Wulf, *Phys. Rev.*, **A11**, 365 (1975).
57. R. G. Priest, *J. Phys.*, **36**, 437 (1975); *J. Chem. Phys.*, **65**, 408 (1976).
58. W. H. de Jeu, *J. Phys.*, **38**, 1265 (1977).
59. R. Bartolino, J. Doucet, and G. Durand, *Ann. Phys. (France)*, **3**, 389 (1978).
60. D. Guillon and A. Skoulios, *J. Phys.*, **38**, 79 (1977).
61. J. J. Benattar, A. M. Levelut, and L. Strzelecki, *J. Phys.*, **39**, 1233 (1978).
62. A. de Vries, *Mol. Cryst. Liq. Cryst. Letters*, **49**, 143 (1979).
63. A. de Vries, *Mol. Cryst. Liq. Cryst. Letters*, **49**, 19 (1979).
64. A. de Vries, *Mol. Cryst. Liq. Cryst. Letters*, **49**, 179 (1979); *J. Chem. Phys.*, (July, 1979).
65. J. E. Lydon and C. J. Coakley, *J. Phys.*, **36**, Cl-45 (1975).
66. J. W. Goodby and G. W. Gray, *J. Phys.*, **40**, C3-363 (1979).
67. L. Richter, D. Demus, and H. Sackmann, *J. Phys.*, **40**, C3-41 (1979).
68. J. Doucet, A. M. Levelut, and M. Lambert, *Phys. Rev. Letters*, **32**, 301 (1974).
69. A. M. Levelut and M. Lambert, *C.R. Acad. Sc. (Paris)*, **272**, 1018 (1971).
70. J. Doucet, M. Lambert, and A. M. Levelut, *J. Phys.*, **10**, C5a-247 (1971); *Mol. Cryst. Liq. Cryst.*, **24**, 317 (1973).
71. A. M. Levelut, J. Doucet, and M. Lambert, *J. Phys.*, **35**, 773 (1974).

72. J. Doucet, J. P. Mornon, R. Chevalier, and A. Lifchitz, *Acta Cryst.*, **B33**, 1707 (1977).
73. J. Doucet, M. Levelut, and M. Lambert, *Acta Cryst.*, **B33**, 1710 (1977).
74. A. M. Levelut, *J. Phys.*, **37**, C3-51 (1976).
75. J. Doucet, A. M. Levelut, and M. Lambert, *Phys. Rev. Letters*, **32**, 301 (1974).
76. H. Hervet, F. Volino, A. J. Dianoux, and R. E. Lechner, *Phys. Rev. Letters*, **34**, 451 (1975); F. Volino, A. J. Dianoux, and H. Hervet, *J. Phys.*, **37**, C3-55 (1976); A. J. Dianoux, H. Hervet, and R. E. Lechner, *J. Phys.*, **38**, 809 (1977).
77. F. Volino and A. J. Dianoux, *Phys. Rev. Letters*, **39**, 763 (1977).
78. J. J. Benattar, A. M. Levelut, L. Liebert, and F. Moussa, *J. Phys.*, **40**, C3-115 (1979).
79. H. Hervet, S. Lagomarsino, F. Rustichelli, and F. Volino, *Acta Cryst.*, **A32**, 166 (1976).
80. J. Doucet, A. M. Levelut, M. Lambert, L. Liebert, and L. Strzelecki, *J. Phys.*, 36, Cl-13 (1975).
81. J. W. Goodby, and G. W. Gray, *Mol. Cryst. Liq. Cryst. Lett.*, **49**, 217 (1979).
82. A. L. Leadbetter, R. M. Richardson, and A. J. Carlile, *J. Phys.*, **37**, C3-65 (1976).
83. J. Doucet and A. M. Levelut, *J. Phys.*, **38**, 1163 (1977).
84. A. Tardieu and J. Billard, *J. Phys.*, **37**, C3-79 (1976).
85. A. J. Leadbetter, J. P. Gaughan, B. Kelly, G. W. Gray, and J. Goodby, *J. Phys.*, **40**, C3-178 (1979).
86. W. Helfrich, *J. Phys.*, **40**, C3-105 (1979).
87. *International Tables for X-Ray Crystallography*, N. F. M. Henry and K. Lonsdale, Eds. (The Kynoch Press, Birmingham, 1952), Vol. 1.
88. A. de Vries, *J. Chem. Phys.*, **70**, 2705 (1979).
89. A. J. Leadbetter, J. Frost, J. P. Gaughan, and M. A. Mazid, *J. Phys.*, **40**, C3-185 (1979).
90. A. J. Leadbetter, J. C. Frost, and J. P. Gaughan, *J. Phys.*, **40**, 375 (1979).
91. A. C. Griffin, M. L. Steele, J. F. Johnson, and G. J. Bertolini, *Noveau J. Chimie*, in press (1979).
92. A. J. Leadbetter, M. A. Mazid, B. A. Kelley, J. W. Goodby, and G. W. Gray, *Phys. Rev. Letters* (1979).
93. A. J. Leadbetter, J. C. Frost, and M. A. Mazid, *J. Phys. Letters*, **40**, L-235 (1979).
94. W. Maier and A. Saupe, *Z. Naturforsch.*, **13A**, 564 (1958); *ibid* **14A**, 882 (1959); *ibid* **15A**, 287 (1960).
95. W. L. McMillan, *Phys. Rev.*, **A4**, 1238 (1971).
96. P. D. de Gennes, *Mol. Cryst. Liq. Cryst.*, **12**, 193 (1971).
97. W. L. McMillan, *Phys. Rev.*, **A6**, 936 (1972).
98. K. K. Kobayashi, *Phys. Lett.*, **A31**, 125 (1970); *J. Phys. Soc. Japan*, **29**, 101 (1970); *Mol. Cryst. Liq. Cryst.*, **13**, 137 (1971).
99. P. G. de Gennes, *Solid State Commun.*, **10**, 753 (1972).
100. F. Bochard, *J. Phys.*, **34**, 411 (1973).
101. F. Jähnig and F. Bochard, *J. Phys.*, **35**, 301 (1974).
102. P. G. de Gennes, *C.R. Acad. Sci.*, **B274**, 758 (1972).
103. R. J. Meyer and W. L. McMillan, *Phys. Rev.*, **A9**, 899 (1974).
104. R. J. Meyer, *Phys. Rev.*, **A12**, 1066 (1975).
105. W. L. McMillan, *Phys. Rev.*, **A7**, 1673 (1973); *ibid*, **A8**, 328 (1973).
106. W. L. McMillan, *Phys. Rev.*, **A7**, 1419 (1973).
107. J. D. Litster, J. Als-Nielsen, R. J. Birgeneau, S. S. Dana, O. Davidov, F. Garcia-Golding, M. Kaplan, C. R. Safinya, and R. Schaetzing, *J. Phys.*, **40**, C3-339 (1979); J. Als-Nielsen, R. J. Birgeneau, M. Kaplan, J. D. Litster, and C. R. Safinya, *Phys. Rev. Letters*, **39**, 352 (1977); *ibid*, **39**, 1668 (1977); H. Birecki and J. D. Litster, *Mol. Cryst. Liq. Cryst.*, **42**, 33 (1977); H. Birecki, R. Schaetzing, F. Rondelez, and J. D. Litster, *Phys. Rev. Letters*, **36**, 1376 (1976).
108. A. J. Leadbetter and P. G. Wrighton, *J. Phys.*, **40**, C3-234 (1979).
109. A. J. Leadbetter and E. K. Norris, *Mol. Phys.*, **38**, 669 (1979).
110. V. K. Pershin and V. S. Zhukov, *Sov. Phys.-Solid State*, **20**, 655 (1979).
111. H. Terauchi, *J. Phys.*, **40**, C3-401 (1979).
112. G. Albertini, B. Dubini, S. Melone, M. G. Ponzi-Bossi, F. Rustichelli, and G. Torquati, *J. Phys.*, **40**, C3-384 (1979).

113. R. S. Khare and C. R. Worthington, *Mol. Cryst. Liq. Cryst.*, **38**, 195 (1977); N. S. Murthy, J. R. Knox, and E. T. Samulski, *J. Chem. Phys.*, **65**, 4835 (1976); E. T. Samulski and A. V. Tobolsky, *Liquid Crystals and Plastic Crystals*, Vol. 1, eds. G. W. Gray and P. A. Winsor (Ellis Horwood Ltd., Chichester, 1974), p. 175.
114. I. G. Chistyakov, *Sov. Phys. Crystallogr.*, **8**, 691 (1964).
115. K. A. Suresh and S. Chandrasekhar, *Mol. Cryst. Liq. Cryst.*, **40**, 133 (1977).
116. E. T. Samulski and D. B. Dupré, *Adv. Liq. Cryst.*, Vol. 4, ed, by G. Brown (Academic Press, Inc., New York, 1979), p. 121.
117. R. Desper, M. N. Alexander, P. L. Sagalyn, and N. S. Schneider, ACS (Polymer Div.) Chem. Preprints, **18**, 73 (1977).
118. A. Blumstein, *Liquid Crystalline Order in Polymers* (Academic Press, New York, 1978).
119. A. Blumstein, Y. Osada, S. B. Clough, E. C. Hsu, and R. B. Blumstein, ACS (Polymer Div.) Chem. Preprints **18**, 14 (1977).
120. S. Chandrasekhar, B. K. Sadashiva, K. A. Suresh, N. V. Madhusudana, S. Kumar, R. Shashidhar, and G. Venkatesh, *J. Phys.*, **40**, C3–120 (1979).
121. J. E. Zimmer and J. L. White, *Mol. Cryst. Liq. Cryst.*, **38**, 177 (1977).
122. A. J. Leadbetter, R. M. Richardson, and J. C. Frost, *J. Phys.*, **40**, C3–125 (1979).
123. A. J. Dianoux, H. Hervert, and F. Volino, *J. Phys.*, **38**, 809 (1977).
124. A. de Vries, A. Ekachai, and N. Spielberg, *Mol. Cryst. Liq. Cryst.*, **49**, 143 (1979).
125. A. de Vries, A. Ekachai, and N. Spielberg, *J. Phys.*, **40**, C3–147 (1979).
126. G. R. Luckhurst and C. Zannoui, *Nature*, **27**, 412 (1977).
127. c.f. L. V. Azároff, *Elements of X-Ray Crystallography* (McGraw-Hill Book Co., Inc., New York, 1968), Chap. 16.
128. M. J. Buerger, *Z. Kristallogr.*, **130**, 173 (1969).