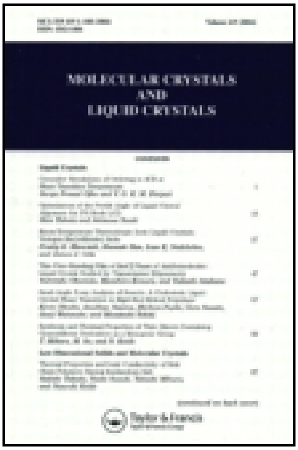

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A Structural Classification of Smectic Liquid Crystals

Adriaan de Vries [a]
[a] Liquid Crystal Institute, Kent State University, Kent, Ohio, 44242, U.S.A.

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A Structural Classification of Smectic Liquid Crystals†‡

ADRIAAN de VRIES

Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, U.S.A.

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A systematic classification of thermotropic smectic phases has been developed, with fourteen different phase types. First, the assumption is made that in *all* smectic phases the molecular packing within the layers is based on a herringbone arrangement of the molecular planes. The specific packing models for the various phases are derived from this herringbone arrangement by the introduction of certain kinds of orientational disorder of the molecular planes. It appears that four different packing models are possible. Second, a distinction is made between phases in which the director is normal to the smectic plane and those in which the director is tilted. Combining this distinction with the four packing models referred to above, one arrives at eight possible layer structures. Third, a distinction is made based on the presence or absence of certain X-ray reflections related to the existence of a well-developed three-dimensional lattice. Incorporation of this distinction leads to a system of fourteen possible smectic phase types. All known layered smectic phases can be classified within this system.

I INTRODUCTION

Most people working in the field of liquid crystal research are familiar with the fact that there are many kinds of smectic phases (i.e., liquid crystal phases with a layer structure), and with the fact that these phases are generally classified as smectic *A*, smectic *B*, etc. This classification has been developed by the group in Halle, East Germany (see, e.g., Ref. 1), and is based on miscibility studies. It has been, and still is, of great value in liquid crystal research, but as the number of different phase types is becoming larger, a drawback that is becoming increasingly apparent is that the letters denoting

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the phase types tell us nothing about their structure or properties. For instance, they give no indication that the difference between phase types *E* and *H* is probably the same as that between *A* and *C*. For this reason we have developed[2,3] a classification based on structure. This classification is very systematic, its symbols are simple and easily understood, the symbol for each phase type gives a significant amount of information about the phase, and differences and similarities between phase types are readily apparent. Also, a simple X-ray powder diffraction pattern and a conoscopic microscopic study will, in general, suffice to determine the type of an unknown phase.

II THE BASIC PACKING

The basis of our structural classification is the molecular packing illustrated in Figure 1. In this figure, the molecular long axes are perpendicular to the plane of the paper and their positions are indicated by the small circles. The lines denote the orientations of the average molecular planes. The molecular axes are in a more-or-less hexagonal arrangement, but the planes are not, and the overall structure has orthorhombic symmetry. The broken lines in Figure 1 indicate the unit cell of the structure in the plane of the drawing.

The molecular packing illustrated in Figure 1 was proposed in 1974 for the smectic *E* phase. It appears to be well established that smectic *E* does indeed have this structure: Three research groups,[4–6] apparently independently of each other, came to the same conclusion. It also is fairly certain that the same molecular packing, only now with the molecular axes *tilted* with respect to the lattice in the plane of the paper, is the structure of the smectic *H* phase.[7,8] The origin of this packing model, however, goes back much further, and to a quite different type of liquid crystal phase. It was first pro-

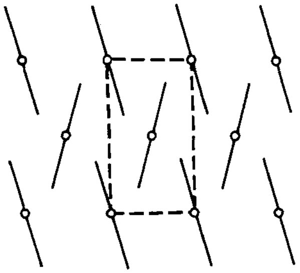

FIGURE 1 Schematic representation of the basic molecular packing, as seen along the long axes of the molecules. The small circles mark the positions of the molecular axes, the full lines indicate the orientations of the molecular planes, and the broken lines outline the unit cell.

posed in 1968 by Gulrich and Brown,[9] as the only molecular packing model that fitted their X-ray diffraction intensity measurements on a *nematic* phase. That it remains a viable model for this phase is illustrated by a more recent paper[10] from another source in which the model was again found to be successful in giving a satisfactory explanation of data on a nematic phase.

Putting a number of liquid crystal phases in sequence of increasing order, e.g., *N*, *A*, *C*, *B*, *G*, *E*, *H*, we see (with reference to the previous paragraph) the following with regard to the applicability of the model of Figure 1 to these phases: It has been proposed as the only satisfactory model for the most disordered phase (*N*), and it has been found to be the correct model for the most ordered phases (*E*, *H*). It also has been proposed elsewhere as the basic model for some of the other phases (*A*,[11] *G*[12]). Thus, it appears likely that the model of Figure 1 will be applicable to *all* liquid crystal phases.

Further confirmation of this hypothesis comes from two considerations. First, we have found[13] that, with intermolecular distances† as commonly found in smectic liquid crystals (about 5 Å), the only possible packing of a

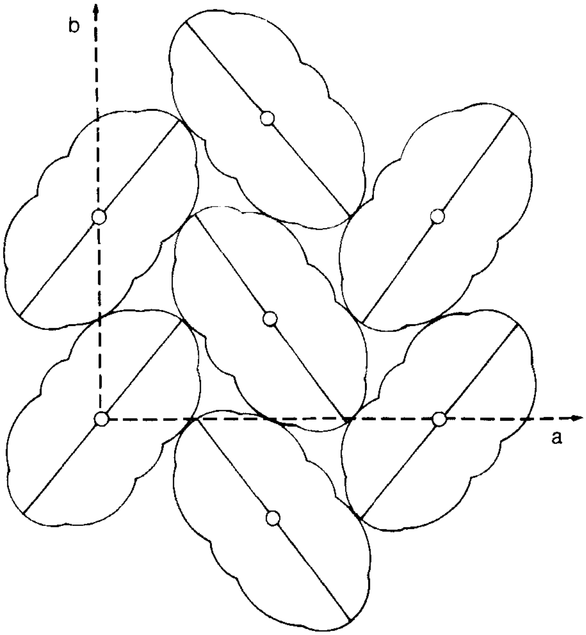

FIGURE 2 A projection of a packing of benzene rings, with a distance of about 5 Å between the centres of adjacent molecules (all rings have one of their C—H bonds perpendicular to the plane of the drawing).

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† By "intermolecular distances" we mean the average distances between the long axes of neighboring parallel molecules.

collection of benzene rings (the most non-cylindrical components of the molecules of the large majority of liquid crystals) is a packing (Figure 2) as in Figure 1. Second, in studying the crystal structures of a number of aromatic compounds we have found[12] that in these structures the molecular packing is also as indicated in Figure 1.

On the basis of the information summarized in the preceding two paragraphs, we have made the assumption which forms the foundation of our structural classification system, viz., that the molecular packing of Figure 1 *is* the basic packing for *all* smectic phases.

If this assumption would be wrong, our classification system would be wrong, too. If it is correct, however, the main features of our classification system follow almost automatically. We feel that the assumption has a firm experimental data base, and that it is further confirmed by the simplicity and applicability of the classification system based on it (see below). Thus, we will take the assumption as correct, and now proceed with developing the classification system.

III OTHER PACKING MODELS

Once we accept the idea that Figure 1 represents the basic molecular packing of all smectic phases, the question arises as to what other packings are possible on this basis. We have found only three.[3] The first, and simplest, modification of Figure 1 is the following. For a given set of molecules with a packing as in Figure 1, it would be impossible to distinguish between the molecular arrangements of Figures 3a and 3b. Also, a transition from Figure 3a to Figure 3b, or vice versa, could be accomplished by a relatively small and easy cooperative rotation of the molecules around their long axis. Thus, it would appear to be quite plausible that a structure as in Figure 1 would at higher temperatures give way to a structure in which the arrangements of Figures 3a and 3b are equally probable and continually changing from the one into the other. This structure is represented in Figure 3c as the superposition of Figures 3a and 3b. It is the first modification of the basic packing of Figure 1. It has an orthorhombic unit cell, as did Figure 1, but this unit cell is now centered in the plane of the paper (i.e., the molecule in the center has the same orientations as the molecules on the corners).

The next modification is as follows. A packing as in Figure 3c (or Figure 4b) would be equivalent to the packings of Figures 4a and 4c. Transitions between Figures 4a, 4b, and 4c would not be as simple as between Figures 3a and 3b, however, because the molecular rotations required are larger and can be expected to have higher energy barriers, and because the positions of the long axes of the molecules also have to change somewhat (as indicated in

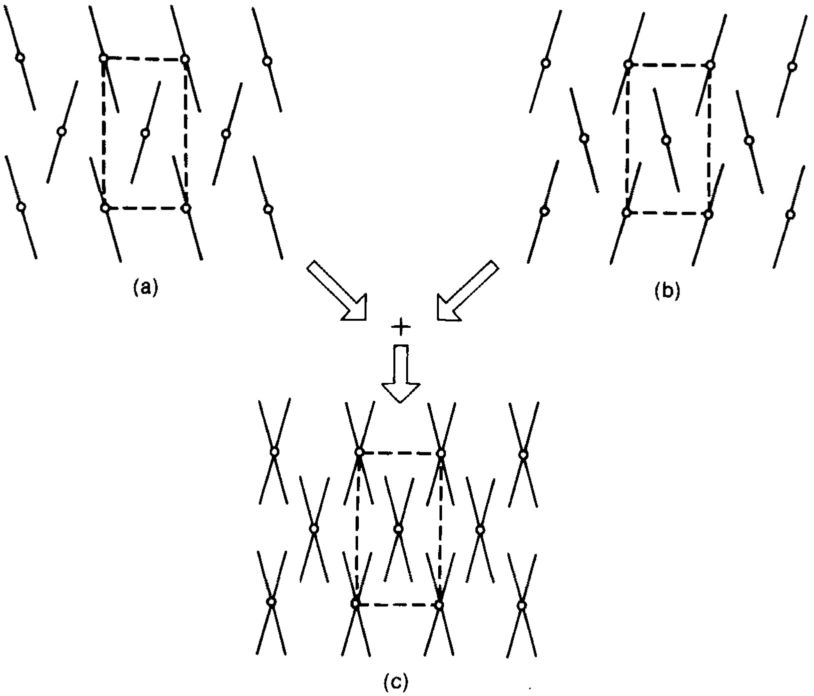

FIGURE 3 Two equivalent schematic representations (*a* and *b*) of the basic molecular packing of Figure 1, and a schematic (*c*) of a packing in which *a* and *b* are equally probable.

Figure 4 by the changes in the orientation of the unit cell marked by the broken lines). If the temperature would be high enough, though, transitions between the arrangements of Figures 4a, 4b, and 4c would probably become possible and result in a structure in which all three arrangements are equally probable and continually changing from one to another. This structure is represented by Figure 4d; it is the second modification of the basic packing of Figure 1. The orthorhombic unit cell of the original structure has now been transformed into a hexagonal unit cell, as indicated by the broken lines in Figure 4d.

The structure represented by Figure 4d was described in the preceding paragraph as one in which the molecular arrangements of Figures 4a, 4b, and 4c were equally probable and continually changing from one to another. A different way of interpreting this structure is to assume that individual smectic layers† would have the structures of Figures 4a, 4b, or 4c, and that these layers would be stacked in a fairly random manner. Thus, Figure 4d

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† Or: regions.[14]

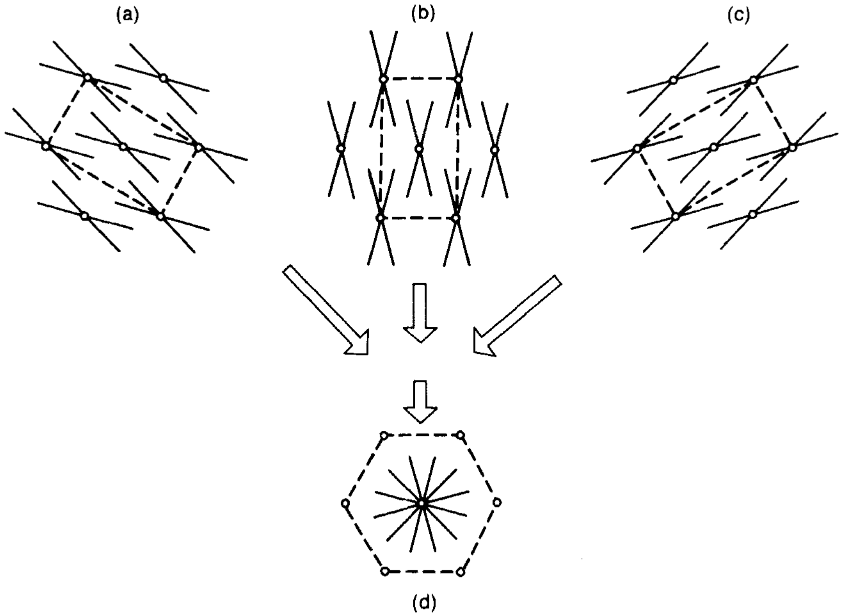

FIGURE 4 Three equivalent schematic representations (*a*, *b*, and *c*) of the packing of Figure 3c, and a schematic (*d*) of a packing in which *a*, *b*, and *c* are equally probable.

would represent the overall average structure for a stack of smectic layers. At a later stage, it may become necessary to make a distinction between phases in which the structure of Figure 4d is achieved by dynamic disorder (the first interpretation given above) and phases in which it is achieved by static disorder (the second interpretation given above), but in this paper we will not make such a distinction.

The third and final modification of the basic packing of Figure 1 is derived from the packing of Figure 4d by replacing the sixfold axis by an infinite-fold axis (Figure 5d). Compared with the structure of Figure 4d (or Figure 5c), all orientations of the molecular plane around the long axis are now equally probable (this is indicated by the full circle in Figure 5d), as are all positions of the molecular axes of the molecules surrounding the central molecule (as indicated by the broken circle). As with Figures 3c and 4d, the various orientations and positions indicated by the circles in Figure 5d should not be thought of as uncorrelated, as if one molecule could have all orientations independent of the orientations and positions of the surrounding molecules. Rather, at any given moment the most probable arrangement for any group of molecules is always assumed to be the basic herringbone packing of Figure 3a or 3b. Averaged over time or place, all orientations of these packings are equally

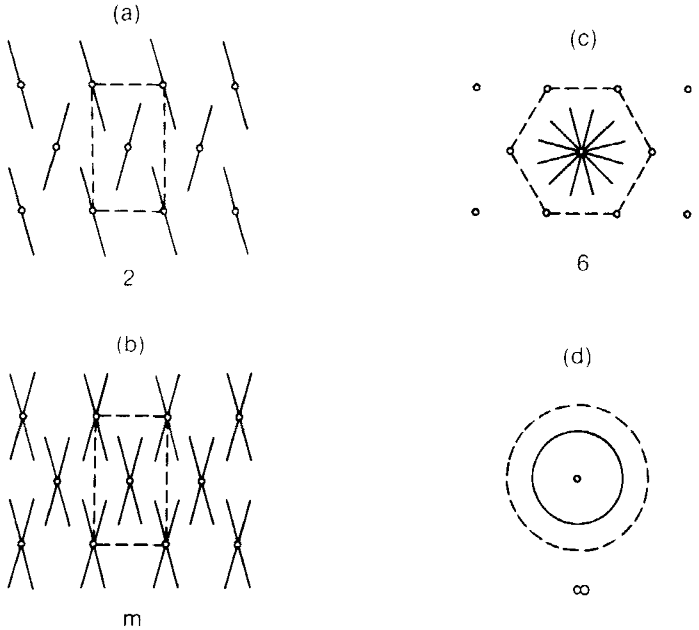

FIGURE 5 Schematic representations of the four possible molecular packings, which have been assigned the symbols *2*, m, *6*, and ∞, respectively.

probable. Figure 5d schematically represents this averaged molecular arrangement.

Thus, we have a total of four† possible molecular packings[3] (Figure 5). Each of these will be referenced below by a single symbol representative of its symmetry.[2] Figure 5a will be represented by the symbol "2", because the structure has twofold rotation axes perpendicular to the plane of the drawing. Figure 5b will be given the symbol "m", because it is derived from Figure 5a via a mirror plane. For Figure 5c we will use the symbol "6", because the structure has sixfold rotational symmetry. And Figure 5d will be indicated by the symbol "∞", because of its infinite rotational symmetry.

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† A fifth possibility would be the recently proposed[15,16] "hexatic" structure. This structure is similar to that of Figure 4d or 5c, but now only the *orientation* of the lattice has long range order, whereas the *positions* of the lattice sites (i.e., the positions of the molecules) have merely short range order. In our classification (Figure 5), the hexatic structure would come between Figure 5c and Figure 5d.

IV FURTHER DISTINCTIONS BETWEEN SMECTIC PHASES

With only four possible molecular packings for about ten different phase types found experimentally, it is clear that additional distinctions, beyond those based on packing, are necessary to arrive at a satisfactory classification system. The first such distinction is, obviously, the distinction between orthogonal and tilted structures. In orthogonal structures, the director is perpendicular to the plane of the smectic layer; in tilted structures, the director is at an angle with respect to the layer normal. It is important that this distinction between "orthogonal" and "tilted" is made on the basis of the *director* rather than on the basis of the *molecules*. In *all* smectic phases there is a certain amount of orientational disorder (measured by the order parameter S) relative to the direction of the molecular long axis, and, as a result, the average of the angle θ between this axis and the layer normal is significantly different from zero, even for orthogonal smectic phases[3,17] (Table I). Because of this, one can say that "in all orthogonal smectic phases the molecules are tilted." These phases are, nevertheless, orthogonal, because the *director* is *not* tilted.

Combining the distinction based on tilt with those based on packing, and making a tentative assignment of the phase types known from miscibility studies,† we arrive at the classification given in Table II (the phase denoted by X is an as yet unnamed phase found recently by us [14,19,20]).

The fact that two phases (G and I) occupy the same spot in the table indicates that still an additional distinction is needed. We will use for this distinction the presence or absence of certain reflections in the X-ray diffraction pattern.‡ When these reflections are present (as in the G phase), the phase definitely has a well developed three-dimensional lattice. When these reflections are absent (as in the I phase), the phase probably has no three-dimensional lattice.

The difference between a two-dimensional and a three-dimensional lattice in a smectic monodomain can be described as follows (see Figure 6). For the three-dimensional lattice, let X and Y be the two axes in the plane of the smectic layer, and let Z be the out-of-plane axis (for simplicity, the lattice drawn in Figure 6a has been chosen to be orthogonal). The X and Y axes

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† Two more phase types, J and K, were recently introduced in a paper by Barrall *et al.*[18] At the Eighth International Liquid Crystal Conference, however, Gray announced the withdrawal of these new phase types; the phases in question had been re-examined and found to belong to previously established phase types.

‡ Similarly, the main difference between the X-ray diffraction patterns of H and G phases is also the presence or absence of certain reflections (compare, e.g., the diffraction patterns of phase V, smectic G, and phase VI, smectic H, of TBBA[7]). The group of reflections indicating the difference between H and G is, of course, different from the group indicating the difference between G and I.

TABLE I

Average molecular tilt angle ($<|\theta|>$) as function of the orientational order parameter (S), for orthogonal smectic phases

S	$<\|\theta\|>$	Corresponding phase
0.80	19.3°	Smectic *A*
0.85	16.5°	Smectic *B*
0.90	13.3°	
0.95	9.4°	Smectic *E*

TABLE II

Assignment of the miscibility phase types to the possible smectic layer structures

Director orientation	Molecular packing 2	 m	 6	 ∞
Orthogonal	E	X	B	A
Tilted	H	G, I	F	C

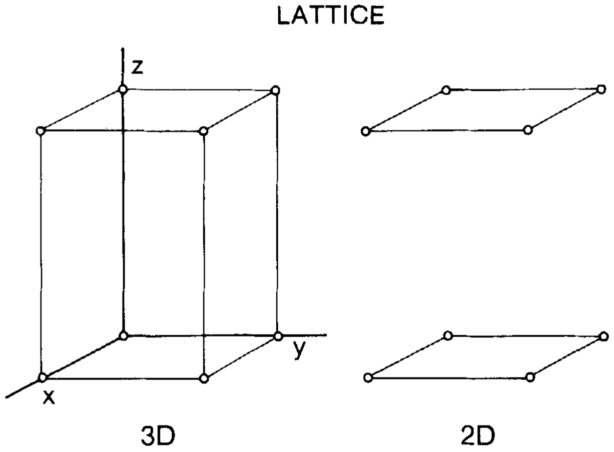

FIGURE 6 Comparison of a three-dimensional lattice with a two-dimensional lattice.

define the two-dimensional lattice formed by the centers of the molecules (the small circles in Figure 6) in each smectic layer. The three axes together define the three-dimensional lattice formed by the molecular centers of a stack of layers in a monodomain (Figure 6a). In a monodomain of a phase with only a two-dimensional lattice, one still has in each layer the lattice defined by the X and Y axes (Figure 6b), and these lattices are still parallel and equidistant, but the *positions* of the lattices are now no longer related in a regular fashion (i.e., there is no Z axis).

The presence or absence of the Z axis has certain definite consequences for the X-ray reflections that can be obtained from a monodomain. In general, a reflection of a three-dimensional lattice is identified by a set of three numbers, or indices, which are usually represented by the letters h, k, and l. The index h relates to the periodicity of the lattice in the X direction, k to the Y direction, and l to the Z direction. If one or more of the indices of a reflection are zero, then that reflection is not affected by the periodicity in the corresponding direction(s). Thus, both the two- and the three-dimensional smectic phases give $00l$ reflections (the inner rings on a diffraction pattern), because these reflections are only sensitive to the layer planes being parallel and equidistant. Also, both may give $hk0$ reflections (outer rings), because these reflections are caused by the lattice within the layers. The hkl reflections,† however, require simultaneous periodicities in all three directions and thus are only present for a *three*-dimensional lattice (Table III). Consequently, the presence of hkl reffections indicates that there is a three-dimensional lattice.

The question might be raised, however, whether the lattice of a three-dimensional smectic phase can be well-enough developed to give observable hkl reflections. In answer to this question, we refer the reader to Table 1 of Ref. 12. The first two columns of this table list the indices and positions of the reflections observed by us for the smectic G phase‡ of 4-*n*-butyloxybenzal-4′-ethylaniline (BBEA). This list contains five observed $00l$ reflections, six

TABLE III

X-ray reflections from three- and two-dimensional lattices in smectic phases

3D	2D
$00l$	$00l$
$hk0$	$hk0$
hkl	—

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† By "hkl reflections" we mean here reflections *other than* the $00l$ and $hk0$ reflections.

‡ At that time called the smectic H phase.

observed *hk*0 reflections, and *twenty-nine* observed *hkl* reflections. Thus, there can be no doubt that the *hkl* reflections can be observed for smectic phases.

The same data from Ref. 12 also allow us to estimate what the diffraction pattern would look like for a powder sample† of a phase like the smectic *G* phase of BBEA. Table IV lists the diffraction angles of the *hkl* and *hk*0 reflections of the series $1\bar{1}l$ ($l = -3$ through $+3$). The diffraction pattern of a powder sample consists of concentric ring-shaped reflections, with larger ring diameters corresponding to larger diffraction angles. The diffraction pattern of a powder sample of the *G* phase of BBEA will contain, therefore, weaker outer rings (the *hkl* reflections‡) in addition to the main outer ring (the $1\bar{1}0$ reflection and other *hk*0 reflections‡ corresponding to the distances between adjacent molecules), some with smaller diameters and others with larger diameters than the main ring. That this is indeed the case may be seen from Figure 7b (the "rings" are incomplete and spotty because the sample was not a good powder sample). The diffraction pattern of a smectic *I* phase, by contrast, shows only one single strong outer ring, with no evidence for the existence of additional outer rings§ (Figure 7a). We conclude, therefore,

TABLE IV

Diffraction angles (2θ) for a series of $1\bar{1}l$ reflections from the smectic *G* phase of BBEA

hkl[a]	2θ
$1\bar{1}\bar{3}$	22.1°
$1\bar{1}\bar{2}$	20.3°
$1\bar{1}\bar{1}$	19.8°
$1\bar{1}0$	20.6°
$1\bar{1}1$	22.6°
$1\bar{1}2$	25.6°
$1\bar{1}3$	29.1°

[a] $\bar{3}$ means: minus 3, etc.

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† By "powder sample" we mean a sample containing small regions of all possible orientations of the structure, like in a random powder of a solid phase.

‡ The *hk*0 reflections are always much stronger than the corresponding *hkl* reflections, because the molecules are always more or less parallel to the *Z* axis.

§ It should be taken into account, of course, that the tilt angle in the *I* phase[19] is significantly smaller than in the *G* phase,[12] and that the outer rings would, therefore, be closer together for a three-dimensional *I* phase. Table V lists the diffraction angles of the 20*l* series of reflections ($l = -2$ through $+2$) of three hypothetical lattices, all three for a hexagonal close-packing of cylinders with a length of 25 Å and a dimater of 5 Å. The three lattices have tilt angles of 30° (representing smectic *G*), 10° (representing smectic *I*), and 0° (representing smectic *B* and *X*), respectively. It may be seen that for a three-dimensional smectic *I* some of the additional outer rings would be expected to be distinguishable, but that this might not be the case for a three-dimensional smectic *B* or *X*.

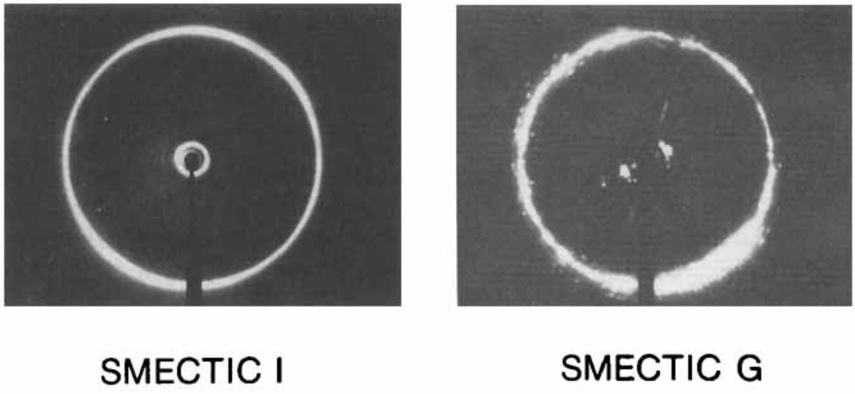

FIGURE 7 X-ray diffraction photographs of a smectic *I* phase and a smectic *G* phase.

TABLE V

Diffraction angles for a series of 20*l* reflections from three hypothetical lattices with tilt angles of 30°, 10°, and 0°, respectively

hkl	Diffraction angles		
20$\bar{2}$	17.9°	20.5°	21.7°
20$\bar{1}$	18.8°	20.2°	20.8°
200	20.5°	20.5°	20.5°
201	22.9°	21.4°	20.8°
202	25.7°	22.9°	21.7°

TABLE VI

Possible smectic phases

		Orthogonal		Tilted	
		∞		m	
PACKINGS	∞	∞∞0	—	∞m0	—
	6	6∞0	6∞1	6m0	6m1
	m	m∞0	m∞1	mm0	mm1
	2	2∞0	2∞1	2m0	2m1
		0	1	0	1
		hkl absent	*hkl* present	*hkl* absent	*hkl* present

that the *G* phase definitely has a three-dimensional lattice, but the *I* phase probably only a two-dimensional one.

V THE CLASSIFICATION

If we assume that the distinction based on the absence or presence of the *hkl* reflections is also applicable to other types of smectic phases, we have now 14 possible smectic phases.† Using the symbols "0" (zero) and "1" (one) to indicate "absence" and "presence", respectively, and the symbols "∞" and "m" to indicate orthogonal and tilted phases,‡ respectively, the symbols for the 14 phases are as listed in Table VI. Each phase is characterized by a set of three symbols. The first one indicates the molecular packing (see Figure 5), the second one refers to the tilt of the director, and the third relates to the dimensionality of the lattice. Table VI shows that the 14 possible phase types can be arranged in a very systematic, simple, and clear manner.

From the tentative assignment, in Table II, of the phase types known from miscibility studies, we can now come to a tentative assignment of these phase types to the possible smectic structures listed in Table VI. This assignment is given in Table VII. Smectic *B* and *X* have been assigned to phases with the symbol "0", because X-ray photographs like those in Figure 1 of Ref. 21, Figure 1 of Ref. 22, Figure 5 of Ref. 23, and Figure 10 of Ref. 13 do not show any *hkl* reflections for these phases. Also, in a recent paper[24] we described the *B* phase of a compound with severely disordered alkyl chains at both ends of the molecule. Since adjacent layers are in contact via these alkyl chains, it appears to us very unlikely that this *B* phase could have the necessary register of adjacent layers required for a three-dimensional lattice. On the other hand,

TABLE VII

Assignment of the miscibility phase types to the possible smectic structures

A	∞∞0	—	—	C	∞m0	—	—
B	6∞0	(B)	6∞1	F	6m0	—	6m1
X	m∞0	(X)	m∞1	I	mm0	G	mm1
—	2∞0	E	2∞1	—	2m0	H	2m1

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† Even though Table II lists 8 combinations of packing and tilt, there are now only 14 phase types rather than 16 (= 2 × 8), because the disordered packing mode (packing symbol ∞) does not allow a three-dimensional lattice.

‡ The symbols "∞" and "*m*" refer to the symmetry of the director relative to the smectic plane. For orthogonal phases, we have a line perpendicular to a plane, and the director is an axis of infinite-fold symmetry (∞). For tilted phases, we have a line tilted with respect to a plane, and the only symmetry element is a mirror plane (*m*) through the director and the normal to the smectic plane.

there do appear to be *B* phases with a three-dimensional lattice,†[25 27] and, as noted in the third footnote on page 11, it might be very difficult to distinguish the *hkl* reflections if they are present. For these reasons, we have also entered *B* and *X* (in brackets) for the corresponding phases with the symbol "1".

With reference to our discussion in the Introduction about the drawbacks of the miscibility classification, it will be clear that our classification symbols (Table VI) give a considerable amount of information about each phase type. With the assignments of miscibility phase types as in Table VII, they indicate, e.g., that the structure of the smectic *E* phase has a simple herringbone packing (Figure 5a), that it is orthogonal, and that it has a three-dimensional lattice. The smectic *H* phase appears to have the same characteristics, except that it is tilted, and this difference between *E* and *H* (orthogonal versus tilted) is seen to be the same as that between *A* and *C*. Other similarities and differences, e.g. in the sequences *A*, *B*, *X* or *C*, *F*, *I*, would also be readily apparent from our structural classification symbols.

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† We do not know how relevant the recent work of Moncton and Pindak[26] on three-dimensional phases is for our distinction between absence and presence of *hkl* reflections, for these authors' results refer to stacks of about 100 layers thick. With a molecular length of 25 Å, this would amount to only 0.25 micron, which is exceedingly small compared to the dimensions of the samples in our X-ray studies (500 microns).

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